
Debates over the Theory of Solution: A Study of Dissent in Physical Chemistry in the English-Speaking World in the Late Nineteenth and Early Twentieth Centuries
Author(s): R. G. A. Dolby
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Debates over the Theory of Solution:

A Study of Dissent in Physical Chemistry in the English-Speaking World in the Late Nineteenth and Early Twentieth Centuries

BY R. G. A. DOLBY*

"I used to think theology
Was rather rough on doubt,
But chemistry with ions beats
Theology all out.

You'd better join the church before
Your course is well begun,
Because you'll need to exercise
The art of faith, my son."
Ellwood Hendricks[1]

"The history of the development of the ionic dissociation hypothesis appears to me to be one of gravest warning, which we should heed before it be too late; the grave ethical value of the lessons to be learned from it should not be overlooked."
H. E. Armstrong[2]

1. INTRODUCTION

Modern physical chemistry is often dated from 1887. In that year J. H. van't Hoff's theory of solution and S. A. Arrhenius' theory of electrolytic dissociation were made the core of a new chemical specialty promulgated by the school formed around Wilhelm Ostwald. The new approach to chemistry encountered resistance, particularly in Britain; it came to dominate British ideas of solution only after more than a decade of strenuous opposition. Arrhenius' theory of electrolytic dissociation was attacked particularly strongly. In the twentieth century, the debate continued in a subdued form in

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*Unit for the History, Philosophy and Social Relations of Science, University of Kent at Canterbury, Canterbury, Kent CT2 7NR, England.

[1] Quoted by James Kendall, *Journal of Chemical Education, 2* (1925), 376.

[2] H. E. Armstrong, *Science Progress, 3* (1909), 656.

Britain, and in America, too, the new theories remained subject to an undercurrent of criticism. Only after the death of the main opponents of the Ostwald school, the emergence of new theories, and changes in the major interests of physical chemists, did the debate finally end.

There is considerable interest in following such a debate, both as an important episode in the history of science and as a case study exploring the methodology of scientific change. A debate is a valuable source of insight into the criteria affecting choices between alternative theories and is useful for revealing the role of dissent in scientific change.

In the course of the present historical study we will see how dissent functioned in one problem area of mature science; we will see that it was regarded as an important part of the process of reaching rational consensus, not an embarrassing and unintended symptom of the breakdown of normal processes. Indeed, there were institutionalized settings for debate. The British Association for the Advancement of Science, and later the Faraday Society, organized meetings for discussions between rival parties; the discussions and debates arising out of papers read to the Chemical Society were reported in a special journal;[3] journals such as the *Philosophical Magazine* accepted polemical notes and papers, and *Nature* published letters in which correspondents developed the debate. There were also informal rules for debate, as is indicated by the remarks the scientists made when they considered that their opponents had become unconstructively polemical, that is, had transgressed the rules.[4] Although the debate over the theory of solutions was at times exceptionally heated, neither side felt that they were upsetting the

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[3] *Proceedings of the Chemical Society,* which commenced publication in 1885.

[4] The following sentence by P. S. U. Pickering, replying to criticisms made by James Walker, is suggestive of what was and was not acceptable in the debate. "Although Dr. Walker took upon himself the task of refuting the objections which I raised against the dissociation theory, he appears to me to have avoided the very objections for which I most sought explanations, though, perhaps, the absence of these explanations will probably be regretted by his friends less than *the absence of that courtesy which those who are seeking after the truth might naturally expect from their fellows, and the absence of which in the present instance was all the more to be regretted as I had not associated Dr. Walker's name with any of the views which I had called into question.*" *Philosophical Magazine* [5], *32* (1892), 40; my italics.

continuity of scientific development, but rather that it was by debate that science would reach the truth most effectively. When some of the textbooks of the Ostwald school expounded the theories of van't Hoff and Arrhenius without referring to the arguments of their critics, the latter considered this to be a perversion of the rational path of science.[5]

In the concluding section, I shall discuss the concept of dissent. I shall stress its usefulness in other historical studies of science and discuss the suggestion that scientific change takes many forms in which dissent is of fundamental importance, so that debate is not restricted to cases of scientific revolutions. This paper is to be considered, therefore, as a contribution to the descriptive methodology of scientific change.

Historiographic Note

In writing the history of the debate over the theory of solutions, two major problems of presentation emerged: the importance of representing sympathetically several incompatible viewpoints on the same issues, and the need to report simultaneous but tenuously connected parts of the debate.

The events in this history occurred in the social realm, in which people's behavior is affected by what they *think* is happening. By reporting the comments made at the time of the debate and later retrospects, I have tried to show that the participants frequently differed widely in their understanding of the course of the debate and of the nature of the final outcome. Since the position of each character tended to change slowly while the center of public attention moved around rapidly during the debate, I could best have demonstrated the essential coherence of each viewpoint by following it through the whole period. To work through the debate as many times as there are characters, however, would overtax the patience of the reader. I have compromised by concentrating on particular characters at particular phases of the debate. Normally, I have indicated the personality and preoccupations of each character when he first makes an important appearance; the reader may refer to these passages when considering subsequent briefer discussions of the later development of his ideas and his later involvement in the debate.

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[5] See in particular the discussion of the issues raised by Armstrong's career, in section 7 below.

Often the debate broke down into separate simultaneous but interacting strands, each of which would be best understood by being followed over an extended period. I have somewhat reduced the complications of bringing them together into a single thread of narrative by ignoring parallel debates in non-English speaking countries, except when they had an immediate effect on the central characters of the British and American debates. The debate in the English speaking world was largely self-contained (though dependent on the prior work of the Ostwald school on the continent), so that the restriction is acceptable. With only a few exceptions (such as the controversy over hydration between Arrhenius and D. I. Mendeleef and his Russian supporters), the debate in other countries was less dramatic and more piecemeal, dominated by unrelated priority disputes and individual misunderstandings, and is therefore less useful historical material.

2. HISTORICAL BACKGROUND TO THE DEBATE

It is possible to trace a continuing line of discussion on the nature of solutions throughout the history and prehistory of chemistry.[6] However, until the last third of the nineteenth century, relatively few chemists dealt with the nature of solutions as a problem in its own right and as a problem around which questions about the phenomena of solution could be organized. In his general discussions of chemical affinity, C. L. Berthollet had dealt with reactions in solution and solubility. But because he believed that chemical compounds could have indefinite proportions, he did not make a sharp distinction between compounds and solutions. In the following decades, Berthollet's ideas stimulated much discussion but few experiments and no decisive advances.[7] The increasing importance of a

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[6] See for example, P. Walden, "Die Lösungstheorien in ihrer geschichtlichen Aufeinanderfolge," *Sammlung chemischer und chemisch-technischer Vorträge, 15* (1910), 277–454. This paper provides a thorough though not exhaustive retrospective survey of ideas of solution, particularly in the eighteenth and nineteenth centuries. See also J. R. Partington, *A History of Chemistry* (London, 1964), *4,* chap. XX.

[7] See F. L. Holmes, "From Elective Affinities to Chemical Equilibria," *Chymia, 8* (1962), 105–145, for a historical account of the tradition. Holmes suggests (pp. 128–129) that the impasse that chemists reached in their discussion of affinity theories in the decades after Berthollet was due to their lack of knowledge of the state of substances in solution (particularly of equilibrium mixtures of dissolved substances), and that, in the early nineteenth century, the number of chemists was still small enough for the less attractive topics to be neglected.

chemistry of definite proportions in the wake of Daltonian atomic theory made questions related to the nature of solutions, which have indefinite proportions, seem peripheral. Chemists studied diverse phenomena of solution to varying extent during this period, but they showed little interest in attempting to draw the material together to give a deeper understanding of the nature of solutions.

Gradually, during the middle part of the nineteenth century, a new question about the nature of solutions came sharply into focus as physical and chemical forces became more strongly contrasted. Chemists asked if solutions, particularly aqueous solutions, were to be understood as containing definite chemical species produced by the combination of the dissolved substance and the water, or if they were to be explained in purely physical terms. One can extract from the literature fairly strong statements of either opinion, supported by different selections of evidence. For example, in 1846 one writer argued that the contraction of total volume that occurs when substances dissolve in water is of a magnitude corresponding to such an immense external pressure that it must be evidence of chemical combination.[8] In 1867 another writer, L. Dossios, considered that a satisfactory treatment of solutions could be derived from a kinetic theory that assumed that the kinetic energy of a molecule was greater than the attraction between two neighboring molecules but less than the total attraction of all the molecules on one another. Dossios argued from analogy with homogeneous bodies: even though the molecules in solution are not all identical, the kind of force that produces cohesion in homogeneous bodies also provides a satisfactory explanation for cohesion in solutions. Saturation occurs when the molecules leaving solution equal in number those reuniting with it. The solubility will increase with temperature, that is, with the increase in molecular movement.[9]

By the 1870's, thermochemistry provided one of the most important sources of information on the state of substances in solution. As is to be expected, when substances pass from the solid to the liquid state, many solids dissolve in water with the absorption of heat. Some others do not. For several chemists, M. Berthelot among them, it was most plausible to attribute the heat liberation to chemical combination of the dissolved substance with the water. Berthelot presented an influential full statement of the hydrate theory of the

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[8] J. J. Griffin, *Philosophical Magazine* [3], *29* (1846), 289-310, 444-467.

[9] L. Dossios, *Vierteljahrsschrift der Zürichischen Naturforschenden Gesellschaft, 13* (1867), 1-21. Dossios' treatment was taken up by W. W. J. Nicol in 1883.

1870's in his 1879 *Essai de mèchanique chimique fondèe sur la thermochimie*. There he considered that solution of salts occurs with the formation in the solution of definite compounds between the salt and the water, analogous to or identical with the hydrates of constant composition known in the crystalline state.[10] Thermochemical evidence looked especially strong for the dilution of strong acids. For example, the full dilution of a sequence of solutions of nitric acid containing from zero to one hundred equivalents of water per equivalent of acid shows that substantial amounts of heat are liberated on dilution until the solution contains six or seven equivalents of water. Berthelot's study of the shape of the heat of dilution curve led him to believe that there may be a definite hydrate with two equivalents of water, and another with five or six. Similar evidence suggested to him that there were several hydrates of sulphuric acid in solution. Berthelot went on to assemble a variety of evidence to show more generally the existence of hydrates in solution and to give some idea of their possible composition.

Berthelot's conception of the importance of hydrates in solution was representative of the positions of other chemists who had a chemical conception of solution. In the 1880's, the most eminent defender of the hydrate theory of solutions was Mendeleef. He had been writing on his conception of solution since 1865[11] but attracted particular attention on this subject outside Russia only after the publication in 1886 of his theory on the determination of hydrates present in solution. The hydrate theory of solution was the most plausible method of explaining the physical changes resembling the manifestations of chemical combination that accompany the formation of a solution. But it had to be combined with a physical theory of the liquid state of solution generally and of the more important processes which occur in solution.

During the second half of the nineteenth century, physicists and chemists combined the kinetic theory of heat with the kinetic theory of gases, making possible a thorough understanding of the quantitative aspects of the gaseous state and of reversible processes involving gases. Their first applications of the theories to the liquid state were speculative in nature, for they were slow to achieve an adequate understanding of reversible processes in solution and to link solution

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[10] M. Berthelot, *Essai de mèchanique chimique fondèe sur la thermochimie* (Paris, 1879), *2,* 162.

[11] P. Walden, *op. cit.* (note 6), pp. 386-390, 408-413.

to the gaseous state. Dossios' work was representative of the first phase of theory development, prior to the application of thermodynamics.

In his third paper on thermodynamics, "On the Equilibria of Heterogeneous Substances," J. W. Gibbs set out a systematic basis for the treatment of chemical phenomena by thermodynamic methods.[12] His general treatment adequately dealt with equilibria in solution, in particular equilibria between gases and solutions, where Henry's Law could be used. However, Gibbs wrote his paper in a compressed, abstract, mathematically elegant style which required mathematical sophistication of the reader and thus limited the distribution of the paper even though its results were of great interest to chemists. It was some time before many interested chemists were in a position to appreciate and exploit Gibbs's work.[13] Other physicists and chemists independently developed less general treatments,[14] but it was not until the late 1880's that the thermodynamics of chemical phenomena became a fashionable area.

In the meantime, a small number of chemists pioneered a physical treatment of solutions that, although less general than Gibbs's in its conception, was far simpler mathematically and was linked to a rich variety of experimental phenomena. It became the basis for a new and prolific school of research, which in turn transformed the peripheral subject area of physical chemistry into a thriving research specialty.[15]

Van't Hoff had risen to eminence as one of the two chemists who in 1874 had advanced the idea of the tetrahedral carbon atom as the basis of a theory of the arrangements of atoms in space capable of explaining the nature of optically active organic compounds. In the

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[12] J. W. Gibbs, *Transactions of the Connecticut Academy, 3* (1875-1878), 108-248, 343-524. Reprinted in J. W. Gibbs, *Scientific Papers* (London, 1906), *1*, 55-353.

[13] L. P. Wheeler, in *Josiah Willard Gibbs* (New Haven, 1951), discusses the distribution of Gibbs's paper and, in an appendix, gives a list of names of those scientists to whom Gibbs sent offprints.

[14] For example, H. von Helmholtz, *Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin, 1* (1882), 22-39, 825-836; *2* (1883), 647-665. J. H. van't Hoff, *Études de dynamique chimique* (Amsterdam, 1884).

[15] A fuller discussion of these developments is given in R. G. A. Dolby, "Social Factors in the Origins of a New Science: The Case of Physical Chemistry" (forthcoming).

1880's, van't Hoff turned to problems of physical chemistry, publishing his influential *Études de dynamique chimique* in 1884. Concerned with chemical affinity, van't Hoff in this work took up the problem of measuring the magnitude of chemical affinity. One possible approach to the problem was, following E. Mitscherlich, to study the attraction of salts for water. Mitscherlich's method of comparing the water vapor pressure of the salt with that of pure water at the same temperature suggested that an implausibly weak force was involved. But a chance discussion with the botanist H. de Vries, his colleague at Amsterdam, about the work of H. Pfeffer on osmotic phenomena immediately suggested to van't Hoff that osmotic pressure would provide a measure of the affinity of a salt solution for water. If a salt solution is separated from pure water by a semipermeable membrane, which allows the passage of water but not of the salt, the water tends to flow into the salt solution, unless its passage is resisted by an externally applied pressure. The pressure required to stop the flow is described as the osmotic pressure. Consideration of osmotic pressure indicated that the affinity of the salt solution for water was far higher than was suggested by Mitscherlich's data. By considering the thermodynamics of the attainment of equilibrium between a solution and a pure solvent connected both through a semipermeable membrane and by the unrestricted passage of vapor, van't Hoff was able in *Études de dynamique chimique* to express the equilibrium in the standard mathematical form that he used for equilibria, $d(\log c)/dT = q/2T^2$.

After the publication of *Études de dynamique chimique,* van't Hoff studied the many idealized reversible processes that the concept of a semipermeable membrane allowed. He quickly found that osmotic pressure corresponds to gas pressure and that the law relating the pressure, volume, and temperature of an ideal gas, $PV = RT$, holds for dilute solutions also. Even the constant, R, was the same for solutions as for gases. Van't Hoff concluded that Avogadro's principle holds for dilute solutions as well as for gases and developed a theory of solutions from these results. It was difficult to make precise direct experimental studies of osmotic pressure, but by extending his thermodynamic reasoning van't Hoff was able to explain the results of F. M. Raoult, who in 1882 had established that the depression of the freezing point of a dilute solution, as the lowering of the vapor pressure of the solvent, is proportional to the molecular concentration of the dissolved substance.

Van't Hoff presented his theory of solution in 1885,[16] expressing his general result as $PV = iRT$, where P is the osmotic pressure, and i is an empirical factor which is characteristic of a given solution. For many substances, i was close to unity in dilute solution, but for electrolytes it was generally much higher, often nearer two or three. This defect of the theory Arrhenius turned into an advantage in a paper published in 1887.[17]

Physical scientists had had difficulty in explaining satisfactorily the nature of electrolytic substances ever since the discovery of the chemical action of electricity at the turn of the nineteenth century. In 1857, R. Clausius had suggested that there must be a small permanent dissociation of electrolytes into electrically conducting ions. The permanent dissociation would explain why current can pass immediately on the application of voltage without first having to produce dissociation. In the 1850's, J. W. Hittorf's studies of ionic transport during electrolysis had shown that the proportion of the current carried by each ion in a salt was usually different. This made it unlikely that during electrolysis the ions were combined in firm molecules. In the 1870's F. Kohlrausch developed the modern methods of avoiding the problems of polarization in measurements of the conductivity of electrolyte solutions. Study of dilute solutions led him in 1874 to his law of the independent migration of ions, according to which the conductivity of a dilute solution is the sum of two constants, one depending on the cation and the other on the anion.

Electrochemical phenomena had long been a source of speculation about the nature of chemical force. The electrochemical theory of J. J. Berzelius, in particular, had been an influential early conception of chemical combination. But Berzelius' essentially qualitative ideas had not proved adequate for later developments in chemical theory or in electrochemistry. In his Faraday Lecture of 1881, the physicist H. von Helmholtz had presented to chemists an electrical conception of chemical combination which was compatible

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[16] J. H. van't Hoff, *Archives des Sciences Exactes et Naturelles, 20* (1886 [for 1885]), 239–302; *Kongliga Svenska Vetenskaps-Akademiens Handligar, 21,* no. 17 (1886), 3–58. These two papers are almost exactly the same except for their final sections. Van't Hoff later described the development of his views in "Wie die Theorie der Lösungen entstand," *Berichte der Deutschen Chemischen Gesellschaft, 27* (1894), 6–20.

[17] S. Arrhenius, *Zeitschrift für physikalische Chemie, 1* (1887), 631–648.

with knowledge of electricity. It was based on Faraday's study of electrolysis and the "modern chemical theory of quantivalence." From Faraday's law and the chemical atomic theory Helmholtz concluded that the ions carry a definite unit of electric charge in electrolysis. (He pointed out that this was in conflict with Berzelius' dualism in which the atoms in binary compounds did not completely saturate each other's electrical forces, so that more complex aggregates of atoms could be built up.) By a chain of reasoning Helmholtz estimated the order of magnitude of electrical forces acting between ions. It seemed sufficient to explain how the voltages used in electrolysis could disrupt chemical compounds. Helmholtz suggested that at least for typical non-aggregated compounds the forces of affinity and the constancy of chemical valency could be explained in terms of the electrical attraction between charged atoms. Although Helmholtz claimed to have avoided speculative assumptions in his treatment, he admitted that "I am not sufficiently acquainted with chemistry to be confident that I have given the right interpretation, the interpretation which Faraday himself would have given if he had been acquainted with the law of chemical quantivalence."[18]

By the 1880's, some physicists studying electrolytic phenomena considered that their primary task was to provide a mechanism for the electrical phenomena and attributed related chemical phenomena to the interaction of electrically charged particles. For example, Kohlrausch, G. Wiedemann, and others during the early 1880's developed Clausius' idea of dissociated ions in their speculations on the effects of an electric current in a conducting solution. They supposed that some of the electrolyte molecules are split into oppositely charged ions, which move freely and independently through the solution at speeds unaffected by the chemical environment and influenced only by such general conditions as viscosity. Under such conditions a small hydrogen ion would move more rapidly through the solution than larger ions. Their approach contrasted with that of chemists who considered chemical interaction between solvent and solute to be an essential feature of solution.

At this stage of the development Arrhenius devoted his doctoral thesis to the problem.[19] He made the bold and chemically implausible suggestion that a significant proportion of the molecules of all

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[18] H. von Helmholtz, *Journal of the Chemical Society, 39* (1881), 303.

[19] Arrhenius' thesis was published in *Bihang till Kongliga Svenska Vetenskaps-Akademiens Handligar, 8,* nos. 13, 14 (1884).

electrolytes are permanently in an active form that conducts electricity. The proportion of molecules in the active form increases with dilution until, at extreme dilution, all the molecules are conductors. He suggested that this variation in the proportion of active molecules is more important than any changes in the resistance of the solution to the passage of ions in measured variations of electrolytic conductivity. Furthermore, it is these conducting molecules that are chemically active, so that the relative strength of acids, for example, can be explained by the concentration of active molecules.

As he later admitted,[20] Arrhenius did not have a great variety of experimental data to support his ideas. Even though he had refrained from stating his belief that the active molecules are charged radicals of the kind that, as physicists speculated, might be produced during electrolysis, the ideas expressed in his dissertation disagreed completely with the prevailing conceptions of the chemical nature of salts and related substances. Arrhenius' ideas were largely ignored, but he did get an immediate positive reaction when he sent a copy of his thesis to Ostwald in Riga. Ostwald was able to use Arrhenius' work to correlate his own measurements of the chemical affinities of acids with measurements of their conductivities. Because of Ostwald's interest, Arrhenius gained the respect of local colleagues and was able to pursue an academic career. Arrhenius spent several years studying in a number of European laboratories.

In 1887, Arrhenius read van't Hoff's formulation of the theory of solutions. He immediately saw that it provided further evidence for the permanent dissociation of electrolytes. If the sodium chloride molecule, for example, is permanently dissociated into two ions, then a salt solution will have twice the molecular concentration suggested by the formula NaCl. This explains why the factor, *i*, in van't Hoff's equation is so close to two for sodium chloride solution. For any electrolyte solution, the factor, *i*, should be the same as the number of ions produced by the dissociation of a molecule.

Arrhenius published his theory in Sweden and in Britain, but its main impact came with its publication in the *Zeitschrift für physikalische Chemie.*[21] In an earlier number of the same volume, van't Hoff

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[20] S. Arrhenius, *Journal of the Chemical Society, 105* (1914), 1418.

[21] Arrhenius said (*Journal of the American Chemical Society, 34* (1912), 361) that an account of the hypothesis was included in a report of the British Association Committee for the investigation of the conductivity of electrolytes. However, Partington (*op. cit.* [note 6], p. 678) says that the report is no

had republished his theory of solutions, mentioning Arrhenius' theory of ionic dissociation as an explanation of the size of *i* for electrolyte solutions.[22]

Physical scientists very quickly recognized a number of important implications of the two mutually supporting theories. When the law of mass action was applied to the equilibrium between normal and dissociated substances, it was found that the calculations did not agree with experiment for the slight variation of conductivity with dilution of most salts, but gave a very good agreement for the much greater variation with weak acids. Several people noted this, but it was Ostwald who published first what is now called "Ostwald's dilution law."[23] In 1888–1889 W. Nernst made another application. By treating the ions of a solution in terms of their motion under an osmotic pressure gradient, Nernst was able to calculate the contact potential between a metal and a solution of its ions, and also between two solutions.[24]

The most important figure in the dissemination of the new treatment of solutions was Wilhelm Ostwald. When, in 1887, he was appointed to the second chair of chemistry at Leipzig, he founded a research school which became the nucleus of a research specialty of physical chemistry. The exploitation of the new treatment of solutions was a central theme of the new specialty. A new journal, *Zeitschrift für physikalische Chemie,* which he founded in the same year, and his many influential textbooks publicized the new area of scientific growth. The graduates of Ostwald's laboratory spread Ostwald's conception of the new discipline in Germany and then in other countries in which they could establish themselves. They became professors specializing in physical chemistry, wrote textbooks

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longer in the British Association files. The publication in *Zeitschrift für physikalische Chemie, 1* (1887), 631-648, embodied two communications read before the Swedish Academy of Sciences and published in *Översigt af Kongliga Svenska Vetenskaps-Akademiens Forhandligar,* 1887.

[22] J. H. van't Hoff, *Zeitschrift für physikalische Chemie, 1* (1887), 481-508.

[23] Arrhenius discusses the work that was being done on this law independently of Ostwald in *Journal of the American Chemical Society, 34* (1912), 361-362. Ostwald's route to the discovery is given by F. G. Donnan in his Ostwald Memorial Lecture, *Journal of the Chemical Society* (1933), p. 325.

[24] W. Nernst, *Zeitschrift für physikalische Chemie, 2* (1888), 613; *4* (1889), 129. A discussion of this and related work is given by J. R. Partington in *Journal of the Chemical Society* (1953), p. 2853.

modelled on Ostwald's, and founded specialist journals similar to the *Zeitschrift für physikalische Chemie.*

It was in America that the new discipline took root most rapidly. At the end of the nineteenth century, the American university system was growing rapidly. Large numbers of Americans were going overseas to qualify themselves for university teaching. Students studying sciences such as chemistry went to Germany, because it provided the best scientific training. Besides being drawn by the reputation of German chemical research, they went to obtain the German degree of doctor of philosophy, which was a suitable qualification for a university teacher and relatively cheap to obtain. The Americans who had gained a German degree by research on a laboratory subject were soon teaching the same way in America; after the founding of Johns Hopkins University as a graduate university in 1878, many other American universities reformed their graduate schools or set up new ones. The students in these American graduate schools in turn went on to teach in other universities, spreading rapidly the interests of the first generations of German trained graduates in any subject suitable for laboratory research by graduate students. In chemistry, it was organic chemistry which dominated Germany in the later part of the century and which benefitted most from the American expansion. But Ostwald's physical chemistry soon became sufficiently fashionable to attract the interest of many young American chemists who were not enamored of organic chemistry, particularly since at that time the fortunes of inorganic chemistry were at a low ebb.

In Britain, the growth of the university system and of chemistry within it was far less rapid. However, the graduates of the Ostwald laboratory were again of great importance in the establishment of British physical chemistry in accordance with the Ostwald program.

3. THE BRITISH DISCUSSION OF ELECTROLYSIS AND SOLUTION 1880-1887

In contrast to the situation in America, where physical chemistry can be represented as expanding almost unresisted into the growing university system, the introduction of the new ideas of the Ostwald school into Britain was strongly affected by earlier chemical opinion then prevalent in Britain. Two relevant general topics were especially important: theories of the nature of solutions and the process of dissolution, and discussion of the role of electricity in chemical action and combination, especially as illuminated by the study of electrolyte solutions.

Solution

The Daltonian atomic theory had accentuated the distinction between stoichiometric compounds and solutions. Chemists had been especially successful at developing an understanding of the former, but problems remained in the treatment of the latter. By the early 1880's, the prevailing opinion held that, when a salt (or any solute) dissolves in water, the solvent first forms hydrates which are then dispersed throughout the liquid. In 1878, for example, W. A. Tilden had maintained that "a solution contains *a mixture of several hydrates, the constitution of which depends partly on the temperature of the liquid, and partly on the proportion of water present.*"[25] A similar view was expressed by the "hydrate theorists" of the 1880's, and after the publicity associated with Mendeleef's development of the hydrate theory after 1886, a number of scientists who had earlier held this view were encouraged to claim priority.[26] But the ideas of the many precursors of the hydrate theory of the 1880's were vague and not related to very much evidence.

In 1883 W. W. J. Nicol mounted an attack on the "hydrate theory" of solution. He presented the theory in an extended quote from Berthelot's *Mécanique Chimique,* which he considered to be the most concise statement of the generally received hydrate theory that he could find.[27] Nicol argued that none of the water molecules in a solution are chemically combined with the solute in a manner analogous to water of crystallization, but that the process of dissolution is to be understood in terms of general attractive forces. A solution is formed when the attraction of the molecules of water for a molecule of the salt exceeds the attraction of the molecules of the salt for one another (at least under conditions where the changes in the water-water attraction have no effect). Nicol amassed experi-

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[25] W. A. Tilden, lecture to Bristol Naturalists' Society, February 1878, published in the Society's *Proceedings* and quoted by Tilden in *The Progress of Scientific Chemistry in Our Own Times,* 2nd ed. (London, 1913), p. 279.

[26] Tilden's retrospect of 1913 illustrates the trend. See also the claim by T. Sterry Hunt for an essay of 1855, made in *Chemical News, 58* (1888), 151-153.

[27] W. W. J. Nicol, *Philosophical Magazine* [5], *15* (1883), 91-92.

mental evidence in support of his position in many papers in the 1880's, engaging also in a polemical exchange with P. S. U. Pickering, who is a major figure in the present history.

Tilden and Nicol were representative of a growing group of British chemists in the mid-1880's who shared an interest in the experimental study of solutions. The meetings of the British Association for the Advancement of Science reflected the rise of interest in the nature of solutions. In the years immediately before 1884 no papers on the subject had been presented; but in 1884 four papers (involving six authors) were read. The following year two committees (involving five members) reported on solutions and continued to report for several years. In 1887 a larger committee (initially with seven members) first reported on the bibliography of solution. The reports of these committees, which did not contain theoretical discussions, reflected the considerable British interest in the nature of solutions predating the theories of Arrhenius and van't Hoff.

H. E. Armstrong and the Role of Electricity in Chemical Action

The development of ideas on electricity and chemical action before 1887 can best be presented by a look at H. E. Armstrong and his activities.[28] Armstrong was the key figure in the opposition to the new physical chemistry in England. He was an extreme individualist, a man who would never yield to the social pressures of a scientific community or follow scientific trends. Armstrong arrived at his position before he knew of the theories of Arrhenius and van't Hoff, and he developed them with a consistency that ignored the tides of fashion that he felt to be moving around him. After fifty years he wrote what he called his "considered message at the end of seventy years of constant study" in a polemical letter criticizing the dissociation theory and restating his nearly unchanged position.[29]

Armstrong had been trained by E. Frankland at the Royal College of Chemistry in London and by H. Kolbe at the University of Leipzig. As his first research he had made a chemical analysis of polluted water for Frankland, and he retained an interest in water throughout his career. In Leipzig he had studied orthodox organic chemistry. Armstrong's personality came to closely resemble Kolbe's—per-

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[28] For a full-length biography of Armstrong, see J. Vargas Eyre, *Henry Edward Armstrong* (London, 1958).

[29] H. E. Armstrong, "Ionomania in Extremis," *Chemistry and Industry, 14* (1936), 916–917.

haps as a result of deliberate imitation. Armstrong also inherited from Kolbe a belief in residual affinity as a feature of chemical combination.

Armstrong had many strands to his career, though the most important were undoubtedly his efforts in chemistry and in education. In education he was against the tendency towards specialization; his wide range of chemical interests, illustrated by the variety of his many contributions to the discussions at meetings of the London Chemical Society, confirms his opposition to specialization.[30] His research followed three main lines: the chemistry of naphthalenes, the chemistry of camphor, and the mechanism of chemical change. His ideas of chemical change led him into conflict with the Ostwald school of physical chemistry.

Many of the issues on which Armstrong developed such strong opinions he had initially taken up by chance. One interest, for example, grew out of circumstances related to an early, part-time position in chemistry at the London Institution.[31] The chair had once been held by W. R. Grove, inventor of the Grove cell, and Armstrong found some of Grove's apparatus in the laboratory. Later he bought a bundle of *Transactions of the Royal Society,* which included Grove's memoirs. The study of these gave him a continuing interest in electrolysis.

Armstrong first stated his ideas on chemical action in 1885, when he was thirty-seven. By this time he had built up an influential position in British chemistry, particularly in his autocratic secretaryship of the Chemical Society (1875–1893). The immediate stimulus to his public speculation was a report by H. B. Baker to the Chemical Society in March 1885. Baker had extended the work of H. B. Dixon on the reactivity of very pure chemical substances and had found that pure carbon and phosphorus are both incombustible in pure oxygen. He believed moisture to be essential for the reactions. In the discussion that followed, Armstrong suggested that all chemical reaction is "reversed electrolysis." He thought that Baker's report was providing evidence that the same kind of aggregation is required for combustion as is involved in electrolysis.[32] Armstrong elaborated his ideas as president of the Chemical Science Section of the British As-

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[30] See the record of *Proceedings of the Chemical Society.*

[31] Armstrong was appointed to the chair of chemistry at the London Institution in 1870.

[32] H. E. Armstrong, *Proceedings of the Chemical Society, 1* (1885), 40.

sociation Meeting at Aberdeen that summer.[33] He attributed special importance to the concept of molecular aggregates. Employing the notion of residual affinities, he insisted that it is rare for atoms to satisfy one another's affinities completely in simple substances. Atoms, he said, will readily aggregate, especially by the mutual attraction of negative radicles, and thus provide the special conditions under which chemical reactions can most readily take place. In solutions, aggregation is influenced by the interaction between solvent and dissolved substance. Armstrong remarked that this kind of aggregation seems to be involved in electrolysis. He noted that, while simple binary liquids like hydrochloric acid and water are not electrolytes, a mixture of them is. Furthermore, of the binary metallic compounds it is the least volatile (and therefore the most associated) that show electrolytic properties.

Armstrong's view of chemical action, although highly speculative, was compatible with the prevailing outlook in chemistry, and Armstrong could employ it in the explanation of chemical phenomena. But, as Armstrong recognized, it was not in accord with an increasingly popular conception of the nature of electrolysis being developed by a number of physicists. In his 1881 Faraday Lecture to the Chemical Society, Helmholtz had expounded a physical view of the relation between electrical and chemical phenomena; Armstrong developed his discussion from a criticism of Helmholtz' arguments.[34] Helmholtz had challenged chemists: "I shall consider my work of today well rewarded if I have succeeded in kindling anew the interest of chemists in the electrochemical part of their science."[35] Armstrong took up the gauntlet. He was keen to speculate on the rela-

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[33] H. E. Armstrong, *Report of the British Association* for 1885 (1886), pp. 945-964, especially pp. 952ff.

[34] Armstrong considered Helmholtz' lecture very influential, even though he disagreed with Helmholtz' reasoning. In 1896, he was to comment that "probably Helmholtz' Faraday lecture was the one Faraday lecture which was distinctly an original contribution, which we can be sure exercised a very important influence on the scientific world. A very large share of the attention which has been drawn to this subject of late years, which van't Hoff, Arrhenius, and others have developed to such an extraordinary extent, has arisen out of the Faraday lecture by Helmholtz. Not only here but in Germany also it attracted very great attention, and was of very much consequence." *Proceedings of the Chemical Society, 12* (for 1896), 28-29.

[35] H. von Helmholtz, *op. cit.* (note 18), p. 304.

tionship of chemical and electrical phenomena, but wished to argue from the considerations that *chemists* held to be most important.

While his criticism of Helmholtz was restricted to some of the assumptions at the basis of Helmholtz' argument, Armstrong attacked directly the ideas being developed by other German physicists. Armstrong's conception of electrolysis gave an essential role to aggregation, with the solvent playing a vital part in aqueous solution. The physicists, on the other hand, treated electrolysis as a process in which current is carried by the dissolved substance, and they explained it by the partial dissociation of the dissolved substance into parts that are even simpler than the chemical molecules. Armstrong was sure that their ideas were very bad chemistry. He thought it nonsense to suppose that the crucial stage in electrolysis was dissociation rather than association and to treat the water in aqueous solutions simply as a resisting medium. Armstrong felt that the chemically active nature of water showed that it must be involved in the electrolytically active components of the solution. He pointed out that the concentration of solutions that show maximum conductivity (as measured by Kohlrausch) is usually close to that of solutions that develop the maximum heat of solution (as measured by J. Thomsen).[36] The approximate agreement, he claimed, must surely be due to the maximum formation of electrolytically active aggregates. As he was later to argue at greater length, it is possible that it is not the dissolved substance but the water which is the actual electrolyte. He saw further support for his belief that chemical action and electrolysis were to be understood in the same (chemically inspired) terms in the work of Ostwald and Arrhenius relating the conductivity of acids to their chemical activity. As Arrhenius had not then explicitly stated that the active components of electrolyte solutions were dissociated solute ions, Armstrong did not appreciate that Arrhenius' result was intended to support an even more extreme theory of ionic dissociation.

In 1885 Armstrong sought the support of a physicist friend, Oliver J. Lodge. In 1884 Lodge had contributed a long paper, "On the Seat of the Electromotive Forces in the Voltaic Cell," to the British Association.[37] Lodge then turned to electrolytic phenomena

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[36] H. E. Armstrong, *Report of the British Association* for 1885 (1886), p. 957.

[37] O. J. Lodge, *Report of the British Association* for 1884 (1885), pp. 464–529; published also in *Philosophical Magazine* [5], *19* (1885), 153–190, 254–

at Armstrong's request, not because research in this area was one of his chief interests. As Lodge explained later,[38] Armstrong was rather hostile to the physical explanations of electrolysis in terms of dissociated ions and to their favorable reception by chemists. He wanted them scrutinized by a physicist. At the Aberdeen meeting in 1885, Lodge discussed the matter in a long paper, "On Electrolysis," but did not come to any firm conclusions.[39] A committee was then appointed to study the matter further. The committee on electrolysis in its physical and chemical bearings gave its first report to the British Association in 1886. Armstrong and Lodge were joint secretaries.

Before the work of the committee had appeared, Armstrong published an elaboration of his views.[40] He distinguished as electrically active: metals; simple electrolytes such as fused silver iodide; pseudo-dielectrics, which behave as dielectrics when pure, but as electrolytes when mixed with other members of their own class (such mixtures are "composite electrolytes"); dielectrics. The discussion was primarily of composite electrolytes. The reasoning can be illustrated by the uncomplicated case of hydrochloric acid and water. Each of the pure substances is a non-electrolyte—Armstrong refused to accept Kohlrausch's work suggesting a small conductivity for pure water—while a mixture of the two is an electrolyte. It seemed incomprehensible to Armstrong that anybody could seriously argue that the

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280, 340-365. Later additions and subsequent discussion were published in *Philosophical Magazine,* including a contribution from Ostwald, *Philosophical Magazine* [5], *22* (1886), 70-71.

[38] O. J. Lodge, *Past Years. An Autobiography* (London, 1931), pp. 190-191. Lodge's recollection is slightly misleading; at that stage Armstrong's opposition was directed mainly against the physicists who were developing Clausius' theory of dissociation. Arrhenius became the main opponent a little later.

[39] O. J. Lodge, *Report of the British Association* for 1885 (1886), pp. 723-772. Lodge's correspondence with Armstrong makes it clear that he was not able to put much time into preparing the paper. He accumulated materials and theories and then told Armstrong that he could not manage the "monotheism" of Armstrong's unitary chemical theory of electrolysis. He considered that the matter needed looking at from *all* points of view. Armstrong Papers (Imperial College Archives): letters from O. J. Lodge, first series, nos. 423-428 (May to December 1885).

[40] H. E. Armstrong, "Electrolytic Conduction in Relation to Molecular Composition, Valency and the Nature of Chemical Change: Being an Attempt to Apply a Theory of Residual Valency," *Proceedings of the Royal Society, 40* (1886), 268-291.

dissociated atoms of hydrochloric acid are the active species, while the water is merely the mechanical means of separating the ions. Since only the mixture is conducting, it seemed more likely to him that the active material is a kind of molecular aggregate of acid and water. An analogy could be drawn between electrolyte solutions and metal alloys, for both show some of the features of chemical combination yet lack definite proportions. The analogy provides a counter example to which Armstrong frequently returned in his later papers. Armstrong noted that a very small percentage of lead can make gold quite brittle and urged that lead can have this effect only if each atom of lead affects larger molecular aggregates of gold. He expected that the formation of a simple compound with contrasting properties would lead to simple additive changes in physical properties. The position Armstrong maintained throughout the later debates was now established. He always stressed the importance of association and insisted that water is too reactive to be ignored in solutions. He drew support for his views from chemical analogies between solutions and other substances.

I want now to return to the main forum of debate on electrolysis, the British Association committee on electrolysis. In the *Report of the British Association* for 1886, Lodge published an important collection of discussions and abstracts of papers and letters, including the latest work by continental scientists. Arrhenius' ideas up to January 1887 were well represented. Lodge included his correspondence with Arrhenius and a long critical abstract he had made of Arrhenius' dissertation of 1883. Lodge was especially appreciative of the second, theoretical part of the dissertation in which Arrhenius had suggested that at all times (and not just when a current is flowing) a substantial proportion of the molecules of an electrolyte are active, both electrolytically and chemically. Arrhenius believed, but had not dared to say until 1887, that the active molecules were in fact dissociated in the manner Clausius had suggested.[41] In commenting on Arrhenius' "Chemical Theory of Electrolytes" Lodge had written: "But it is a bigger thing than this: it is really an attempt at an electrolytic theory of chemistry."[42] He was appreciative of Arrhenius' theory but not committed to it.

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[41] A fuller discussion of Arrhenius' ideas and their development is included in R. G. A. Dolby, *op. cit.* (note 15).

[42] O. J. Lodge, *Report of the British Association* for 1886 (1887), p. 362.

Most of the letters and abstracted papers of overseas authors in the 1886 *Report* were part of a three way discussion between Arrhenius, Kohlrausch, and E. Bouty on the nature of electrolytic conductivity, especially under the simplifying circumstances of extreme dilution. The argument interested physicists rather than chemists. Two problems stimulated the debate over the conclusions to be drawn from experiment: the determination of the conductivity of pure water, which became a major problem as investigations of dilute solutions increased, and the self-induction resulting from the use of alternating current in conductivity measurements. Kohlrausch and Arrhenius disagreed as to whether or not a connection could be assumed between the electrical conductivity and the internal friction of a solution. Arrhenius argued that the most important explanatory factor is the proportion of an electrolyte in the active form, and Bouty claimed that for most electrolytes (those we call "normal") the mobility of each ion is about the same at extreme dilution. There were also British contributions to the committee report, consisting mainly of experimental studies checking the assumptions and assertions of the continental scientists.

In the *Report of the British Association* for 1887 the committee continued the discussion. Again Lodge was the editor of the printed report. The most interesting items in the report are his comparison of the views of Arrhenius and Armstrong, together with a reply by Armstrong.[43] Although Lodge had entered the discussion of electrolysis at Armstrong's request, his treatment was not very critical of Arrhenius. In Lodge's opinion, Arrhenius had provided a perfectly orthodox view of the nature of electrolysis which was of special interest in its application to chemistry. Lodge clearly identified Arrhenius' "active" molecules with the dissociated molecules of Clausius.[44] Lodge's criticisms of Armstrong's views were more severe. Writing as a physicist, he avoided commenting on the chemical features of Armstrong's ideas, but pointed out their physical difficulties. For example, he stressed that any chemical theory that assumes that the electromotive force produces the changes necessary for the passage of electric current should be able to explain why a very small electromotive force is sufficient.

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[43] *Report of the British Association* for 1887 (1888). Lodge, pp. 351–353; Armstrong, pp. 354–357.

[44] O. J. Lodge, *Report of the British Association* for 1887 (1888), p. 351.

In his reply, Armstrong suggested that the experimental results of Arrhenius' work should be separated from the theoretical conclusions.[45] He insisted that Arrhenius was unjustified in stressing dissociation, when association is so important in chemical reactions. He argued for the importance of third substances in chemical reactions, suggesting that we still have much to learn about simple chemical changes. At this early stage in the discussion, Armstrong was still prepared for compromise, though recognizing the difficulties of reconciling chemical and physical considerations. "In conclusion, I would add that I urge these pleas on behalf of my hypothesis with the greatest diffidence, feeling that I am unfortunately unable to fully appreciate the force of the mathematical and physical arguments."[46] After stressing the uncertainties of the current state of understanding of intramolecular structure, he went on: "It is impossible at present to quantify peculiarities and relationships which are patent to the chemist, but these must be taken into account; and for this reason it is all-important that chemists and physicists should cooperate."[47] Armstrong and Arrhenius continued to exchange criticisms after 1887.

The Early Ideas on Solution of P. S. U. Pickering

One of the most prominent, though not authoritative, figures in the debates of the 1880's and 1890's was P. S. U. Pickering.[48] Pickering was a man of private means who showed great independence of outlook. One of his first published papers had been a criticism of a view expressed by his tutor at Oxford.[49] Pickering did his experimental studies by himself, without any laboratory assistant

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[45] As previously explained, Armstrong had earlier argued that Arrhenius' and Ostwald's data supported his theory.

[46] H. E. Armstrong, *Report of the British Association* for 1887 (1888), p. 357.

[47] *Ibid.*

[48] The most useful biographical source on Pickering is T. M. Lowry and E. J. Russell, *The Scientific Work of the Late Spencer Pickering F.R.S.* (London, 1927). The correspondence between Arrhenius and Ostwald reprinted in *Aus dem wissenschaftlichen Briefwechsel Wilhelm Ostwalds,* ed. Hans-Günther Körber (Berlin, 1969), pt. 2, suggests that Pickering was the English opponent of the new theory who was the most trouble to the Ostwald school.

[49] E. J. Russell, *Journal of the Society of Chemistry and Industry, 39* (1920), 448R. The tutor was W. W. Fisher; the paper appeared in *Journal of the Chemical Society, 33* (1876), 409.

or attendant; he published only a very few joint papers, mostly based on the work of his women students at Bedford College, London.[50] He developed a number of highly original methods, some of which might have been more valuable had he discussed them with another scientist in their development. Sometimes he based them on highly doubtful assumptions. He had the odd habit of giving his experimental results with more figures than he considered reliable. The apparent overprecision of his figures misled many of his opponents into thinking that he was ignorant of the errors in his work and naive of the uses of mathematics in chemistry.[51]

Pickering was readily drawn into controversy, and his discussions of the nature of solutions are not the only example of his polemical exchanges. Pickering's ideas about solution developed out of his studies of sulphates and of sulphuric acid, in which a great variety of chemical and physical methods were used to draw chemical conclusions. Independently of Armstrong[52] and of E. J. Mills[53] he had developed a theory employing the notion of residual valences to explain such molecular aggregate compounds as hydrated salts and double salts.[54] In 1886, he published a series of thermochemical papers, building on the work of Thomsen and Berthelot. Among his studies were experiments investigating the heat changes in dilutions of solutions. The irregularities in the curves obtained by plotting heat of dissolution against concentration for hydrated salts at various temperatures led him to conclude that different hydrates were being formed in the solutions at various temperatures.[55]

In the same year he published a paper on water of crystallization which discussed the difficulties in the general notion of hydration and water of crystallization.[56] When Tilden criticized the experimental basis of this paper,[57] Pickering accepted some of the criti-

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[50] *Ibid.*

[51] See the discussion by T. M. Lowry in T. M. Lowry and E. J. Russell, *op. cit.* (note 48), pp. 8–9.

[52] H. E. Armstrong, *Proceedings of the Chemical Society, 1* (1885), 40; *Report of the British Association* for 1885 (1886), pp. 945–964.

[53] E. J. Mills, *Philosophical Magazine* [4], *28* (1865), 364.

[54] P. S. U. Pickering, "Atomic Valency," read to the Chemical Society in December 1885. *Proceedings of the Chemical Society, 1* (1885), 122–125; published in full as a pamphlet in 1886.

[55] P. S. U. Pickering, *Journal of the Chemical Society, 49* (1886), 260–311.

[56] P. S. U. Pickering, *Journal of the Chemical Society, 49* (1886), 411–432.

[57] W. A. Tilden, *Proceedings of the Chemical Society, 2* (1886), 198–199.

cism and repeated the work.[58] His comment in accepting the force of the criticism revealed the problems of his method of working in relative isolation. "A worker is no doubt apt to be misled by having had for a long time too close and, perhaps, a one-sided view of his own work, but something must also be subtracted from the critic's opinion, from the fact that he has not followed the work in the whole of its progress, especially so when he himself has performed work of a similar nature, but under totally different conditions, and with different and comparatively imperfect instruments."[59] Even when his isolated reasoning had not led him astray, Pickering's work was often so different from that of his fellow scientists that it was not clearly understood or appreciated. The intuitive insights that the experimental worker gains from intimate experience of his materials can only be communicated to fellow workers with very similar interests.

In 1886, in the course of his discussion of hydration and water of crystallization, Pickering came into conflict with W. W. J. Nicol. Nicol had argued[60] that water of crystallization does not exist in solution at all. The two men carried their debate through a number of meetings of the Chemical Society and published rival experimental papers in *Philosophical Magazine.*[61]

A convenient summary of Pickering's position before 1887 is contained in a paper read to the British Association in 1886.[62] He described the "hydrate theory of solution" as the view that there were chemical compounds of definite proportions between solvent and solute; against this he argued that solutions contain molecular compounds of indefinite proportions, held together by residual valences. When a solid dissolved, the molecular aggregates of the solid state were broken down into simpler forms (which absorbed heat) and replaced by aggregates with the liquid (which evolved heat).

Another aspect of Pickering's work which was soon to lead him

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[58] P. S. U. Pickering, *Journal of the Chemical Society, 51* (1887), 290-356.

[59] *Ibid.,* p. 291.

[60] W. W. J. Nicol, *Philosophical Magazine* [5], *16* (1883), 121-131; *18* (1884), 179-193.

[61] For examples of their polemical exchanges, see Nicol, *Proceedings of the Chemical Society, 2* (1886), 220-222; *3* (1887), 40-42 (the papers and the subsequent discussion are reported); *Chemical News, 54* (1886), 191; *Journal of the Chemical Society, 51* (1887), 389-396; and Pickering, *Journal of the Chemical Society, 51* (1887), 75-77.

[62] P. S. U. Pickering, *Chemical News, 54* (1886), 215-217.

into direct opposition to the theories of the Ostwald school of physical chemistry was his explanation in 1887 of heats of neutralization.[63] He employed his idea of residual valences, arguing that because the affinities of acids and bases are only partially saturated, they readily combine with one another to form molecular aggregates.

In 1887 and the years following, the main direction of Pickering's experimental work was to be reoriented by Mendeleef's hydrate theory. But before considering the further development of Pickering's career, the early impact of the work of the Ostwald school should be discussed.

3. EARLY STAGES OF THE CONFRONTATION, 1887-1888

The Penetration of the Ideas of the Ostwald School into Britain and Early Reactions of its British Supporters

The theories of van't Hoff and Arrhenius and their development within the Ostwald school were quickly regarded, by supporters and opponents alike, as a unified theory. I shall frequently have occasion to refer to the unified theory below and will use the suitable, neutral label "the Ostwald school theory." There is adequate justification for using Ostwald's name rather than that of Arrhenius or van't Hoff, because, as one commentator wrote, "Prof. Ostwald is one of the warmest supporters of the physical theory, and has done more, perhaps, than any other, to make it what it now is."[64] Scientists at the time referred to the theory as "the new theory of solution" or "the physical theory of solution," or by some longer locution. Their briefer labels, however, often had polemical connotations.

The theory of the Ostwald school gained its first exposure in England through the direct intervention of some of the continental enthusiasts, and through the expositions of a very limited number of early British sympathizers. Arrhenius' theory was given very early publicity. Arrhenius had been in contact with the British Association electrolysis committee, and his 1887 theory was first made public in a letter to the committee which was circulated among the members.[65] M. M. P. Muir, a Cambridge chemist, best known as a textbook writer and historian of chemistry, had been giving sympa-

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[63] P. S. U. Pickering, *Journal of the Chemical Society, 51* (1887), 593-601.

[64] J. W. Rodger, *Nature, 45* (1891), 193.

[65] See note 21.

thetic expositions of Ostwald's work since 1879. In 1887, Ostwald had given van't Hoff's theory of solutions in the second volume of his influential *Lehrbuch der allgemeinen Chemie,* and in 1889, Muir had made extensive use of Ostwald's *Lehrbuch* in the second edition of his *Principles of Chemistry.* Muir's influence, however, was mainly through his textbooks and the only early supporter of the Ostwald school theory among leading British research chemists was William Ramsay.[66]

Ramsay had done a little experimental work on solutions since the mid-1880's, and when Raoult's method of determining molecular weights in solution became the subject of active British discussion at the meeting of the Chemical Society in May 1888, Ramsay was among those presenting papers employing the method. Ramsay was equally enthusiastic about van't Hoff's theory, which built on Raoult's method. On June 9, 1888, he read a translation of van't Hoff's 1887 paper to the Physical Society.[67] At about the same time, Ramsay began corresponding with Ostwald. He soon caught Ostwald's enthusiasm for Arrhenius' theory and for the possibilities of the new approach to the study of solutions. Later he became a close friend of Ostwald.

Ramsay had to overcome some confusions before he clearly understood all the implications of the Ostwald school theory, in particular the electrolyte dissociation theory. An early source of difficulty for a great number of chemists was the distinction between the dissociated ions of an electrolyte and the same substance in the free state—between an ion of sodium and a free sodium atom, for example. Arrhenius, in his 1887 memoir, had stressed that in solution the dissociated atoms have a high electric charge and so cannot easily be separated from one another. But his notation did not at first indicate the difference. Thus, in a note to the British Association,[68] Arrhenius wrote about water being very slightly "dissociated into H and OH," without indicating immediately that the separate parts have high electrical charges. Muir in his 1889 discussion of

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[66] There are two book length biographies of Ramsay: W. A. Tilden, *Sir William Ramsay: Memorials of his Life and Work* (London, 1918); M. W. Travers, *A Life of Sir William Ramsay* (London, 1956).

[67] Ramsay's translation was published in *Philosophical Magazine* [5], *26* (1888), 81-105.

[68] S. A. Arrhenius, *Report of the British Association* for 1888 (1889), p. 353.

Arrhenius' theory[69] repeated Ostwald's summary of the distinction (but pointed out that as we do not yet know the significance of an electric charge on an ion, Arrhenius' distinction does not *explain* the difference between electrolyte ions and the products of gaseous dissociation). Ramsay was initially far more confused, as M. W. Travers shows in his biography.[70] For example, when Ostwald wrote to him describing an experiment to demonstrate the electrostatic production of ions, Ramsay sent on the letter to Lodge (as Secretary to the British Association electrolysis committee), referring to it as an argument for the existence of free atoms of potassium and chlorine (rather than free ions). Ostwald's letter was published in *The Electrician,*[71] a journal that had been selected that year as a suitable medium for communications among the electrolysis committee between the annual meetings of the British Association. In the letters that were published in subsequent issues, a number of confusions became evident. Lodge, for example, criticized the experiment when he failed to replicate it. Ostwald replied that Lodge should have read the original paper on which the letter to Ramsay was based; he would then have seen that, far from being the *crucial* experiment that Ramsay had thought it to be, it was an "ideal experiment." However, a comparable experiment had subsequently been carried out.[72]

Armstrong's Reaction to the Ostwald School Theory, 1888-1889

In 1889 the British Association published Arrhenius' "Reply to Professor Armstrong's Criticisms Regarding the Dissociation Theory of Electrolytes."[73] The reply, written soon after van't Hoff and Arrhenius had developed their theories, made a point by point criticism of Armstrong's ideas and also of the work of Armstrong's student, H. Crompton. Armstrong appended two notes, commenting on the reply, and giving a general discussion of the current state of

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[69] M. M. P. Muir, *A Treatise on the Principles of Chemistry,* 2nd ed. (Cambridge, Eng., 1889), p. 462.

[70] M. W. Travers, *A Life of Sir William Ramsay* (London, 1956), pp. 89-93.

[71] W. Ostwald, *The Electrician, 22* (1889), 493-494.

[72] The exchange took place in *The Electrician, 22* (1888-1889), 493-494, 676, 691-692; *23* (1889), 30, 44; ending with an abstract of a paper in which an actual experiment was detailed in *23* (1889), 300-301, 323.

[73] S. A. Arrhenius, *Report of the British Association* for 1888 (1889), pp. 352-355.

ideas on electrolysis.[74] Arrhenius' note and the discussion by Armstrong show the sorts of misunderstandings that may be associated with the early stages in the confrontation and development of theories, and which are most naturally described as "incommensurable." While Arrhenius was developing a theory that built only on the quantitative phenomena of dilute solutions, Armstrong was evaluating theories that made the most sense in terms of the general understanding chemists had of chemical reactivity. Not dilute solutions, but solutions with comparable numbers of solvent and solute molecules appeared to be the most natural as a basis for theoretical study. By Armstrong's standards, the behavior of dilute solutions was irregular and complex, the Ostwaldians making far too much out of idealized simplifications of solution behavior. Arrhenius clearly believed that the role of water in electrolysis was minimal, and that, when alcohol was substituted for water and solvent, the main reason for the decrease of the conductivity of the electrolyte was the higher resistance of alcohol to the passage of ions. Armstrong immediately found such a view of the role of the solvent implausible. Indeed the ionists increasingly abandoned the view of the solvent as inert. At this early stage of the debate, the position that each side developed was—by later standards—frequently based on unreliable experiments and buttressed by implausible or speculative claims. It was consequently easy for negative attitudes to form and harden over issues that to later scientists did not seem to merit so much fuss.

In the discussion that Armstrong, as chemical secretary of the electrolysis committee, added to the 1888 report after the summer meeting, he criticized both Arrhenius' theory and, indirectly, van't Hoff's theory of solution. Armstrong was able to refer to J. J. Thomson's *Applications of Dynamics to Physics and Chemistry* (1888), one of the first English responses to the theories of van't Hoff and Arrhenius. Thomson accepted van't Hoff's conclusion that the work of Pfeffer and Raoult showed that the molecules of a dissolved substance exert the same pressure as they would in the gaseous state for equal volume and equal temperature.[75] But he did not accept that knowledge of the structure of the molecule of the solute could be

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[74] H. E. Armstrong, *Report of the British Association* for 1888 (1889), pp. 355-356, 356-360.

[75] J. J. Thomson, *Application of Dynamics to Physics and Chemistry* (London, 1888), p. 175.

derived from the van't Hoff relationship. Thomson's treatment suggested that any physical influence that would change the mean Lagrangian function of the water on the two sides of a semipermeable membrane (such as the evolution of heat on dilution) would lead to the observed relationship of osmotic pressure and concentration.[76] More studies were needed to investigate different solvents and to make more use of the relationship with absolute temperature. Thomson was more critical of Arrhenius' dissociation theory, although he did not mention it by name. He wrote:

> Indeed the theory has recently been stated that in dilute aqueous solutions the dissolved acid or salt is in most cases dissociated and that to a very considerable extent; thus it has been stated that in dilute solutions of HCl as much as 90 per cent of the acid is dissociated. The reasons given for this conclusion do not seem to me to be very convincing, and the experimental results on which they are based seem to admit of a different interpretation. The supporters of this theory urge that for the salt to produce the effect which in some cases it does, it is necessary to suppose that the molecules of the salt exert a greater pressure than they would if they occupied the same volume at the same temperature when in the gaseous condition. This reasoning is founded on the assumption that all the effects due to the dissolved salt may be completely explained merely by supposing the volume occupied by the solvent to be filled with molecules of the salt in the gaseous condition. Now though we may admit that the salt does produce the effects that would be produced by this hypothetical distribution of gaseous molecules, still it does not follow that these are the only effects produced by the salt. The salt may change the properties of the solvent and the effects attributed to the dissociation of the molecules may in reality be due to this change.[77]

Naturally, Armstrong was pleased that a physicist as eminent as J. J. Thomson should come to this conclusion; as part of his critique of the dissociation hypothesis he quoted part of the above passage. Armstrong went on to say that dissociation of gaseous hydrogen chloride only occurs to a tiny extent at temperatures of 1300–1500°. "That a gas of such stability should be almost entirely dis-

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[76] *Ibid.*, pp. 189–190.
[77] *Ibid.*, pp. 212–213.

sociated by mere dissolution in water is to me incredible."[78] He summarized his general opinion of the advocates of the dissociation theory in a final paragraph.

> Arrhenius, Ostwald and others regard both electrical conductivity and chemical activity as similarly conditioned by the degree of dissociation—in their opinion, very active substances, such as sulphuric acid, are to a large extent dissociated in solution; inert substances, such as acetic acid, are but to a slight extent dissociated in solution. But the adherents of this school all overlook the fact that there are two distinct theories of chemical interchange: the older theory that the interacting molecules initially combine and that the resulting complex then splits up—which may be termed the integration theory; and the more modern dissociation theory. I am led to regard the former as the more comprehensive and generally applicable, especially as comparatively so few compounds are electrolytes, and I venture to think that physicists also would incline to my belief if they would assume a somewhat different mental attitude towards the facts, and would seek to fully unravel the entire series of changes involved in chemical interactions.[79]

Armstrong's remarks to the electrolysis committee on van't Hoff's theory were brief and limited to attacking its status as a buttress of the Arrhenius theory. He had, however, set out his view of Raoult's method of determining molecular weights more fully in a paper and in discussions at the Chemical Society in 1888 and 1889. As secretary of the society, he reported his own comments thoroughly. Although he appreciated the law expressing the analogy between the osmotic pressure of the solutions and the pressure of an ideal gas, labelling it as a "masterly generalisation,"[80] he doubted that very much could be inferred from it as to actual molecular structure. In particular, he doubted that Raoult's method reliably gave actual molecular weights, or that it gave acceptable evidence that electrolytes are really dissociated. In his reasoning he invoked the case of the atomic heats of the elements. By using Dulong and Petit's law, we can infer something about the *atomic* heat of the elements, even though our measurements are actually made on *molecular* sub-

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[78] H. E. Armstrong, *Report of the British Association* for 1888 (1889), p. 356.

[79] *Ibid.*, p. 357.

[80] *Ibid.*, p. 356.

stances. Similarly, even though solutions might be made of large molecular aggregates, variations in the behavior of these aggregates might, by Raoult's method, tell us something about the chemical units of which they are composed. If this was so, we could not legitimately infer that electrolytes, for example, are dissociated into separate atoms, or that colloids have very high molecular weights.[81]

It should be noted that Raoult's work on molecular weights put Armstrong's theory into a crisis situation. For the simplest interpretation of the quantitative studies of freezing point depression was that the molecular weights of most substances in solution are very close to their fundamental formulae. Armstrong blurred the issue; he could not really explain why there should be such a sharp quantitative relationship between freezing point depression and fundamental formulae. It was an argument for electrolyte dissociation that he could not easily evade.

Mendeleef's Hydrate Theory and its Critics 1887–1889

An important development of 1887 from the point of view of the British opponents of the Ostwald school theory was a method suggested by Mendeleef to study hydration in solution. Basing it on Berthelot's similar but less precisely expressed ideas,[82] Mendeleef presupposed that all the water in a solution is combined with the dissolved substance and that there will be changes in the solution properties at different concentrations as one hydrate is replaced by another. In his paper[83] Mendeleef found that, although a plot of the density of a solution against the percentage composition gave a relatively continuous curve, the differential of the density gave a series of straight lines when plotted against composition. Each of these straight lines was represented as due to varying proportions of two hydrates in equilibrium. As the percentage concentration was increased, the points of discontinuity indicated where a higher hydrate had disappeared, leaving a single hydrate containing a lower proportion of water. As concentration increased still further, an increasing

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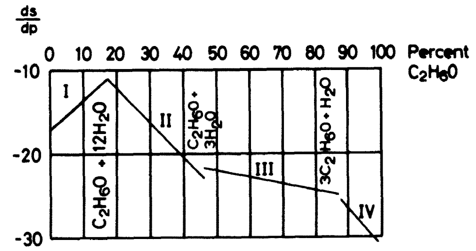
[81] H. E. Armstrong, *Proceedings of the Chemical Society, 5* (1889), 42–43, 98, 109–113.

[82] P. S. U. Pickering, "Solutions," in *Watts Dictionary of Chemistry,* ed. M. M. P. Muir and H. F. Morley, revised ed. (London 1894), *4,* 492.

[83] The English version of Mendeleef's paper appeared in the *Journal of the Chemical Society, 51* (1887), 778–782.



Graph of the rate of change of specific gravity with change in percentage composition of an ethanol-water mixture.

amount of the next lower hydrate appeared in the solution.[84] (See graph.) The method was in principle applicable to any property successive hydrates displayed differently; their succession could be revealed by manipulating the basic curve of solution property against concentration in a variety of ways.

Mendeleef's theory was taken up enthusiastically by some British chemists but was also criticized by Arrhenius and other members of the Ostwald school at early stages in its development. It had to develop in the face of fierce opposition.

Perhaps the first English chemist to take up the method was Armstrong's student Crompton.[85] Armstrong added a note to Crompton's paper,[86] recapitulating his own position and commenting enthusiastically on the support that Crompton's use of the method had given his own theoretical but qualitative arguments. Armstrong welcomed the method as a general method for demonstrating the nature and significance of hydration in solution, but he made no experimental use of Mendeleef's method after this time. It was Pickering who developed it into a major research program. He had remarked on the importance of the method when Crompton's paper was first read,[87] and he was soon applying it in his experimental work.

In an early paper exploring the method, Pickering applied it to his studies of the heat of dilution of solutions.[88] Armstrong had become much more critical of the method, commenting after the reading of Pickering's paper that many chemists would probably hesitate to

[84] The graph is from D. I. Mendeleef, *Journal of the Chemical Society, 51* (1887), 780.

[85] H. Crompton, *Journal of the Chemical Society, 53* (1888), 116-125.

[86] H. E. Armstrong, *Journal of the Chemical Society, 53* (1888), 125-133.

[87] P. S. U. Pickering, *Proceedings of the Chemical Society, 3* (1887), 128.

[88] P. S. U. Pickering, *Proceedings of the Chemical Society, 4* (1888), 35-37.

accept Mendeleef's explanation until evidence of the existence of definite hydrates had been obtained by investigating a greater range of properties for the nature of their dependence on the composition of the solution. If measurements on many properties indicated the same changes in hydration, Mendeleef's interpretation would come closer to being conclusive. Armstrong also pointed out, however, that the method was unlikely to be definitive, as there could be more than two hydrates present in a solution at a given concentration.[89] Very soon Pickering, too, was dissatisfied with Mendeleef's use of the method, particularly as the data Mendeleef had used did not lead to his graphical results when replotted. Pickering also came to agree with Armstrong that there might be more than two hydrates of a solute present in a solution of a given concentration.[90] Nevertheless, Pickering was convinced that the irregularities in the curves of variation of solution property with dilution *did* indicate the formation of successive hydrates. Pickering was to develop the method experimentally in a series of papers in the early 1890's, but his work continually was criticized, particularly by members of the Ostwald school.

As early as 1889 Arrhenius published a paper in *Philosophical Magazine* that was critical of Mendeleef's idea and its English supporters.[91] He attempted to show that the method was fallacious, depending for its conclusions on the magnification of experimental errors. He argued that the phenomena of dilute solution, which Mendeleef had wished to explain in terms of hydration, were quite satisfactorily accounted for by the Ostwald school theory. There could only be a very small amount of hydration in very dilute solutions, and the close agreement of the Ostwald school theory with experimental data implied that what hydration there was could not vary significantly with concentration.

Since Pickering's work had at that stage only appeared in abstract,[92] he complained that Arrhenius was premature in his criticism, and that when the paper was published in full, it would be seen that it was Arrhenius who was mistaken.[93] The first exchanges between Pickering and Arrhenius were characterized by the mixture of

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[89] H. E. Armstrong, *Proceedings of the Chemical Society, 4* (1888), 37.

[90] See for example P. S. U. Pickering, *op. cit.* (note 82), p. 493.

[91] S. A. Arrhenius, *Philosophical Magazine* [5], *28* (1889), 30-38.

[92] The abstract was in *Chemical News, 60* (1889), 278.

[93] P. S. U. Pickering, *Philosophical Magazine* [5], *28* (1889), 148. The full paper appeared eight months after Arrhenius' criticisms. *Journal of the Chemical Society, 57* (1890), 64-184.

acrimony and argument at cross-purposes that is typical of early stages of scientific debate. Each side thought that the other used a misleading selection of experimental results and processed its results with a method that presupposed the conclusion being sought. The hydrationists preferred to study concentrated solutions, while the Ostwald school restricted themselves to dilute solutions. But the differences were most marked in the methods of treating the experimental data. Arrhenius was seeking simple quantitative regularities and so was encouraged to smooth the results heavily so as to indicate only the broadest patterns in the data. Pickering, on the other hand, was using quantitative study only to back up qualitative arguments about the complexity of solutions. In contrast, Arrhenius suggested that since Mendeleef, Crompton, and Pickering had not agreed on the solution compositions at which they found discontinuities in their curves (and so had concluded that different hydrates were present in solution), they were measuring only their own experimental errors. The oddest feature of Pickering's method was that, following Crompton, in order to get a set of straight lines, he used the *second* differential of the curve obtained by plotting solution property against percentage composition. And as the initial graphs were not regular enough, he obtained his second differentials by smoothing the curve of the first differential. Arrhenius insisted that any irregularities that remained in the second differential were merely the result of insufficient smoothing at the intermediate stage.[94] Pickering was heated in his reply.

> Professor Arrhenius attacks me on the subject of this smoothing of the curves, remarking that "if Mr. Pickering had 'smoothed' his curves properly, he would evidently have removed these angular points or sudden changes of curvature." The question hinges on the interpretation of the word "properly." Professor Arrhenius seems to think that the "proper" amount of smoothing to be made is such that all sudden changes of curvature should be obliterated; and this too in an investigation the sole object of which is to ascertain whether there are such sudden changes or not. I must beg to differ with him. The "proper" amount of smoothing I take to be such as will allow but little more error in the experimental points than the known errors of the determinations, or than that which seems to be the probable error according to the irregularities of consecutive points in the figure. If with such smoothing we are led

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[94] S. A. Arrhenius, *Philosophical Magazine* [5], *28* (1889), 37-38.

> to conclusions which are obviously false, or which are at variance with the results obtained from independent sources, then and only then must we admit some further source of error, and increase the smoothness of our drawings.[95]

Pickering remained quite unrepentant during the 1890's in his use of the method, although he came to prefer the direct detection of irregularities in the curve of solution properties by fitting a bent rule to the graph of the original experimental data.[96]

In 1889, Pickering felt that he had achieved a major triumph for his method. He discovered that on cooling his solutions he was occasionally able to crystallize out the hydrate that his curve-fitting techniques had suggested should be present. The first success was $H_2SO_4,4H_2O$, a previously unknown hydrate.[97] Thus, in 1890, Pickering felt prepared to go into the offensive against the Ostwald school. In papers contributed to the *Journal of the Chemical Society,* to *Philosophical Magazine,* and at the meeting of the British Association in Leeds, he expounded his hydrate theory and attacked what he saw as the weak points of the Ostwald school theory.[98]

4. THE LEEDS MEETING OF THE BRITISH ASSOCIATION IN 1890

The Leeds meeting was important in many strands of the debate on the theory of solution and deserves a full discussion. Under the stimulus of the disagreements within the electrolysis committee of the British Association, a joint session of the physics and chemistry sections was organized at the 1890 meeting. It was labelled a discus-

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[95] P. S. U. Pickering, *Philosophical Magazine* [5], *29* (1890), 429.

[96] The use of a bent rule, or lathe, was elaborated in later papers in the face of much criticism. A full and sympathetic discussion of the issue is given by T. M. Lowry in T. M. Lowry and J. Russell, *op. cit.* (note 48), pp. 57-80.

[97] The first announcement was made in *Chemical News, 60* (1889), 68.

[98] See in particular, P. S. U. Pickering, *Journal of the Chemical Society, 57* (1890), 331-369, in which he explained the implications of the crystallization of previously unknown hydrates of sulphuric acid and began the attack on the Ostwald theory. In *Philosophical Magazine* [5], *29* (1890), 427-434, Pickering replied to Arrhenius' criticisms. In *Philosophical Magazine* [5], *29* (1890), 490-501, he attacked an obsolete version of Raoult's method of deriving molecular weights from measurements of freezing point depressions and then criticized the aspects of the Ostwald theory that he mistakenly thought were based on this work. At the British Association meeting Pickering presented his paper, "The Present Position of the Hydrate Theory of Solution," *Report of the British Association* for 1890 (1891), 311-322.

sion "on the theory of solution and its connection with osmotic pressure." The leading experts from Europe were invited, and although Arrhenius could not come (a note from him was read by Ostwald's British student, James Walker) Ostwald and van't Hoff attended. Van't Hoff warned Ostwald before the meeting that he had heard that they would be attacked; he should bring his dictionary.[99] Most of the discussion took place in the sessions on Saturday September 6th, Monday September 8th, and the informal meetings in between.

Saturday: G. F. FitzGerald

On Saturday the electrolysis committee reported. Among the papers read was a discussion of electrolytic theories by the Irish physicist, G. F. FitzGerald.[100] FitzGerald was to lead the opposition of British physicists to the Ostwald school theory. He had a greater reputation among his colleagues than that which history has left him. In part this was because he was at his most impressive in critical discussion; it was then that he earned great respect for his opinion. A number of the physicists who were not actively involved in the debate over the theory of solutions came to distrust those features of the new theories of physical chemistry that he had commented on. FitzGerald was also a friend of Ramsay and an acquaintance of Armstrong, and his opinion was taken seriously by the chemists.[101] He had been a member of the electrolysis committee since its creation in 1887 and was its chairman in 1890. At the Saturday session his paper was introduced as being "in preparation for a discussion on the extreme dissociation theory of solution supported by these recent investigations [the works of Ostwald, van't Hoff, and Arrhenius], as opposed to the more customary view held by chemists, and having reference also to Dr. Armstrong's views of residual affinity. . . ."[102] FitzGerald favored a modification of the classical Grotthus theory of electrolysis. If, when polarized by an electromotive force, the molecules draw one another apart at a rate proportional to the polarization, the Grotthus theory can explain why Ohm's law holds for

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[99] Letter from van't Hoff to Ostwald, 19 September 1890, in Ostwald's correspondence, *op. cit.* (note 48), pp. 226–227.

[100] G. F. FitzGerald, *Report of the British Association* for 1890 (1891), pp. 142–144.

[101] See, for example, the introduction to *The Scientific Writings of the Late George Francis FitzGerald,* ed. J. Larmor (Dublin, 1902).

[102] *Report of the British Association* for 1890 (1891), p. 142.

very small currents in electrolysis.[103] The limits of modification were clear, however, for "there seem to be very serious difficulties in supposing that uncombined atoms are for any time free in the liquid. . . ."[104] FitzGerald considered it plausible that, as Armstrong had suggested, double decomposition takes place by association, but the matter should be investigated further. He went on: "There are some other phenomena that have been explained upon the supposition that free atoms are gadding about in a liquid. Such are the lowering of the boiling [sic] and freezing points of solutions of salts, and their effect on osmotic pressure."[105] He then went on to sketch how these effects might be a product of the nature rather than the number of the molecules of an electrolyte. If the electrolyte molecules were more easily polarized, that is, turned in an effective direction more often than other molecules, they might be able to produce twice the osmotic pressure. And changes in boiling and freezing points were to be explained by exceptional effects of electrolytes on the normally constant molecular affinity of salts for water.

On Saturday also, a paper was presented by W. N. Shaw, "Report on the Present State of our Knowledge in Electrolysis and Electrochemistry."[106] The paper was a half digested review of the literature in which no clear conclusions were drawn as to the claims of the two main sides.

Informal Discussion between Saturday and Monday

It was in the informal discussion, especially on Saturday and Sunday, that the debate over the theory of solutions became liveliest. As Ostwald told the absent Arrhenius, FitzGerald brought up a whole series of objections on Saturday night and on Sunday; Ostwald and van't Hoff talked to him all day.[107] The best account of the informal discussion was given by the Leeds professor of chemistry, Arthur Smithells, in a contribution to Ramsay's biography.

> The Leeds Meeting of the British Association in 1890 is memorable as marking the first Ionic Invasion of England in the persons of

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[103] G. F. FitzGerald, *Report of the British Association* for 1890 (1891), p. 143.

[104] *Ibid.*, p. 143.

[105] *Ibid.*

[106] W. N. Shaw, *Report of the British Association* for 1890 (1891), pp. 185–223.

[107] Letter from Ostwald to Arrhenius, 23 September 1890, in Ostwald's correspondence, *2*, *op. cit.* (note 48), p. 71.

van't Hoff and Ostwald. It was, of course, in the early days of the ionic theory of solution and I remember Ostwald remarking that the united ages of himself, van't Hoff and Arrhenius were less than a hundred years.

Ramsay and Ostwald met for the first time as fellow-guests in my house, which became accordingly a sort of cyclonic centre of the polemical storm that raged during the whole week. No meeting within my experience has more fully illustrated the fact that the most interesting and stimulating proceedings of the British Association are those which occur outside the section rooms. The discussion was, as I have said, incessant. I remember conducting a party to Fountains Abbey on the Saturday and hearing nothing but talk of the ionic theory amid the beauties of Studley Royal. The climax, however, was reached the next day—Sunday. The discussion began at luncheon when FitzGerald raised the question of the molecular integrity of the salt in the soup and walked around the table with a diagram to confound van't Hoff and Ostwald. After luncheon the party adjourned to the garden and was gradually increased by the arrival of strolling philosophers until it assumed quite large proportions. I regret that at this distance I cannot recall the names, but believe that it included, in addition to Ramsay and those named, Lodge, Armstrong, Pickering, Otto Petterson, and there were some others.

The discussion continued throughout the afternoon with alternating vehemence and hilarity. I have a particular recollection of FitzGerald walking restlessly about with his hand clasped on his brow and declaring in his rich Irish brogue, "I *can't* see where the energy comes from." Ramsay, as you can imagine, was no silent spectator. Being a convinced ionist, he was eager in helping out the expositions of Ostwald, whose English at that time was imperfect and explosive, and his wit and humour played over the whole proceedings. I wish I could do more justice to him and to the occasion. I believe it effected a good deal towards forming friendships, promoting goodwill and removing misunderstandings, and certainly it was the beginning of relations of great mutual sympathy and regard between Ramsay and Ostwald, which lasted till they were divided by their respective national sympathies at the unhappy outbreak of war.[108]

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[108] As quoted by W. A. Tilden, *op. cit.* (note 66), pp. 117–118.

Monday

The formal discussion on Monday started with a paper by Pickering.[109] Pickering was too much of an individualist to give a very good impression to the ionists.[110] Much of his paper was directed to an exposition of his hydrate theory, which he considered superior to the Ostwald school theory. Among his criticisms of the electrolyte dissociation theory were a number of points that, although often expressed in a way that showed ignorance of the development of chemical thermodynamics in the 1880's, reflected serious difficulties. For example, no one then considered the possibility that salts might be ionized even in the solid state, and early investigators thought it a matter of chance that the quantity of energy required to dissociate the solid salt into separate atoms was so close to that obtained by combining atoms with high electric charges. No energy was admitted to be available from combination of the electrolyte and solvent. Pickering pointed with scorn to some of the chance equalities of energy changes which the dissociation theory presupposed in the process of dissolution. He noted that the high heat of solvation of anhydrous salts would also be surprising unless hydration in solution is recognized as the explanation. However, his arguments did not influence the ionists, because in their eyes Pickering was obviously confused about the nature of energy changes. It takes a very sympathetic study of Pickering's critical remarks to winnow out the telling criticism from the confusions and misunderstandings.

In the subsequent discussion FitzGerald made the longest contribu-

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[109] P. S. U. Pickering, *Report of the British Association* for 1890 (1891), pp. 311-322.

[110] See, for example, the comments by M. W. Travers, *op. cit.* (note 66), p. 92. Pickering is presented as an unsuitable figure to lead the anti-ionist camp. Certainly, Pickering had misunderstood many features of the theories of van't Hoff and Arrhenius. See also, T. M. Lowry and J. Russell, *op. cit.* (note 48), pp. 45-46. The ionists' dismissal of Pickering was not complete, however. In the discussion which followed Pickering's paper, a note from Arrhenius was read which criticized Pickering's recent work. But as Ostwald said in his autobiography, "Arrhenius had calculated a great number of Pickering's own measurements in the freezing point depression of sulphuric acid and had found remarkably good correspondence, evidence that Pickering's measurements were incomparably better than his theory." *Lebenslinien* (Leipzig, 1927), *2,* 135; my translation.

tion.[111] Particularly because of Ramsay's respect for his friend's incisive critical mind, FitzGerald was the anti-ionist whose opinion was taken most seriously by the Ostwald camp. In the informal discussions they had convinced FitzGerald that the Ostwaldian theory *could* account for the energy changes associated with the production of charged dissociated ions in solution, but he still considered that the truth was more complicated than they recognized. Among his other comments, FitzGerald criticized van't Hoff's suggestion that the osmotic pressure of dilute solutions is produced by the kinetic pressure of solute particles unable to penetrate the semipermeable membrane. For FitzGerald the debate settled little except preliminary misunderstandings. Later he was to criticize the Ostwald school theory more sharply; he had apparently remained unaffected by the ionists' arguments. His opposition to their theory continued unabated until his early death (at the age of fifty) in 1901.

Armstrong, who was undoubtedly the leading chemist in opposition to the Ostwald school theory, did not develop his position significantly at the Leeds meeting. In the published discussion he concentrated on just a few of the difficulties of the theory that he had previously set out. But one feature of his argument gained critical notice from Ostwald. In his publications both before and after the 1890 meeting—and probably in conversation as well—Armstrong frequently appealed to the chemists' intuitive feelings or chemical common sense. For example, in an earlier discussion of the contrast that, the dissociationists claimed, existed between the highly stable hydrogen chloride gas and the highly dissociated hydrogen chloride solution, he had said: "Such a conclusion may enable certain mathematical problems to be solved in an apparently satisfactory manner, but it is hardly one which a *chemist's common sense* would lead him to accept forthwith, in the absence of any explanation accounting for so extraordinary a difference between a dissolved substance at a low temperature and the same substance in a gaseous state at a high temperature."[112] At the Leeds meeting, Ostwald dismissed this kind of argument with the remark that Armstrong should distinguish between chemical facts and chemical feelings. The facts, Ostwald claimed, were in support of the theory of his school, and the feelings would change quite easily. "Chemists will speak in a year or two as

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[111] The discussion is recorded in *Report of the British Association* for 1890 (1891), pp. 323-338.

[112] H. E. Armstrong, *Proceedings of the Chemical Society, 5* (1889), 113. My italics.

quietly of the free ions as they now speak of the uncombined mixture of hydrochloric acid and ammonia in the gaseous state [of ammonium chloride]."[113]

Neither side triumphed at the Leeds meeting on theories of solution. The formal meeting concluded with J. H. Gladstone's remark that there had been a rapprochement and increased mutual understanding between the two sides.[114] Ostwald's comments on the meeting indicate that he, at least, thought that it had been relatively successful for the ionists.

> I do not think I am wronging our hosts in supposing that the invitation had been given first of all with the friendly intention of persuading us that we were in error and of sending us back home again after a good lesson. And during the first few days our adversaries alone held the floor, so that one might have thought up to a certain point that we were already scientifically dead. But when, after long and lively personal discussions, the representatives of the modern ideas finally had a chance to speak, even at the public sessions, the appearance of things was not slow in changing, and we were able to separate from our hosts in amiable fashion and not without triumph.[115]

Even if Ostwald thought that the debate had been relatively successful from the ionist point of view, the British opposition continued to argue against the new theories, and particularly Arrhenius' theory of electrolyte dissociation through the 1890's.

5. THE DEBATES OF THE 1890'S

Further Development of the Hydrate Theory

In the early 1890's Pickering continued the polemic. His primary target in his criticisms of the Ostwald school theory was Arrhenius' theory of electrolyte dissociation, but he also attacked van't Hoff's view of osmotic pressure. Although van't Hoff had established a quantitative relationship, Pickering considered it to be of limited value to him since he believed that van't Hoff's conception of the underlying molecular processes was defective. He welcomed a paper

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[113] W. Ostwald, *Report of the British Association* for 1890 (1891), p. 334.

[114] J. H. Gladstone, *Report of the British Association* for 1890 (1891), p. 338.

[115] Quoted in translation. G. Bruni, "The Scientific Work of J. H. van't Hoff," *Annual Reports of the Smithsonian Institution* (1913), p. 779. See also E. Cohen, *Jacobus Henricus van't Hoff* (Leipzig, 1912), p. 282.

by R. H. Adie, read at the Chemical Society in 1891, in which Adie reported irregularities of the osmotic pressures of solutions.[116] Pickering stated that the irregularities told strongly against the physical theory of solution and developed his criticisms further: "Mr. Adie has touched on one of the most fundamental objections to the present physical theory of solution—the existence of osmotic pressure—for this is due to the impermeability of a membrane to the dissolved substance; and how can it be contended that if the molecules of the latter were single, and still more if they were dissociated into ions, they cannot get through holes which the water molecules have no difficulty in threading?"[117]

Pickering's most important work in the 1890's was his development of the Mendeleef method of studying hydrates in solution. Colleagues attacked him for his faith in the method, and particularly for his use of a flexible lathe to process his results, and his adherence to the method more than anything else served to isolate him from the other opponents of the Ostwald school. A discussion of his method at the Chemical Society on 4 June 1891[118] revealed the character of the criticism. Other chemists were worried by difficulties in working out an adequate mathematical theory of the method and they could not decide whether or not the discontinuities obtained were due to errors in experiment and to the smoothing of curves. The major obstacle they encountered was that they could not reproduce Pickering's results. As one critic, Rücker, pointed out, "as in the case of all other experimental methods, the final test of validity is whether concordant results are obtained by different observers. . . ."[119]

In the same discussion Armstrong indicated that even for those who accepted the importance of hydration, Pickering's work was objectionable.

> It appeared to him . . . that Mr. Pickering's conclusions were in many respects open to question from a chemist's point of view; he thought, in fact, that Mr. Pickering both proved too much and was illogical. Prepared as the speaker was to believe in the existence of hydrates in solution, he could not imagine that so large a number as was suggested would arise, or that the 102 breaks in the sulphuric acid curves, for example, could possibly be interpreted

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[116] R. H. Adie, *Proceedings of the Chemical Society,* 7 (1891), 25–26.

[117] P. S. U. Pickering, as reported in *Proceedings of the Chemical Society,* 7 (1891), 26–27.

[118] See *Proceedings of the Chemical Society,* 7 (1891), 105–109.

[119] *Ibid.,* p. 107.

> as evidence of as many distinct hydrates. There was no independent evidence to support such a conclusion.
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> Then he thought Mr. Pickering was illogical, because he interpreted all the breaks as indicative of hydrates, notwithstanding that he asserted—doubtless, with justice—that both water and sulphuric acid in the pure state consisted of complex molecules: surely in this case, as change would set in at either end of the curve, it must be impossible to say which of the breaks are to be interpreted as indicative of change in the composition of the complex molecules of acid and water respectively, which are due to the formation of hydrates consisting of simple water and acid molecules and which are due to the formation of hydrates, say, of simple water and complex acid molecules."[120]

Pickering had ready replies to most of the objections raised in the discussion, and although there is no evidence that he convinced a significant number of the scientists he addressed, he remained active in his advocacy of the method until he gave up his research on the subject in about 1896.

In a series of papers, mostly in *Philosophical Magazine,* Pickering widened the experimental data on which his version of the hydrate theory was based, proposed explanations in terms of an increasing range of phenomena, and engaged in a running battle with younger members of the Ostwald school. Following the early attacks by Arrhenius on the British hydration theorists, in 1891 James Walker took up the Ostwaldian cause.[121] Walker set out a collection of criticisms similar to those that Arrhenius had employed, showing Pickering's misunderstandings of the Ostwaldian theory and picking out the more objectionable features of Pickering's own arguments.[122] When Pickering replied in 1892,[123] he suggested that his criticisms of the Ostwald school theory in earlier years no longer applied in full, as the official ionist position now conceded that the dissociated ions are probably hydrated, and that the heat of their hydration may help to stabilize the ionized solution. However, in case the old view lingered on, Pickering presented some thermochemical studies intended to show the implausibility of any theory of solution that treats the ions as moving so freely through the solution that their behavior

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[120] *Ibid.,* p. 106.

[121] For an account of Walker's career, see *Journal of the Chemical Society* (1935), pp. 1347–1354.

[122] J. Walker, *Philosophical Magazine* [5], *32* (1891), 355–365.

[123] P. S. U. Pickering, *Philosophical Magazine* [5], *34* (1892), 35–46.

shows a quantitative analogy with gas molecules moving through empty space. He also replied to Walker's criticisms, although he apparently felt that the Ostwaldian had overstepped the bounds of the etiquette of scientific debate.

An even more heated exchange took place between Pickering and H. C. Jones; it began in *Berichte der Deutschen Chemischen Gesellschaft* and transferred to *Philosophical Magazine*. Pickering had attempted to carry the debate to the Ostwaldians' home territory, arguing that the hydrate theory was better able to explain the freezing point depressions of dilute solutions than was the Ostwald school theory. Jones replied, and the series of polemical papers followed.[124] Jones was later to become the most enthusiastic American popularizer of the Ostwaldian school; his far from impartial textbooks and historical retrospects have had great influence. Like Arrhenius and Walker, Jones claimed in 1893 that Pickering's methods of calculation depended on the magnification of random experimental error, and he presented rival data in support of the ionic dissociation theory. Pickering pointed out that Jones's work disagreed significantly with his own and suggested some sources of error which Jones—in Pickering's view—had not avoided. When Pickering applied his own method of graphical analysis to Jones's data, Jones reacted strongly. "Mr. Pickering has applied his method of curve drawing to my results from sodium chloride, which differ from his to the extent of more than 50 per cent, and with it claims to have found the same 'breaks' as in his own results. He has thus shown the true value of his method, which seems to be largely independent of the experimental data."[125]

Pickering was not as foolish about experimental accuracy as Jones seems to have thought. He explained the difference between Jones's results and his own as probably being due to error in instruments which he had eliminated in his own work by the use of several thermometers.[126] Such a systematic error would not significantly affect the arguments his calculations were intended to support. And with

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[124] P. S. U. Pickering, *Berichte der Deutschen Chemischen Gesellschaft, 25* (1892), 1314; *26* (1893), 1221, 1977; *Journal of the Chemical Society, 65* (1894), 293-312; *Philosophical Magazine* [5], *37* (1894), 162-164; H. C. Jones, *Berichte der Deutschen Chemischen Gesellschaft, 26* (1893), 551, 1635; *Philosophical Magazine* [5], *36* (1893), 465-497; *Proceedings of the Chemical Society, 10* (1895), 101, discussion 101-104.

[125] H. C. Jones, *Philosophical Magazine* [5], *36* (1893), 484-485.

[126] P. S. U. Pickering, *Philosophical Magazine* [5], *37* (1894), 163.

backing from E. H. Davies he pointed out to Jones at a meeting of the Chemical Society that he had not introduced new errors in the treatment of Jones's data. He had not subtracted one experimental figure from another, thus making the error in the result greater than that in either of the initial figures, as Jones had claimed, but had subtracted from Jones's data a precisely calculated quantity, designed to magnify the variation already present in the data.[127]

After this exchange Pickering was still prepared to refer to his treatment of Jones's result as further support for the hydrate theory. But Jones, in a later retrospect, considered that nothing of value remained after his own and other criticisms of the Mendeleef hydrate theory. "More accurate work has shown that most, if not all of the irregularities in the Mendeleef plot of solution property against percentage concentration are due to experimental error; and that there is not the slightest evidence for the theory of Mendeleef."[128]

Jones's conclusion is rather uncharitable, as by 1899 he was developing his own solvate theory, which he presented as a natural development of the Ostwaldian theory. While it is certainly the case that Pickering denied the existence of dissociated ions, even if they were solvated, his arguments were not restricted to the Mendeleef method, and many were of value to *any* theory of solvation. There was a much greater degree of continuity between the old hydration theories and Jones's later work than Jones found it expedient to recognize.

Pickering summarized his work on the hydration theory in his article on "Solutions" in *Watts Dictionary of Chemistry* in 1894.[129] The editors of this edition of the dictionary had decided to invite Arrhenius and Pickering to contribute rival entries.[130] Pickering's position remained essentially unchanged after this article.

Other Developments in the Early 1890's

During the early 1890's Ostwald was producing illustrations and arguments in support of the Ostwaldian theory. He gave quantitative

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[127] P. S. U. Pickering, *Proceedings of the Chemical Society, 10* (1895), 101–102; E. H. Davies, *ibid.*, p. 103.

[128] H. C. Jones, *A New Era in Chemistry* (London, 1913), p. 166.

[129] P. S. U. Pickering, *op. cit.* (note 82), pp. 492–496.

[130] The article by Arrhenius was on solutions in general; Pickering contributed a summary of the general and particular arguments in support of the hydrate hypothesis.

explanations in terms of the ionic dissociation hypothesis of such properties as the magnetic rotation and the color of electrolyte solutions. Some of his expositions appeared in English. When Ostwald's paper "Chemical Action at a Distance" appeared in *Philosophical Magazine,*[131] it attracted critical discussion. Like the earlier exchange over the example of electrostatic production of electrolysis, Ostwald's latest presentation was construed by the British as an *argument* for the Ostwaldian theory, although Ostwald only claimed to be presenting yet another type of phenomenon that could be anticipated and explained satisfactorily by the new theory. The behavior of silver dipped in dilute sulphuric acid provides an example of chemical action at a distance. Although no appreciable action normally takes place, the silver will dissolve if it is connected to a platinum wire dipped in a solution containing an oxidizing agent such as acidified potassium bichromate, and if the two solutions are connected through a semipermeable membrane. Ostwald described a number of such experiments, most of which were already known, and showed how readily they were explained in terms of the Arrhenius theory. Indeed, Ostwald claimed:

> The description of some of the experiments, which are communicated here, was completely worked out at my writing table, *before I had seen anything of the phenomena in question.* After making the experiments on the following day, it was found that nothing in the description required to be altered. I do not mention this from feelings of pride, but in order to make clear the extraordinary ease and security with which the relations in question can be considered on the principles of Arrhenius' theory of free ions. Such facts speak more forcibly than any polemics for the value of this theory.[132]

Pickering, however, was not impressed. He argued[133] that the same phenomena could as readily be explained on the more traditional principles of the Grotthus theory. Because one always requires a liquid-liquid contact in chemical action-at-a-distance experiments, one can always describe chains of solute molecules as stretching from one electrode to the other, the only observable effects being at the

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[131] W. Ostwald, *Philosophical Magazine* [5], *32* (1891), 478–480.

[132] *Ibid.*, p. 156.

[133] P. S. U. Pickering, *Philosophical Magazine* [5], *32* (1891), 478–480.

electrodes. "All these experiments seem to be on a par with one described some time ago by Professor Ostwald, consisting in the production of a small amount of electrolysis by a current of electrostatic origin: experiments which are perfectly consistent with the old electrochemical theory, dressed up in the garb of the dissociation theory and then presented to us as proof positive of this theory."[134]

Similar objections were made by J. Brown in a paper read at the British Association meeting that year (1891) and published in *Philosophical Magazine* the following year. Brown also discussed further experiments by Ostwald which had been described in *Zeitschrift für physikalische Chemie*, and he drew the conclusion that Ostwald had yet to point to any crucial experiments. Both of the rival theories could explain the known experimental results.[135]

Ostwald's tendency to present his arguments as if there was no serious rival to the Ostwald school theory for the treatment of solutions was a constant annoyance to many British scientists.[136] His textbooks in particular drew criticism on this point. For example, in a review of Ostwald's *Solutions*, the reviewer commented: "As a concise account of the new theory of solution Professor Ostwald's work is most valuable; but it is somewhat to be regretted that he did not give some indication of the older theories, of which not a word is said. Indeed, a student taking up the book and having no previous knowledge of the subject would be led to suppose that the theory here put forward is the universally accepted one, whereas it is really regarded by the majority of chemists as quite untenable."[137] Another reviewer of *Solutions* made similar comments and provoked an exchange of letters with Ostwald.[138] The reviewer, J. W. Rodger, referred to the theory of the Ostwald school as the "physical" theory and contrasted it with the hydrate or "chemical" theory; he criticized Ostwald for concentrating so heavily on physical factors, when chemical considerations suggest that solutions are far more

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[134] *Ibid.*, pp. 479–480.

[135] J. Brown, *Philosophical Magazine* [5], *33* (1892), 82–89.

[136] That this tendency was to some extent deliberate is revealed in a letter from Ostwald to Arrhenius, 2 January 1892. Ostwald reported with obvious pleasure that the section on solutions of his *Lehrbuch der allgemeinen Chemie*, which had just been translated into English, contained no mention of Pickering. See Ostwald's correspondence, *op. cit.* (note 48), p. 103.

[137] James L. Howard, *Philosophical Magazine* [5], *33* (1892), 146.

[138] J. W. Rodger, *Nature, 45* (1891–1892), 193–195, 342–343, 487. W. Ostwald, *ibid.*, pp. 293–294, 415, 606.

complex than the physical picture assumes.[139] Ostwald, in his reply, objected to the contrasting of "physical" and "chemical" processes and theories of solution. "It has never been maintained, either by me or by any other representative of the newer theory of solutions, that no interaction takes place between the solvent and the dissolved substance; on the contrary, I have for years greatly encouraged research work directed towards making clear the nature of such interactions."[140] Ostwald went on to give his version of the relationship of the two theories of solution.

> I beg Mr. J. W. R. to recall the history of the rivalry between the two "theories." Van't Hoff and his successors developed the law of solutions entirely without polemical strife, because, since the fundamental ideas of van't Hoff's theory were entirely new, there was nothing at all in its territory to combat, as till then there was nothing there. The attacks upon van't Hoff were begun by an investigator who had until then directed his attention exclusively to the phenomena which I have above characterised as individual, and who was evidently unprepared to deal with such colligative properties. The defence had to consist in an unceasing clearing up of misconception. Now, the greatest of these misconceptions is, that both "theories" are rivals. The existence and form of the laws founded by van't Hoff and his successors stand at present beyond question. . . . But what has until now been known as the hydrate theory has not been in a position to give any information whatever in regard to these laws; none of them have been discovered with its aid, and since it has for its subject not the colligative but the individual properties of solutions this will not be otherwise in future.[141]

The rest of Ostwald's letter and much of the later exchange were concerned with the use of the word "theory." The debate degenerated into a terminological disagreement, Ostwald arguing that theories were merely collections of laws, and Rodger that theories should also satisfactorily *explain* the laws they relate. Accusations of inconsistency of usage further obscured the issue.

Ostwald's textbooks soon were the guide for a large number of

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[139] J. W. Rodger, *ibid.*, pp. 193–195.
[140] W. Ostwald, *ibid.*, p. 293.
[141] *Ibid.*, p. 294.

textbooks of physical chemistry in English. Most of these English textbooks were written by members of the Ostwald school and followed closely his presentation. They were criticized by many later anti-ionists for giving students a far from impartial view of the status of the rival theories of solution.[142] Some English textbooks, however, did attempt to give a fair perspective on the two theories from a British point of view. One such book was written by W. C. D. Whetham, later William Cecil Dampier. In the early 1890's Whetham had published experimental work that he considered gave experimental support to the electrolyte dissociation theory.[143] In his textbook *Solution and Electrolysis* (1895) he wrote enthusiastically about the theory of ionic dissociation, less so about the value of treating dissolved substances in solution as if they were in a quasi-gaseous state. He attempted to be fair to Armstrong and Pickering, discussing their ideas briefly and suggesting how Pickering's more effective arguments for the hydration of dissolved substances could be absorbed into the Ostwaldian theory. "We can, in fact, regard a considerable mass of the solution, containing, perhaps, several molecules and dissociated ions of salt, and hundred molecules of solvent, as chemically one large molecule, the parts of which are nevertheless to some extent physically independent of each other."[144] Whetham was to develop this compromise in the following years.

The beginnings of a search for compromise were apparent, but the debate was far from over. In his presidential address to the Chemical Society in 1895 Armstrong showed himself to be as intransigent as ever. After a discussion of the development of his own arguments, he set out his current evaluation of the dissociation hypothesis. "Whatever view may ultimately be taken of the hypothesis—whether it can be retained as a permanent addition to our theories or not—its introduction has been eminently fruitful of results, and an already too voluminous literature of the subject has grown with surprising rapidity. Yet it appears to me that it has been accepted by a particular

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[142] See, for example, J. J. Howard, *Philosophical Magazine* [5], *33* (1892), 144-147; A. Smithells, *Nature, 62* (1900), 76-77; L. Kahlenberg, *Journal of the American Chemical Society, 24* (1902), 485-486; H. E. Armstrong, *Science Progress, 3* (1909), 65-66.

[143] See, for example, W. C. D. Whetham, *Philosophical Magazine* [5], *38* (1894), 392-396.

[144] W. C. D. Whetham, *Solution and Electrolysis* (Cambridge, Eng., 1895), p. 212.

school–at the head of which stands Ostwald, and who regard and treat all unbelievers as heretics worthy of the stake–not as a mere working hypothesis, but as an absolute creed, without any sufficient attempt being made to discuss its general probability."[145] Armstrong went on: "Personally, I am still entirely unconvinced of the validity of the hypothesis, although no one can be more willing to admit that in so far as *weak* solutions are concerned, a 'law' has been discovered which is broadly true in *mathematical form,* however open to question the fundamental premises may be on which it is based. I am satisfied that the phenomena of chemical change are, as a rule, far more complex in character than is assumed by the advocates of the hypothesis."[146]

The Exchange in *Nature* 1896-1897

In 1896 the debate continued with new life, drawn particularly from a prolonged exchange of letters in *Nature*. The exchange took place against the background of FitzGerald's "Helmholtz Memorial Lecture" at the Chemical Society in 1896.[147] FitzGerald's lecture has been varyingly assessed as "profound and brilliant"[148] and as "rambling and irrelevant."[149] In general it was favorably received by the opponents of the Ostwald school theory. In his lecture FitzGerald moved from an evaluation of parts of Helmholtz' work to discussion of some of the dangers of applying thermodynamics to chemistry without sufficient care. Every application of the second law of thermodynamics should be to a reversible reaction, and a complete cycle should be examined so that all thermodynamic changes are recognized. As an example of the errors that may result from unjustified applications, FitzGerald mentioned a recent publication that presented a proof that osmotic pressure is proportional to absolute pressure, unjustifiably assuming that all the heat supplied was doing osmotic work.[150] A lesson was to be learned for mathematical chemistry: "It is as risky for a chemist to apply mathematics as for a mathematician to lecture to chemists: we should work in co-operation."[151] FitzGerald attacked Ostwald's argument that when

[145] H. E. Armstrong, *Journal of the Chemical Society, 67* (1895), 1124.
[146] *Ibid.,* pp. 1124-1125.
[147] G. F. FitzGerald, *Journal of the Chemical Society, 69* (1896), 885-912.
[148] J. Lister, *Proceedings of the Chemical Society, 12* (1897), 26.
[149] J. R. Partington, *op. cit.* (note 6), p. 679.
[150] G. F. FitzGerald, *op. cit.* (note 147), p. 898.
[151] *Ibid.,* p. 899.

an electrolyte is subject to electrostatic induction, the superficial induced charges are due to a layer of electrified ions on its surfaces. "If there were no forces other than electrical ones, these ions would fly off the surface like dust."[152] He then moved on to a discussion of the theory that solutions and gases are analogous.

> So much advance has been made by assuming that bodies in solution behave in some important respects like the same body in the gaseous state, that there has been a serious danger of assuming the physical conditions are at all like. The dynamical condition of molecules in solutions is essentially and utterly different from that of a molecule in a gas. The essential condition for applying any known dynamical theory of gases to calculate their behaviour is that the time during which two molecules are within the sphere of one another's action is small compared with the time during which they are apart, and that consequently the chances of three or more molecules being in simultaneous collisions is very small. . . . Now this essential condition for the application of the dynamics of a gas to molecules in solution is very far indeed from being fulfilled. A molecule is never outside the sphere of action of its neighbors.[153]

Indeed, FitzGerald's calculations suggested that a molecule in solution was within the sphere of influence of between a hundred and a million of its neighbors. "It is, no doubt, a most remarkable thing that osmotic pressure should be even roughly the same as what would be produced by the molecules of the body in solution if in the gaseous state, but to imply that the dynamical theory of the two is at all the same, or that the dynamical theory of a gas is in any sense an *explanation* of the law of osmotic pressures is not at all in accordance with what is generally meant by the word 'explanation'."[154] FitzGerald did not just object to the van't Hoff theory of solutions; he went on to attack the idea that electrolytes show enhanced osmotic effects because they are dissociated. He sketched an alternative explanation, which was more qualitative and also more in line with Armstrong's chemical arguments. The Ostwald school were satisfied with superficial mathematical regularities when they should have been seeking mechanical explanations.

The immediate stimulus for the correspondence in *Nature* was a

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[152] *Ibid.*, p. 902.

[153] *Ibid.*

[154] *Ibid.*, p. 903.

suggestion by the physicist J. H. Poynting as to how osmotic pressure might be accounted for, not as an additional pressure produced by the dissolved molecules, but from some kind of association between the solvent and solute. Poynting hoped to avoid the dissociation hypothesis in his explanation of the higher osmotic pressure of electrolytic substances.[155] The British climate of scientific opinion, influenced by men like FitzGerald and Armstrong, made the dissociation hypothesis something to be avoided if possible. Poynting's idea, in part based on an earlier paper of 1881,[156] was that the mobility of molecules of a solvent is affected by internal or external pressure; the effect of a dissolved substance is analogous to negative pressure—the solute molecules slow down the solvent in their neighborhood. Since it may be argued that electrolytes affect the solvent more than non-electrolytes, the greater effect of their molecules allows for their additional osmotic pressure. Poynting's proposed mechanism stimulated W. C. D. Whetham to write a letter to *Nature,*[157] and thus establish that journal as the forum for a continued exchange. Developing the theme of the concluding part of his textbook published the previous year,[158] Whetham argued for compromise. He suggested that Poynting's mechanism of osmosis was quite compatible with the dissociation theory. He showed for example that, if each ion unites with a certain amount of the solvent, then the dissociation of a molecule into its ions will have a greater effect on the solvent and so raise the osmotic pressure. "Thus Professor Poynting's conditions would be satisfied, and at the same time the advantages of the dissociation theory would be retained."[159] This argument Poynting accepted.[160] After a discussion with Ramsay he announced that he now accepted that ions move independently of one another in solution. Provided that the ions associated with the solvent, their indirect effect on osmotic pressure could be understood in terms of the mechanism he had postulated.

Armstrong then joined the discussion with a polemical letter filled with uninhibited rhetoric. He criticized the deviousness with which the Ostwaldians evaded criticism and described the new breed of

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[155] J. H. Poynting, *Philosophical Magazine* [5], *42* (1896), 289-300.

[156] J. H. Poynting, *Philosophical Magazine* [5], *12* (1881), 32-48, 232.

[157] W. C. D. Whetham, *Nature, 54* (1896), 571-572.

[158] W. C. D. Whetham, *op. cit.* (note 144), p. 44.

[159] W. C. D. Whetham, *Nature, 54* (1896), 572.

[160] J. H. Poynting, *Nature, 55* (1896), 33.

chemists turned out by the school as nominally chemists, but as chemists without "chemical feeling." It seemed to him that in chemistry two parties were emerging that had nothing in common. He concluded his letter by commenting on the corruptive tendency of the Ostwald school in science education to present dogmatically as fact hypothetical ideas of atomic dissociation.[161] Armstrong's letter stimulated three other scientists to reply. O. J. Lodge showed that he had become a moderate advocate of the ionist cause; he was also concerned that Armstrong's intemperate language might have given the false impression that he wished to keep chemistry free of all trespassers.[162] Whetham, employing moderate language, tried to bring the debate back from polemics to serious discussion by replying to the detailed points in Armstrong's objections.[163] Whetham realized that it was the manner rather than the substance of Armstrong's letter that was intended to have the greatest impact, and he admitted that to read the letter as serious argument "considerable mental agility is needed to follow *all* the metaphors which Professor Armstrong crowds into a single sentence. . . ."[164] E. F. Herroun, another anti-ionist, was the third scientist to respond to Armstrong.[165] Herroun had devoted most of his work to the measurement of the electromotive force of cells, a topic on the borderlines of physics and chemistry. Most of his papers were published by the London Physical Society. Herroun believed that the arguments of the anti-ionists had been put very strongly, and that the ionists were employing unfair techniques of scientific debate. "It seems to me a duty of teachers to protest against the growing tendency there seems to be of putting forward the crude hypotheses of the ionist school, as though they had some claim to acceptance as well established scientific laws, about which no reasonable doubt exists. So far from this being the case, the arguments commonly advanced in support of the theory seem to consist mainly of the misapplication of physical laws to a few carefully selected cases, aided by plausible but misleading assertions."[166] Herroun devoted the bulk of his letter to questions that he felt exposed errors in the ionists' position, especially as it appeared

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[161] H. E. Armstrong, *Nature, 55* (1896), 78-79.

[162] O. J. Lodge, *Nature, 55* (1896), 150-151.

[163] W. C. D. Whetham, *Nature, 55* (1896), 151-152.

[164] *Ibid.,* p. 151.

[165] E. F. Herroun, *Nature, 55* (1896), 152.

[166] *Ibid.,* p. 152.

in Ostwald's *Outlines of General Chemistry,* the "Bible of the ionists." He asked that the ionists answer these questions and that the uncommitted—"those who are at present only partly dissociated"—reflect upon them until satisfactory explanations appear.

Early in 1897 Pickering again contributed to the arguments of the anti-ionists.[167] He claimed in a letter to *Nature* that the theories of osmotic pressure and of ionic dissociation are to be treated only as numerical regularities rather than as acceptable theories. "For a theory to be acceptable it should, at the very least, be reasonably probable, and should not violate any fundamental and well-established facts; it should stand the test of any apparently crucial experiments brought forward to settle between it and its rivals, and, I think I may add, it should give some explanation, not simply of the behaviour of matter in the condition in question, but also of why matter ever assumes such a condition."[168]

The Ostwaldian theory, he argued, did not meet these conditions, while the hydrate theory did. The Ostwald school had yet to explain why thermally stable compounds fly apart when exposed to water molecules which are represented as being inert. The question of the thermochemical relationships involved in dissociation had yet to be resolved. As both electrolysis by electrostatic discharge and "chemical actions at a distance" were adequately explained by older theories, the Ostwaldians had yet to produce a significant crucial experiment. As support for his side of the debate Pickering proposed two crucial experiments which he claimed the Ostwald school theory could not handle. Referring to his arguments that solvation makes the particles of the dissolved species too large to pass through a semipermeable membrane, he claimed to have experimental evidence that while pure water and pure propyl alcohol can penetrate a semipermeable vessel, only the solvent of a dilute solution of one in the other is able to pass through.[169] Pickering's second crucial experiment was based on the claim that the freezing points of solutions of sulphuric acid and water in acetic acid suggest

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[167] P. S. U. Pickering, *Nature, 55* (1897), 223-224.

[168] *Ibid.,* p. 223.

[169] It was not until 1905 that Pickering's argument was dealt with. The effect was shown to be transient, disappearing at equilibrium and so not justifying Pickering's conclusion. See A. Findlay and F. C. Short, *Journal of the Chemical Society, 87* (1906), 819-822; F. C. Short, *Philosophical Magazine* [6], *10* (1905), 1.

that the sulphuric acid and the water are associated rather than that the acid is dissociated.

No committed ionist replied to Pickering. Whetham wrote that he was sceptical of the gaseous theory of solutions but in favor of the dissociation theory.[170] Although he could think of no answer to the first crucial experiment, he suggested that Pickering's second experiment was not crucial, as the ionists did not need to assume that sulphuric acid is dissociated when dissolved in acetic acid. He suggested, furthermore, that his own compromise proposal that the ions are highly hydrated could explain Pickering's observations completely. Whetham then suggested that a different list of observations from those that Pickering had discussed provided the strongest evidence for the dissociation theory. The velocity with which an ion travels through a dilute solution in electrolysis is independent of the nature of the other ions present. The conductivity of a dilute solution is proportional to its concentration rather than to the square of the concentration (as would be required by a theory of electrolysis like Grotthus' which explained ion transport by a mechanism of collision between solute molecules). Basing his calculations on the assumption that the ions move independently and at different velocities, Whetham derived the potential difference between two solutions in contact that differ only in concentration. In the British Association meeting of 1897, Whetham outlined his compromise again. He concluded that, although ions travel independently and are free from one another for most of their existence, "it must be particularly noticed that this freedom from each other does not at all prevent the ions from forming chemical combinations with the solvent molecules. Neither does it throw any light on the fundamental nature of solutions."[171] Poynting's mechanism for osmotic pressure had provided a satisfactory alternative to the van't Hoff analogy with ideal gases.

The later part of the exchange in *Nature* in 1897 consisted largely of a discussion between leading theoretical physicists. In his endeavor to give his position respectability Armstrong had earlier quoted supporting remarks by leading physicists: in his letter of the previous November he had referred to Rayleigh's agreement with FitzGerald

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[170] W. C. D. Whetham, *Nature, 55* (1897), 606–607.

[171] W. C. D. Whetham, *Report of the British Association* for 1897 (1898), pp. 244–245.

on the dangers of pushing formal analogies too far and supposing a real dynamical similarity between gases and solutions.[172] Rayleigh replied to affirm his support for van't Hoff's work.[173] He agreed that van't Hoff's supporters had often been careless in the phraseology they used and that they may thus have turned some distinguished physicists and chemists against the theory. To support the extension of Avogadro's law to dilute solutions, Rayleigh gave an alternative derivation. In the following issue a week later, Kelvin presented a counter argument. He stated that in the absence of knowledge of the solvent-solvent, solute-solute intermolecular forces, there was no satisfactory theoretical argument for applying Avogadro's law to solutions. Kelvin concluded by referring with approval to FitzGerald's "Helmholtz Memorial Lecture."[174] Two months later Gibbs argued in a letter to *Nature*[175] that it was not necessary to know very much about intermolecular forces to show that Avogadro's law applied to dilute solutions. He showed that his theoretical treatment in his 1875-1878 paper, "On the Equilibrium of Heterogeneous Substances,"[176] was able to deal with the problem. Another contribution to the discussion in *Nature* was a report of a lecture by the physicist J. Larmor, originally given to the Cambridge Philosophical Society.[177] Larmor referred to the theoretical treatments of osmotic pressure implicit in the work of Helmholtz and Gibbs which made van't Hoff's law indisputable. He also suggested what kind of processes in dilute solutions would make the result comprehensible.

The *Nature* debate ended with a final exchange between Pickering and Whetham.[178] Pickering made it clear that he was not prepared to accept Whetham's compromise. His abhorrence of dissociated ions remained even when their advocates admitted that they might be hydrated. "When a theory can only explain observed facts by driving us to assumptions of the existence of such compounds as H_xH_2O and

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[172] H. E. Armstrong, *Nature, 55* (1896), 78.

[173] Rayleigh, *Nature, 55* (1897), 253-254.

[174] Kelvin, *Nature, 55* (1897), 272-273.

[175] J. W. Gibbs, *Nature, 55* (1897), 461-462.

[176] J. W. Gibbs, *Transactions of the Connecticut Academy, 3* (1874-1878), 108-248, 343-524.

[177] J. Larmor, *Nature, 55* (1897), 545-546.

[178] P. S. U. Pickering, *Nature, 56* (1897), 29; W. C. D. Whetham, *ibid.,* pp. 29-30.

$SO_{4y}H_2O$, I venture to think that that theory must be somewhat shaky."[179] Whetham concluded that only differences of opinion remained. "Such a view of the dissociation theory [with solvated ions] seems to me to offer many advantages. It may be contrary to some *opinion*, but I do not think that any *facts* have yet been pointed out which refute it. Till they are, it may possibly be of use as a working hypothesis in the investigation of that complicated structure which we call a solution."[180] Admitting that ions are hydrated was the main concession the ionists made to Pickering's camp. Pickering refused to accept even hydrated ions and any further development of the subject could only have seemed degenerative to him.

The 1896-1897 discussion in *Nature* marks the end of the first decade of opposition to the Ostwald school theory. Although the chief opponents of the theory became increasingly entrenched in their positions, the main issues were becoming clearer. Among physicists the near consensus was emerging that van't Hoff's law was theoretically satisfactory for dilute solutions but that the underlying mechanism of osmosis was still far from being elucidated. Chemists like Whetham who were searching for compromise agreed that many erroneous claims had been made by the early ionists, and that in particular a full understanding of the nature and stability of ions required recognition of the active role of the solvent. Unlike the American H. C. Jones, the British usually recognized the importance of at least some of Pickering's and Armstrong's arguments. But the debate was still far from over. In spite of the confrontations, neither side had come to a full understanding of the other. Each side still developed its own strong points and in referring to the other stressed only the opponent's weaker points. With some change in the leading personalities and locations of the debate about the turn of the century, the argument was to continue for more than another decade. The main opposition to the growing numbers of Ostwaldian physical chemists came from L. Kahlenberg and from Armstrong and their respective students. The work of these two men can be described separately. Since the crusading phase of Kahlenberg's opposition did not continue as long as that of Armstrong, I shall first consider the former and discuss the American situation.

[179] *Ibid.*, p. 29.

[180] *Ibid.*, p. 30.

6. KAHLENBERG'S INFLUENCE ON CRITICAL DISCUSSION OF THE THEORY OF SOLUTION IN AMERICA AND BRITAIN

The Development of Kahlenberg's Opposition

The American chemist Louis Kahlenberg developed his opposition to the theories of Arrhenius and van't Hoff in a different manner from the English. After taking his first degrees at the University of Wisconsin, he went to Germany, as was the American custom, to further his chemical education. He studied at Leipzig in 1894, and in 1895 he obtained his doctorate with Ostwald. He also spent some time with other German chemists, returning to the University of Wisconsin in 1896.[181] Kahlenberg later wrote that during his student days and for several years afterwards he had been enthusiastic over the theories of Arrhenius and van't Hoff. It was while seeking to establish new experimental facts to support the theories further that he continually observed contradictory phenomena.[182]

The development of Kahlenberg's opposition can be followed in the succession of papers and reviews he wrote around the turn of the century. In his early experimental papers he unquestioningly employed the dissociation theory where appropriate. The first doubts appeared in a study of non-aqueous solutions. The success of the theory for aqueous solutions may make it seem natural to apply the theory to non-aqueous solutions without further question, he said, but one ought to ask whether or not in non-aqueous conducting solutions the dissolved substance is dissociated. "In view of the opposition that the theory had to meet at the time of its promulgation, and in view of the fact that even at present a number of scientists are opposed to it, we may well hesitate to apply this theory (which is based primarily on a study of aqueous solutions) to non-aqueous solutions without a firm experimental basis for doing so."[183] At the end of the same paper, in which the dissociation theory turned out to be inadequate to explain the experimental

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[181] There is a biography of Kahlenberg by N. F. Hall, *Transactions of the Wisconsin Academy of Science, Arts and Letters, 39* (1949), 83-96; *40* (1950), 173-183; it contains a useful bibliography of the work of Kahlenberg and his students (though it must be used with caution as there are many errors and omissions).

[182] L. Kahlenberg, *Transactions of the Faraday Society, 1* (1905), 49.

[183] L. Kahlenberg and A. T. Lincoln, *Journal of Physical Chemistry, 3* (1899), 13-14.

results, Kahlenberg wondered whether or not "after its glorious success in explaining the properties of aqueous solutions of acids, bases and salts, the dissociation theory will need the help of its old rival, the hydrate theory (perhaps in somewhat modified form), to explain the facts in the case of non-aqueous solutions."[184] Later the same year, Kahlenberg expressed his doubts more strongly.

> From the facts here presented, it seems clear that solutions may conduct electricity fairly well and yet the dissolved substance may possess a normal molecular weight, i.e., it may be not dissociated. But this point once established, the question arises, cannot conduction then in all solutions be explained without assuming electrolyte dissociation? To be sure then the high osmotic pressure and corresponding low molecular weights found in so many cases, in aqueous solutions of electrolytes for instance, would have to be accounted for otherwise than by the dissociation hypothesis.[185]

Kahlenberg's early critical studies were based on work on the dissociative power of solvents and on concentration cells in non-aqueous solutions. Kahlenberg was also working on physiological chemistry (his first position after returning from Germany was in the pharmacy department at Wisconsin) and he was finding more evidence of the limitations of the dissociation theory, even in aqueous solutions. The Ostwald school attributed many of the properties of acids to the presence of the hydrogen ion. For example, they related the sourness of the taste of acids to the concentration of hydrogen ions. In contrast, Kahlenberg found that many acid salts tasted much more sour than suggested by the theory.[186] In a parallel study of the toxic effect of acid sodium salts on sensitive plants his conclusion was again critical of the dissociation theory.[187]

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[184] *Ibid.*, p. 34.

[185] L. Kahlenberg, *Journal of Physical Chemistry, 3* (1899), 398.

[186] L. Kahlenberg, *Journal of Physical Chemistry, 4* (1900), 33-37. Kahlenberg's paper generated a brief exchange with T. W. Richards over the explanation of the sour taste. T. W. Richards, *Journal of Physical Chemistry, 4* (1900), 207-211. L. Kahlenberg, *Journal of Physical Chemistry, 4* (1900), 533-537. Kahlenberg also responded to critical comments in reviews by A. A. Noyes in *Review of American Chemical Research, 6* (1900), 73, 147, 157; *Zeitschrift für physikalische Chemie, 36* (1901), 613-615. See L. Kahlenberg, *Journal of Physical Chemistry, 5* (1901), 380fn.

[187] See, for example, L. Kahlenberg and R. M. Austin, *Journal of Physical Chemistry, 4* (1900), 553-569.

Around the turn of the century Kahlenberg also began to write unfavorable reviews of uncritical expositions of the Ostwald school theory. For example, in 1900 in his review of a textbook by H. C. Jones he wrote that although the book viewed the dissociation theory most favorably, during the last year or so facts had begun to accumulate, especially about non-aqueous solutions, that the theory could not explain. "It seems at present that even before the theory of electrolytic dissociation will have found its way into regular chemical textbooks, it will have undergone radical modifications from its present form, or will perhaps have been superseded by more adequate explanations."[188]

Two years later, Kahlenberg used stronger language: "A brief treatise on general physical chemistry which devotes such an undue proportion of its space to the exposition of the theory of electrolytic dissociation and its applications (without even attempting to indicate the shortcomings of this hypothesis) as this book does, can at the present stage of the development of the science, hardly claim to present the subject in a fair, well-balanced form."[189]

By 1901 Kahlenberg was engaged in a systematic program designed to show the untenability of the Ostwald school theory. He published a number of general papers, summarizing his arguments, and with his students he published studies extending the experimental basis of his case. The first of the general papers appeared early in 1901.[190] The paper was introduced by Kahlenberg's version of the history of the Ostwaldian theory. After its promulgation in 1887,

> the theory at once met with great opposition, notably in England, and it was by no means received with open arms on the continent. But the hypothesis inspired experimental investigation, and the results of this phenomenal activity (which at first centred in Ostwald's laboratory at Leipzig, but spread rapidly to other parts

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[188] L. Kahlenberg, review of H. C. Jones, *The Theory of Electrolytic Dissociation and Some of its Applications* (New York, 1900), in *Journal of the American Chemical Society, 22* (1900), 228-229.

[189] L. Kahlenberg, review of J. L. R. Morgan, *The Elements of Physical Chemistry,* 2nd ed. (New York, 1902), in *Journal of the American Chemical Society, 24* (1902), 486.

[190] L. Kahlenberg, "The Theory of Electrolytic Dissociation as Viewed in the Light of Facts Recently Ascertained," *Journal of Physical Chemistry, 5* (1901), 339-392.

> of Germany, to various other countries of Europe and to America) soon silenced the opposition in Germany and gradually diminished it also in England. It must not be supposed, however, that this silence meant that all were convinced. The silence seemed to result on the one hand because of a recognition of the futility of the debate with the knowledge of existing facts, and because of a recognition of, if not admiration for, the enthusiasm displayed by the adherents of the theory. . . .[191]

Kahlenberg attributed the success of the theory to its ability to relate the factor *i* in van't Hoff's theory of solutions to measurements of electrical conductivity for the limited range of aqueous solutions on which measurements had been made. He explained that "in view of the few experimental data at hand in 1887, and the fact that many of them had not been determined with accuracy, the poor agreement, of a goodly number of values at least, was readily overlooked in view of the generalities that the theory sought to bring, generalities which were soon incorporated without proper qualifications into text-books."[192]

The Ostwald school had tended to neglect non-aqueous solutions (most of the early studies of non-aqueous solutions were made by French-speaking scientists), believing that non-aqueous solutions yielded "normal" molecular weights and were generally nonconductors. Kahlenberg reviewed his earlier work to show that such solutions did not behave as the Ostwald school believed. "In the face of these facts the theory of electrolytic dissociation is untenable in the case of non-aqueous solutions."[193]

Kahlenberg devoted the greater part of his 1901 paper to experimental studies of aqueous solutions; he concluded from his studies that there were many cases of dilute solutions for which the dissociation theory failed to account except by using a large number of ad hoc stratagems, and that the theory failed to account quantitatively (and sometimes even qualitatively) for more concentrated solutions. Kahlenberg went on to list all other counter arguments he could muster. He referred to his physiological experiments on sour taste and toxicity. He reviewed the difficulties others had expressed about the thermochemical features of the theory. He mentioned the well-known problem of reconciling the dissociation theory with the law of mass action, particularly for strong electrolytes. He criticized

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[191] *Ibid.*, p. 340.

[192] *Ibid.*

[193] *Ibid.*, p. 344.

the Ostwald school in this connection: "It is really unfortunate that in discussing problems of equilibrium into which strong electrolytes enter (their solubility for instance) the adherents of the dissociation theory should go right ahead with their mathematical equations and deductions as though they were in full accord with the law of mass action."[194]

Kahlenberg was particularly harsh on the dissociation theory when he discussed its application to analytical chemistry. He agreed that some physical scientists might find the language of the dissociation theory helpful, but he insisted that it was untenable to assert that the new terminology, combined with an attempt to apply the law of mass action to electrolytes, constitutes a foundation for analytical chemistry. "The very fact that chemistry has not received much benefit from Professor Ostwald's little book on 'The Scientific Foundations of Analytical Chemistry', in the way of improving existing analytical methods and discovering new ones speaks for itself."[195]

Next Kahlenberg rejected some of the more popular explanations that are expressed in terms of the dissociation theory. He argued that the additive properties of solutions need not imply dissociation, since properties such as molecular specific heat could be related additively to atomic heats in cases where there was no question of dissociation. He found the readiness of electrolytes to undergo rapid reaction to be an inadequate argument for their dissociation; non-conducting substances and mixtures can also react rapidly—as in many well-known explosives. Even the actual phenomena of electrolysis did not require Arrhenius' theory; Kahlenberg considered that Clausius' hypothesis was quite sufficient to explain all the facts.

The abandonment of the dissociation theory would require some other explanation of the high value of i in van't Hoff's equation for dilute solutions of electrolytes. Kahlenberg sought to overcome the difficulty by arguing that the van't Hoff law was of only limited validity, so that one had to expect deviations from it. In particular

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[194] *Ibid.*, p. 381. The scientists engaged in the debate discussed here never paid much attention to the failure of strong electrolytes to behave in accordance with the law of mass action; the problem was probably too far removed from chemical intuition. It was, however, this issue which proved crucial in the further development of the dissociation theory. See H. Wolfenden, "The Anomaly of Strong Electrolytes," *Ambix, 19* (1972), 175-196.

[195] L. Kahlenberg, *Journal of Physical Chemistry, 5* (1901), 382.

Kahlenberg attacked the analogy between gases and dilute solutions. He seemed to think that to ridicule the idea that the solute in dilute solutions behaves like a gas in the volume of the solution was to undermine the whole of van't Hoff's theory of solutions.[196] Kahlenberg admitted that, as with ideal gases, the gas equation is supposed to hold strictly only for infinitely dilute solutions. But, he insisted, one has a right to expect from a modern theory of solutions that with increasing concentration a solution should behave at least qualitatively as a gas does with increase of pressure. He argued that for practical purposes a normal solution is rather dilute and showed that often there is not even qualitative agreement with gas behavior over a given range of concentration.[197]

In two years Kahlenberg's initial disquiet about the dissociation theory had grown into an attack on the theory of dissociation in general and also on van't Hoff's theory of solutions. "It is solely because of the rapid growth of the erroneous idea that the deductions drawn from the indiscriminate application of the simple gas equation to solutions and from the notion that all well-known facts harmonize with the theory of electrolytic dissociation, that I have felt compelled to call attention to the real status of the experimental facts underlying these deductions. It is hoped that this will stimulate to renewed experimental activity, for surely our theory of solutions leaves much to be desired."[198]

Early Reactions to Kahlenberg

Kahlenberg's first general paper and those that followed attracted a certain amount of sympathetic attention as well as the scathing reaction of dedicated Ostwaldians. A. A. Noyes, for example, reviewed the paper scornfully: "The author's view seems to be that because the theory does not alone explain all the relevant phenomena of all kinds of solutions, it is unjustifiable or inadvisable to employ it at all. It is scarcely necessary for the reviewer to add that the theory has received far too many approximately quantitative verifications to be overthrown by such facts as are cited by the author."[199]

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[196] The significance of van't Hoff's analogy between gases and dilute solutions is discussed further in the section on the nature of osmotic pressure.

[197] L. Kahlenberg, *Journal of Physical Chemistry, 5* (1901), 389.

[198] *Ibid.*, p. 391.

[199] A. A. Noyes, *Review of American Chemical Literature,* 7 (1901), 157.

A similar but more moderate response appeared in *Nature,* in a letter by the British chemist H. M. Dawson. After commenting on points of detail, Dawson wrote:

> Although, therefore, the publication contains a large number of valuable empirical data, yet it cannot be allowed for one moment that the ionic theory has been shown to be untenable. It is far from the wish of the writer to minimise the difficulties which do admittedly confront the theory of ionic dissociation. It must not, however, be supposed that the theory has received its final and complete form; the possibilities of its rational expansion and development to explain existing irregularities are far from being exhausted. A warning note may be sounded against a too ready assumption that new experimental data prove the untenability of the theory without very careful consideration of what exactly is, and is not, stipulated by the theory.[200]

The American Electrochemical Society

A second general paper by Kahlenberg appeared in 1902 in the *Transactions* of the American Electrochemical Society.[201] He added little but rhetoric to his earlier arguments.

The American Electrochemical Society requires consideration in its own right in the present historical study: it reported the discussions at its meetings, providing historians with valuable information about the interactions of American electrochemists. Kahlenberg later described the climate of opinion in the early meetings. He characterized the first decade of activity of the society as dominated by discussion of the fundamental electrochemical theories and concepts. He considered this due to the impact of Arrhenius' electrolytic dissociation theory, which, although promulgated in 1887, only gained a foothold after Ostwald propagandized it and applied it to ordinary chemical reactions in aqueous solutions. "So it is not surprising," he wrote, "that the American Electrochemical Society, too, in its early years, should have busied itself to a considerable degree with the discussion of the pros and cons of this new electrochemical theory. On the whole our membership, following perhaps the lead of the English scientists, was rather loath to adopt

[200] H. M. Dawson, *Nature, 65* (1902), 415.

[201] L. Kahlenberg, "Current Electrochemical Theories," *Transactions of the American Electrochemical Society, 1* (1902), 119-124, discussion 124-125.

Arrhenius' theory. Be that as it may, the members were certainly by no means completely stampeded by it; they were, in general, content to make use of it as a working hypothesis as far as this could be done.''[202]

Kahlenberg's account agrees with the record in the *Transactions* of the society. The air of caution about the dissociation theory at the society meetings reflected the hostility to the theory of several of the organizers of the society. Kahlenberg was one of the six vice-presidents elected at the first meeting. Another opponent of the theory was C. J. Reed, an electrochemical engineer who was considered the "prime mover in the organisation of the society"[203] and who was the first secretary of the society.[204] The first president of the society, J. W. Richards, was unenthusiastic.[205]

The most useful record of opinion in the society about the electrolytic dissociation theory was the general discussion on the topic held in September 1903. One of the introductory papers was by W. D. Bancroft, a graduate of the Ostwald laboratory and founder of the *Journal of Physical Chemistry*. After briefly describing the dissociation theory and its applications, he gave the following description of its status at the time:

> The electrolytic dissociation theory has carried the chemical world by storm. It is not too much to say that those who have never accepted the theory no longer exert an effective opposition. Every day, however, it becomes clearer that the early adherents of the theory are now working along two divergent lines. One group of men has been interested in increasing the number of facts to which the theory applies. These men have been very successful. . . . Other men, prominent among whom is Kahlenberg, have felt that the interesting things about a theory are its limitations. They have also been successful, and we now know a great deal about the shortcomings of the electrolytic dissociation theory. . . . The final result is that the electrolytic dissociation theory applies only

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[202] L. Kahlenberg, *Transactions of the American Electrochemical Society, 51* (1928 [for 1927]), 42.

[203] *Transactions of the American Electrochemical Society, 1* (1902), 8.

[204] See, for example, C. J. Reed, *Transactions of the American Electrochemical Society, 3* (1903), 278; *4* (1903), 177-182; *5* (1904), 142.

[205] See, for example, J. W. Richards, *Transactions of the American Electrochemical Society, 5* (1904), 40-41.

> to infinitely dilute solutions, which is much the same as excluding the whole of chemistry.[206]

Many of the members who contributed to the main discussion, including a number of Leipzig graduates, agreed that although the theory had been very useful as a working hypothesis, there were many objections to it, some of which were serious. The Canadian W. Lash Miller, who had studied under Ostwald, expressed a slightly different attitude: after reporting some experimental results which were apparently contrary to the theory, he gained laughter and applause when he admitted that one reason for not abandoning the dissociation theory was that it was very handy in giving lectures; so he looked for an explanation compatible with the theory.[207]

Within the American Electrochemical Society, therefore, there were a number of scientists who, like Kahlenberg, perceived serious problems for the dissociation theory. However, in the absence of a better theory they were willing to continue to use it as a basis for research, even though its use was beginning to lead to artificial complications just as theories of cycles and epicycles had become increasingly complicated in the history of astronomy.[208] Some of the participants expected the present theory to be succeeded by a revolutionary alternative.[209]

Kahlenberg saw the dissociation theory as being in an irremediable state of crisis and wished to reject it completely. He had come to think that it was corrupting the path of physical chemistry.

Further Experimental Work by Kahlenberg; the Debate between Fernekes and Smith

As an alternative to the Ostwald school theory Kahlenberg favored explanatory mechanisms which give an active chemical role to the solvent. He developed these ideas in a paper published in 1903.[210]

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[206] W. D. Bancroft, *Transactions of the American Electrochemical Society, 4* (1903), 175-176.

[207] W. Lash Miller, *Transactions of the American Electrochemical Society, 4* (1903), 185.

[208] The analogy with astronomy was raised by H. S. Carhart, *Transactions of the American Electrochemical Society, 4* (1903), 186-187. Much of the language of the discussion invites the application of T. S. Kuhn's term "crisis."

[209] *Ibid.*, p. 187.

[210] L, Kahlenberg, *Journal of the American Chemical Society, 25* (1903), 380-392.

He measured the rate of interaction between magnesium and various aqueous solutions. He found considerable variation in the rate of evolution of hydrogen and claimed that that result supported the idea that the solution is the product of chemical interaction between solvent and solute. The dissociation theory, he argued, is unable to explain his results, and his alternative chemical conception will be a valuable aid to further research, particularly as it does not focus attention on very dilute solutions.

Kahlenberg's ideas were employed in an extended exchange between one of his students, G. Fernekes, and an advocate of the dissociation theory, G. M. Smith. Fernekes had made an experimental study of the reactivity of sodium and potassium amalgams in various aqueous solutions.[211] In another experimental context, Arrhenius had once suggested that ions of sodium or potassium in solution would hinder the entrance of more of these metals from an amalgam into the solution.[212] Consequently a solution of potassium chloride, for example, should slow the reaction of potassium amalgam, but not of sodium amalgam. In his experimental work Fernekes found that the potassium salt slows the reaction of both potassium and sodium amalgams with the solution. He presented this result as evidence against the dissociation theory and in favor of Kahlenberg's idea that the process of dissolution involves a chemical reaction between solvent and the dissolving substance. The nearly equal retardation of the reaction of both amalgams by sodium and potassium chlorides could be explained if the reaction rate depended on the availability of free water.

Smith replied,[213] arguing that Fernekes' result *is* compatible with the ionic theory. He explained that when sodium amalgam is placed in potassium chloride solution, potassium exchanges with the sodium in the amalgam (where it can be detected experimentally) until the amalgam and the solution contain both elements. As a result of such an exchange, both types of cations retard the reaction of either metal with the water. Fernekes' response was to introduce the case of barium amalgam which reacts three times as strongly with pure water as with potassium chloride solution, although no potassium can be detected in the amalgam.[214] Smith replied by

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[211] G. Fernekes, *Journal of Physical Chemistry*, 7 (1903), 611–639.

[212] S. A. Arrhenius, *Zeitschrift für physikalische Chemie*, *11* (1893), 805.

[213] G. McP. Smith, *Journal of Physical Chemistry*, *8* (1904), 208–213.

[214] G. Fernekes, *Journal of Physical Chemistry*, *8* (1904), 566–570.

describing further experiments in which an ion exchange took place in the amalgam. He concluded: "While all the phenomena of solutions may not be capable of explanation by the ionic theory, it is nevertheless very rash to claim that it has been shown 'conclusively' that this theory has outlived its usefulness."[215]

The debate between Fernekes and Smith might be said to illustrate the point that, when each side is supported by enthusiasts, there is virtually no end to the moves that can be made to avoid accepting the other's case as conclusive.

In another experimental study of 1904, Kahlenberg argued that electrode potentials depend not merely on the metal involved, but also on the solvent and any solute in the solution.[216] Bancroft agreed in the subsequent discussion that Kahlenberg's evidence cast doubt on the assumptions underlying the use of the van't Hoff-Raoult formula.[217]

The Discussion of Kahlenberg's Work in Britain, 1904-1905

At the end of 1904 Kahlenberg read a general paper to the recently formed Faraday Society in Britain.[218] In it Kahlenberg most clearly summarized his arguments against the theories of dissociation and solution. The paper was widely discussed: most chemists who remarked on it felt that Kahlenberg had gone too far in his rejection of the basic theories of physical chemistry. Many shared the view that, although supporters of the dissociation theory had made many claims that Kahlenberg was right to criticize, these claims were not essential to the theory. Both the extreme dissociationists and Kahlenberg were wrong to emphasize these claims.

> The objections raised [by Kahlenberg] will, I think, serve as a salutary corrective to the tendency which to my mind pervades contemporary chemical thought to exaggerate the scope of the ionic theory and to use facts which neither contradict nor support it as arguments in its favor.[219]
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> The author [Kahlenberg] seemed to attack the dissociation

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[215] G. McP. Smith, *Journal of Physical Chemistry, 9* (1905), 35.

[216] L. Kahlenberg, *Transactions of the American Electrochemical Society, 6* (1904), 53-65; discussion pp. 65-66.

[217] W. D. Bancroft, *ibid.*, p. 65.

[218] L. Kahlenberg, *Transactions of the Faraday Society, 1* (1905), 42-53; discussion pp. 53-64.

[219] H. J. Sand, *ibid.*, p. 58.

> theory as if everything that had been written in favor of it formed a chapter of an orthodox Bible. The previous speakers had already shown that Dr Kahlenberg criticised many views which were not really held by the majority of modern electrochemists, and as regards the physiological action of electrolytes, Nernst differed from Arrhenius.[220]

As in the earlier discussion at the American Electrochemical Society, Kahlenberg and his audience diverged on the methodological question of whether or not a theory with as many problems as the theory of electrolyte dissociation was better than no theory at all. R. Abegg argued in a communication: "If one wishes to overthrow any successful theory, it is not sufficient for the progress of science to point out its difficulties—in that case not one theory in science would be valid!—but it is necessary to find another theory likely to explain not merely the difficulties of the old one but also the many phenomena and observations already embraced by it, a procedure a classical example of which you see in the history of the theories of light."[221] Kahlenberg replied that he was not hankering for more theories. "The pathway of the progress of science is strewn with defunct theories, and not always has a new theory replaced an old one. I would not depreciate the value of a working hypothesis, but I would also not minimise the power it has to lead the biased investigator astray."[222]

The paper Kahlenberg presented to the Faraday Society attracted the critical attention of H. C. Jones, an enthusiastic American supporter of the Ostwaldian theory. Kahlenberg had quoted work done by Jones and his students as evidence against the Arrhenius theory. Jones was annoyed, for he had presented the results as a natural development of the Ostwaldian program. He concluded his reply to Kahlenberg by quoting an earlier comment: "These substances, instead of presenting any exception to the theory of electrolytic dissociation fall directly in line with the theory, as so many similar cases have done. Indeed, it is interesting to see how many exceptions to the theory of electrolytic dissociation disappear as experimental methods become more refined and experimental work more accurately carried out. The amount of evidence for the

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[220] H. Borns, *ibid.*, p. 60.
[221] R. Abegg, *ibid.*, p. 57.
[222] L. Kahlenberg, *ibid.*, p. 64.

general correctness of this most fruitful generalisation is at present so large that any apparent exception will be accepted only after it has been very thoroughly substantiated by repeated experiments."[223] Kahlenberg insisted that it was Jones's data not his interpretation that supported the case against the electrolyte dissociation theory, and he cited criticisms that pointed to the arbitrariness of Jones's method of relating his results to the Ostwaldian theory.[224]

Kahlenberg on Osmotic Pressure

In his paper read to the Faraday Society, Kahlenberg had mentioned preliminary results he had obtained in a study of osmotic pressure. This work was published in 1906.[225] His main point of attack was the analogy between gases and dilute solutions. Kahlenberg argued that semipermeable membranes act by selective solubility and that the thermodynamical idea of a passive semipermeable membrane was a fiction. Membranes can only become more nearly semipermeable if their selective action through differential solubility becomes more pronounced. Kahlenberg presented a model of the action of such a membrane: he described experiments in which three layers of fluid, chloroform, water, and ether, are contained in a vessel in such a way that chloroform is underlying water and water underlying ether. As ether is soluble in water it can pass through into the chloroform layer to form a solution of chloroform and ether. But chloroform is almost insoluble in water and so must remain in the lowest layer. Thus the water acts as a semipermeable layer. In the course of the experiment the ether layer disappears, most of it passing through into the lowest layer. Kahlenberg claimed that the model was adequate to explain the qualitative and quantitative results of studies with semipermeable membranes. Just as no liquid is completely insoluble in another, Kahlenberg argued, no membrane is completely semipermeable. Consequently the experimenter will not obtain equilibrium until the separated liquids are of the same composition. It was not customary to stir

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[223] H. C. Jones, *Philosophical Magazine* [6], *10* (1905), 157. The comment was originally made in *American Chemical Journal, 27* (1902), 22.

[224] L. Kahlenberg, *Philosophical Magazine* [6], *10* (1905), 662-664. The critic of Jones's method was J. J. van Laar, *Chemisch Weekblad, 2* (1905), 1-16.

[225] L. Kahlenberg, *Journal of Physical Chemistry, 10* (1906), 141-209.

the liquids in measurements of osmotic pressure, which meant that it took some time to reach a point of apparent equilibrium across a semipermeable membrane. In this time, leakage due to incompleteness of semipermeability could substantially affect the measurement. Kahlenberg proposed that, as in solubility measurements, the separated liquids should always be stirred. Then one would obtain maximum osmotic pressure more quickly and diminish the effects of leakage. Kahlenberg presented the new sets of measurements obtained in this way as evidence of the inadequacy of van't Hoff's law, even as an idealization. "To speak of the osmotic pressure of any isolated solution without specifying what membrane separates it from what other liquid is nonsense, in the light of the facts here presented. And further, to assume that solutes are polymerized or dissociated in dilute solutions because the osmotic pressures developed by the latter in given cases happen to deviate from values computed from the gas laws is evidently equally unjustifiable practice."[226]

There was considerable interest in the mechanism of osmosis at the time, and Kahlenberg's paper attracted some attention. An early forum for discussion was the correspondence columns of *Nature*, which had published an abstract of Kahlenberg's paper.[227] The Earl of Berkeley and E. G. J. Hartley objected to Kahlenberg's experimental methods, and Whetham disagreed with Kahlenberg over the theoretical significance of his work.[228] Whetham told Armstrong, who also joined the exchange, that he had an impartial attitude toward the dissociation theory:[229] "I hold no brief for the [electrolytic dissociation] theory, as Professor Armstrong seems to imagine, and if it ever ceases to be the best hypothesis in the field, I shall willingly abandon it. Consistency always seems to me to be the meanest of virtues, and in matters scientific it may become the most deadly of vices."[230]

But even with such a Popperian attitude, Whetham considered that Kahlenberg's paper carried little weight against the theory of solu-

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[226] *Ibid.*, pp. 207-208.

[227] L. Kahlenberg, *Nature, 74* (1906), 19.

[228] The Earl of Berkeley and E. G. J. Hartley, *Nature, 74* (1906), 54-55, 245. W. C. D. Whetham, *ibid.*, pp. 54, 102-103, 195-296. L. Kahlenberg, *ibid.*, p. 222.

[229] H. E. Armstrong, *Nature, 74* (1906), 79.

[230] W. C. D. Whetham, *Nature, 74* (1906), 103.

tions or the electrolyte dissociation theory. Whetham distinguished between the ideal concept of osmotic pressure employed in thermodynamics and the experimentally determined osmotic pressure. Whatever Kahlenberg was able to show experimentally could not affect the thermodynamic proof. "Defining osmotic pressure as the hydrostatic pressure needed to keep a solution in equilibrium with its solvent across an ideally perfect semipermeable membrane, we obtain a conception, possibly of less chemical and physiological importance, which nevertheless enables us to develop a thermodynamic theory of solution; and this theory has been verified experimentally in cases where we have reason to suppose that the actual conditions approach the ideal."[231]

Kahlenberg initially accepted Whetham's distinction between the two concepts of osmotic pressure, commenting only that the ideal thermodynamic concept has no counterpart in reality and ought to be relabelled in a way that does not involve the term "osmotic."[232] But by 1909 he reacted more strongly. In a reply to criticisms by the Dutch physical chemists E. Cohen and J. W. Commelin[233] he wrote:

> It is a well-known dodge of the thermodynamicists to claim that they are not concerned with the mechanism of osmosis and that which produces osmotic pressure, for they simply require to know the magnitude of the latter in order to proceed with their computations. Right here lies the strength, but also the great weakness of thermodynamic methods. *What we want to know above all things is what causes osmosis and osmotic pressure in order to put us into a position to discuss more intelligently the results of osmotic experiments, and to determine to what extent such results are actually useful in forming a true basis for a tenable theory of solutions.*[234]

Kahlenberg was convinced that the thermodynamic approach to the theory of solutions could be of little value since it claimed to be merely an idealization and did not represent the actual osmotic processes. The approach was also misleading for the physical

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[231] W. C. D. Whetham, *Nature, 74* (1906), 295.

[232] L. Kahlenberg, *Transactions of the Faraday Society, 3* (1907), 26.

[233] E. Cohen, *Chemisch Weekblad, 3* (1906), 290; E. Cohen and J. W. Commelin, *Zeitschrift für physikalische Chemie, 64* (1908), 1-52.

[234] L. Kahlenberg, *Journal of Physical Chemistry, 13* (1909), 97-98. Italics in original.

chemist, he argued, as thermodynamicists *are* concerned with measurements of the magnitude of osmotic pressure, and they tend to pay disproportionate attention to those experiments that show approximate agreement with the gas laws.[235]

In 1907 Kahlenberg submitted a paper to the general discussion of osmotic pressure held by the Faraday Society. He added little to his earlier views, and his work did not attract very much discussion. A. Findlay and Whetham commented on the distinction between thermodynamic and experimental concepts of osmotic pressure. Findlay commented on the role each had played in the past and accused Kahlenberg of being the source of the confusion surrounding the concepts. Both Findlay and Whetham tried to make clearer the limitations and the significance of the thermodynamic concept.[236]

Kahlenberg's Later Position

Kahlenberg's views on the Ostwaldian theory did not go through any further significant development. His final position was summarized in an address given in 1909, "The Past and Future of the Study of Solutions."[237] He suggested that the Ostwald school theory should now be rejected even as a working hypothesis, but that the historian should remember at least its enthusiasm. "The pages of the history of chemistry that record this experimental work on dilute solutions will ever maintain their brilliant luster, for they reflect the enthusiastic efforts of scores of active young hands and minds that were urged on by a most inspiring leader, an able teacher and experimenter and a most loveable man—Wilhelm Ostwald. Without him the theories of van't Hoff and Arrhenius would scarcely have gained a foothold."[238] He summarized his previous arguments against the Ostwald school theory and sketched an alternative chemical theory of solution. The physical theory had distracted attention from older chemical theories, which should be returned to. "Before the advent of the physical theories of solutions considerable work was done in ascertaining the chemical relationships that must exist between solvent and solute in order that solution may take place; but during

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[235] *Ibid.*, p. 98.

[236] A. Findlay, *Transactions of the Faraday Society, 3* (1907), 32. W. C. D. Whetham, *ibid.*, p. 36.

[237] L. Kahlenberg, *Science, 31* (1910), 41–52.

[238] *Ibid.*, p. 43.

the last two decades this work has been practically discontinued, which is particularly unfortunate. It clearly indicates, however, how our so-called modern conceptions of solutions, which have been pressed upon the scientific public by a species of propagandism that is, and it is hoped will remain, quite unrivalled in the history of chemistry, have really stood in the way of progress."[239] The new path for the study of solutions should be to develop chemical insights into solution and should be experimental rather than mathematical: "In the study of solutions, just as in the study of chemical compounds in the narrower sense of the word, we are continually confronted with discontinuities. Now discontinuities can not be handled by mathematicians at present. . . ."[240]

Occasional remarks in his writings from the later part of his career reveal that Kahlenberg continued his undiminished hostility to the Ostwald school theory; to a decreasing proportion of his students he still assigned experimental work designed to show its limitations. According to a biographer,[241] it so discouraged him that his criticisms of the dissociation theory had not been accepted, that he became dogmatically empirical in his approach, ignoring most developments in physical chemistry. "His distrust of theory drove him into a dogmatic empiricism which severely limited his scope, and led him on occasion to condone in himself and in graduate students mere ignorance in the name of healthy scepticism."[242] His own evaluation of his lack of success is reflected in remarks made in a discussion in 1927. After referring to his studies showing the defects of the Nernst-Thomson rule, which relates the dissociative power of a solvent to its dielectric constant, he said: "These facts are not mentioned in the so-called standard books on physical chemistry, for they do not fit in with the theoretical views there promulgated."[243]

Methodological Discussion of the Issues Raised by Kahlenberg

It is appropriate to review some of the general methodological issues raised by Kahlenberg's career. We have seen that, like Arm-

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[239] *Ibid.*, p. 49.

[240] *Ibid.*, p. 51.

[241] N. F. Hall, *Transactions of the Wisconsin Academy, 39* (1949), 89–90.

[242] *Ibid.*, p. 90.

[243] L. Kahlenberg, *Transactions of the American Electrochemical Society, 51* (1927), 557.

strong and Pickering, Kahlenberg was of a polemical temperament. He distrusted mathematical and idealized physical concepts and techniques as they did. However, because he was a rebel from within the Ostwald camp, he presented his case against the Ostwald school theory in a form that differed methodologically from that of the English opposition. His claim was not that the theory was a novel approach which attempted to bypass by illegitimate means the established chemical theories, but rather that the initially plausible theory had outlived its usefulness. "Like other theories founded upon too narrow a basis of induction, it has gradually been outgrown—the facts are too much for it."[244] Unfortunately, as Kahlenberg saw it, the defenders of the Ostwald school theory continued on their old path, while their theory became increasingly incongruous. "To be sure, these investigators and also some others still try to 'harmonize' their results with the theory of electrolytic dissociation, but their efforts at this remind one strongly of the attempts of the ardent advocates of the old phlogistic theory, when they sought to harmonize the fact that bodies are heavier after they are burned, with the hypothesis they wished to uphold at all hazards."[245] Kahlenberg wrote of one such attempt to save the theory: "It is in fact nothing more than to arbitrarily make the behaviour of all solutions conform to a Procrustean bed."[246]

Once he had proved to his own satisfaction that both the theory of electrolyte dissociation and the gaseous theory of solution were not literally true, Kahlenberg treated them as working hypotheses, founded upon partial analogies. Moreover, he argued, they had now become a hindrance in research. He believed it was better to have no theory at all than to keep a misleading one. This attitude set him apart from most of his colleagues.

Much of his work was devoted to criticizing the analogies used by the Ostwald school theorists and to replacing them by ones more natural to a chemist. He insisted that the interpenetration of substances in solution is produced by chemical affinity. In the continuum noted by Thomas Graham from adhesion to solution to chemical action, it is concentrated solutions which show the greatest comparability with chemical action. "It thus becomes evident that in

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[244] L. Kahlenberg, *Journal of Physical Chemistry, 5* (1901), 391.

[245] L. Kahlenberg, *Transactions of the American Electrochemical Society, 1* (1902), 121.

[246] *Ibid.*, p. 122.

investigating solutions we must begin with the most concentrated and end with the most dilute; the latter will appear simply as a limiting case."[247] In such a way Kahlenberg built up arguments to show that it was most productive to study concentrated rather than dilute solutions.

Again, Kahlenberg found the analogies of the Ostwaldian theory to be misleading when they were used to explain the mechanisms of the key processes of solution. He insisted that the process of dissolution, for example, is best viewed as the mutual interaction of solvent and solute. To explain the dissolution of metallic magnesium in aqueous solutions the ionic theories provide a far less reliable guide than a theory in which solutions are "a chemical combination of solvent and solute according to variable proportions."[248] Kahlenberg considered van't Hoff's analogy between gases and dilute solutions especially misleading. It was based only on a limited selection of aqueous solutions at infinite dilution; at higher concentrations, the behavior of solutions deviates from ideal gas behavior in quite a different manner than does the behavior of real gases. As far as the process of osmosis was concerned, Kahlenberg felt that the thermodynamicists' approach exhibited a brutal disregard for the facts. The thermodynamic idealization of osmotic pressure ignored the actual processes except in the rare cases of quantitative agreement between practical and theoretical results.

Kahlenberg attacked van't Hoff's theory of solution primarily to eliminate it as a source of support for Arrhenius' theory. Van't Hoff's theory was not nearly exact enough to be "corrected" by introducing the additional parameter of variable dissociation suggested by Arrhenius. Kahlenberg considered that whatever was of value in Arrhenius' speculations was already contained in Clausius' earlier theory. Once the quantitative basis for Arrhenius' theory had been undermined, chemists could return to the view that electrolyte solutions were like other solutions, and they could seek the mechanism of the passage of electricity in some other way. Kahlenberg believed that electrolytic conduction is probably similar to other types of conduction. Electrolysis requires electrodes as well as a conducting liquid, and it is possible that all the chemical effects

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[247] L. Kahlenberg, *Transactions of the Faraday Society, 1* (1905), 50.

[248] L. Kahlenberg, *Journal of the American Chemical Society, 25* (1903), 390.

take place at the surface of the electrode and that concentration changes in the solution are a secondary effect. Typical electrolytes contain both a metal, which conducts, and a nonmetal, which insulates; often, as with the chlorides of tin, compounds with a higher proportion of nonmetal such as stannic chloride insulate, while compounds with a lower proportion such as stannous chloride are electrolytes. Thus electrolytic conduction appeared to Kahlenberg to be part of a natural gradation of properties between metallic conduction and insulation.[249]

Kahlenberg was an experimental scientist who tried to establish the real nature of a limited range of phenomena in which, he believed, mathematical relationships were hidden, if present at all. As the appropriate method of investigation in such circumstances he chose to stay close to the experimental phenomena, using analogies and guiding hypotheses only where they allowed him to draw the results together into an explanation of the basic processes without directing him into unproductive lines of investigation. Thus his opposition to the Ostwald theory came from his belief that it was based on an idealization of the facts rather than the facts themselves and that the analogies it contained conflicted with intuition and began to hamper research as chemists studied a wider range of types of solutions.

7. THE CONTINUATION OF THE DEBATE IN BRITAIN

H. C. Crompton

As professor of chemistry at the Central Technical College, London, Armstrong attracted a small but active group of graduate students. A number of these were set to work on projects designed to support Armstrong's crusade against the Ostwald school theory. One of the first of Armstrong's students was H. C. Crompton. Crompton made an independent theoretical contribution to the debate and hence deserves brief consideration. Unlike the other students, who did routine experimental work for Armstrong, Crompton attempted to develop theoretical and physical arguments for aspects of Armstrong's position at the level of the arguments of the opposing physical chemists. I have already noted Crompton's early application

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[249] L. Kahlenberg, *Transactions of the American Electrochemical Society*, *13* (1908), 265-272.

of Mendeleef's method of detecting hydration in solution. In 1897, after an inconclusive study of latent heats of solution, Crompton attempted to calculate theoretically the effect of association between the solvent and the solute on van't Hoff's law of osmotic pressure.[250] Associated liquids can be identified by deviations from Trouton's formula, and associated solutes from modifications of the expected properties of the solutions. Crompton argued that, as a general rule, unassociated liquids dissolve unassociated compounds, and associated liquids dissolve associated compounds. The Ostwald school had been misled by the special behavior of water: water, as the electrolytes that dissolve in it, is associated, but its degree of association is reduced by the addition of electrolytes. Crompton developed the subject by quantitative means and reached the conclusion that

> the hypothesis of electrolytic dissociation is entirely unnecessary for the explanation of those exceptions to van't Hoff's law observed in the case of freezing point reductions. Put briefly, the case is this—the exceptions are no exceptions at all, it is the law that is wrong. No account is taken of association in the liquid state, either for the solvent or dissolved substance, as, in fact, Dr. Armstrong and others in this country have so repeatedly pointed out, and it is this that necessitated the introduction by van't Hoff of the by now celebrated coefficient, *i*, for aqueous solutions, upon which the hypothesis of electrolytic dissociation was founded.[251]

Crompton continued with qualitative arguments, repeating a number of Armstrong's arguments.

In the discussion that followed Crompton's presentation of his theoretical results to the Chemical Society,[252] it became clear that Crompton's treatment, even if not seriously in error, failed to provide an alternative to the ionists' account of the facts.

Later that year Crompton again attempted to give theoretical support to Armstrong's view. His attention had been drawn "to the fact that Planck . . . has long since proved that association could have no effect on the osmotic pressure of liquids."[253] Crompton argued that

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[250] H. Crompton, "The Theory of Osmotic Pressure and the Hypothesis of Electrolytic Dissociation" *Journal of the Chemical Society, 71* (1897), 925–946.

[251] *Ibid.*, pp. 941–942.

[252] *Proceedings of the Chemical Society, 13* (1897), 112–115.

[253] H. Crompton, *Proceedings of the Chemical Society, 13* (1897), 225. The reference to Planck is to a discussion between Planck and Wiedemann, *Zeitschrift für physikalische Chemie, 2* (1888), 241, 343.

Planck's reasoning was circular: Planck had assumed that there is no change in the association of the liquid on vaporization, and he had neglected the volume change involved in association. However, Crompton's arguments were not well received; it was fairly clear that he was not at all effective at such a level of theoretical argument. Indeed, he abandoned theoretical work, returning to experimental studies of latent and specific heats of gases and liquids, in which he showed the effects of molecular association without developing theoretical interpretations from the experimental results. Crompton's failure in theoretical work is informative about Armstrong's approach: the approach was inadequate at a rigorous, theoretical level of argument beyond chemical analogy and the chemists' intuitive sense of plausibility.

Further Development of Armstrong's Views

In 1900 the physics and chemistry sections of the British Association held a joint discussion on ions.[254] This was an inconclusive affair, in which the familiar protagonists once more outlined their positions. Some also ruminated on the implications for ionization in liquids of the recent discovery of the electron and the growing understanding of ionization in gases. But the new developments raised far too many problems for easy assimilation.[255]

In his later publications[256] Armstrong wrote that he had made an important development of his position after the 1900 British Association discussion. He came to think that he had been paying too much attention to the dissolved substance, and that it must be the structure of water itself which was of critical importance, the dissolved substance merely modifying this structure. In the case of electrolytes, the modification was to produce a greater proportion of electrolytically active components. This idea, a natural development of his arguments since the early 1880's, was presented in his article on chemistry in the 1902 edition of the *Encyclopedia Britannica* (after a reasonably impartial presentation of the electrolyte dissociation theory).[257] Armstrong based his theory of the active role of water on the idea that oxygen could associate with more than two atoms; he thus made possible the building up of the molecular ag-

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[254] Although reported by title only in the *Report of the British Association* for 1900, a brief account of the meeting was given in *Nature, 62* (1900), 564.

[255] *Ibid.*

[256] H. E. Armstrong, *Proceedings of the Royal Society, A81* (1908), 80.

[257] H. E. Armstrong, *Encyclopaedia Britannica,* 10th ed. (Edinburgh, 1902), second of the new volumes, pp. 736-741.

gregates in which he had believed for so long. He suggested that some aggregates might have their radicles so arranged as to be electrolytically active, while others did not; in no case were the radicles free. He elaborated the theory to its greatest extent in 1908.[258]

T. M. Lowry

Another of Armstrong's students to become involved in the discussion of the theory of solutions around the beginning of the twentieth century was T. M. Lowry. Lowry moved to physical chemistry from organic chemistry and because of his limited mathematical knowledge worked at experimental topics. Like Armstrong, Lowry regularly attended and addressed scientific meetings. But unlike Armstrong he was not a controversialist and sought to resolve controversies by finding descriptions that revealed common ground between opposing theories.[259] His tendency towards reconciliation is revealed in one of his early contributions to the theory of solutions. In a development of Whetham's compromise between ionic dissociation and hydration, Lowry suggested that not merely were ions hydrated, but that the ions owed their existence to the added hydration accompanying dissociation. Lowry later gave the following account of the origin of his idea and of its place in the debate.

> The writer can claim to look upon this controversy with some measure of personal interest since, while still at school he was first attracted to the study of chemistry by the fascination of the theory of electrolytic dissociation, and in particular of its dramatic correlation of the conductivity of an electrolyte with the freezing point of the solution. Soon afterwards, as a student of Professor Armstrong—then, as now, a consistent critic of the "new" theory of solutions,—he was faced with the necessity of finding for his own use a scheme which should be compatible with the two rival points of view. This he found in the idea that *both* views were correct, that their incompatibility was imaginary and not real, and that the hydration of the ions not only provided a way of reconciling the two theories of solution, but also supplied a motive for the electrolytic dissociation of a salt which (as Armstrong had

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[258] H. E. Armstrong, "Hydrolysis: Hydrolation and Hydronation as Determinants of the Properties of Aqueous Solutions," *Proceedings of the Royal Society, A81* (1908), 80-95.

[259] C. B. Allsop and W. A. Waters, *British Chemists,* eds. A. Findlay and W. H. Mills (London, 1947), p. 407.

> pointed out) was conspicuously absent from the original "naked" theory of electrolytic dissociation.[260]

When Lowry presented his paper to the Faraday Society,[261] he learned in the subsequent discussion that parallel developments had already taken place on the continent.[262] Nevertheless, Lowry's work and his search for compromise continued to play an important part in the papers and discussions of the Faraday Society.

The Nature of Osmotic Pressure 1887-1907

By the middle of the first decade of the twentieth century, the Faraday Society had become the most important British forum for the discussions and controversies over the theory of solutions. "General discussions" were to become an enduring feature of the society, and the first two of these recorded in the *Transactions* were on "Osmotic Pressure" and "Hydrates in Solution"—both topics that would have invited further critical scrutiny of the Ostwald school theory.

Until about 1907 the discussions of the nature of osmotic pressure had been marked by considerable confusion. The Faraday Society meeting may be considered the occasion at which the British reached a common understanding of what had and had not been established.

A major source of the continuing misunderstandings was van't Hoff's original paper of 1887.[263] His statements had allowed his readers to attribute to him contradictory accounts of the mechanism of osmotic pressure. In one passage he wrote that given a vessel, *A*, containing a solution separated from its solvent by a semipermeable membrane, "it is known that the attraction of the solution for water will cause water to enter into *A*. . . ."[264] A page later, van't

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[260] T. M. Lowry, in T. M. Lowry and J. Russell, *The Scientific Work of the Late Spencer Pickering F.R.S.* (London, 1927), p. 32.

[261] T. M. Lowry, *Transactions of the Faraday Society, 1* (1905), 197-206; discussion 206-214.

[262] The reference was to Werner, *Zeitschrift für anorganische Chemie, 3* (1893), 294.

[263] J. H. van't Hoff, *Zeitschrift für physikalische Chemie, 1* (1887), 481-508. Later references are to the translation in *Alembic Club Reprints,* No. 19 (Edinburgh, 1961).

[264] *Ibid.,* p. 6. One Ostwaldian physical chemist who took this sentence as indicating van't Hoff's own understanding of the source of osmotic pressure was A. Findlay. See, for example, *Osmotic Pressure* (London, 1913), p. 69 and footnote.

Hoff wrote of the analogy between gases and solutions: "We wish to emphasise in this connection that we are not here dealing with a fanciful analogy, but with one which is fundamental; for the mechanism which according to our present conceptions produces gaseous pressure, and in solutions osmotic pressure, is essentially the same. In the first case it is due to the impacts of the gas-molecules on the containing walls, in the second to the impacts of the dissolved molecules on the semipermeable membrane. The molecules of the solvent present on both sides of the membrane, since they pass freely through it, need not be taken into consideration."[265]

Van't Hoff's memoir contains another source of confusion for its readers, for a literal interpretation of the passage just quoted gives the wrong sign to the osmotic pressure. Van't Hoff seemed to imply that additional pressure would have to be applied to the solvent side rather than the solution side of the membrane to produce equilibrium.[266] Eventually chemists agreed that the problem is trivial. Gases behave just as solutions do, as was shown experimentally when a container with a palladium septum (which is only permeable to hydrogen) was filled with hydrogen on one side and a mixture of gases on the other. The hydrogen flowed through the septum to reach the same partial pressure on each side. At equilibrium, the other gases present on one side created an excess hydrostatic pressure on that side of the septum.[267] Analogously, the solvent attempted to flow through a semipermeable membrane into the solution. Unless a hydrostatic pressure is applied to the solution, equilibrium can only be reached at infinite dilution. Thus, although the magnitude of the osmotic pressure is proportional to the concentration of the solute, it is actually the external pressure required to stop the entry of the solvent into the solution. Any chemical action between solvent and solute increases the osmotic pressure, but that effect can be neglected at the very low concentrations to which van't Hoff's analogy of gases and liquids applied. Neither of the two mechanisms that van't Hoff mentioned were essential to his

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[265] J. H. van't Hoff, *op. cit.* (note 263), p. 7. Kahlenberg considered this account of the mechanism of osmosis sufficiently authoritative to believe that an attack on the analogy between gases and dilute solutions was an attack on the whole theory of solutions.

[266] This point is made, for example, by J. G. Rhodin, *Transactions of the Faraday Society, 3* (1907), 81-85.

[267] W. Ramsay, *Philosophical Magazine* [5], *38* (1894), 206-218.

theory. Indeed, when giving a theoretical proof that Boyle's law applies to dilute solutions, van't Hoff treated the two mechanisms as alternatives with equal status. "If we consider osmotic pressure to be of kinetic origin, that is as arising from the impacts of dissolved molecules, we have to prove proportionality between the number of impacts in unit time and the number of impinging molecules in unit volume. . . . On the other hand if we see in osmotic pressure the effect of an attraction for water, its magnitude is obviously proportional to the number of attracting molecules in unit volume, with the proviso (which is fulfilled in sufficiently dilute solutions) that the dissolved molecules are without action on one another, and that each contributes on its own account a constant amount to this attractive action."[268]

Another matter that had further obscured the discussion of osmotic pressure was an early confusion over the appropriate units to employ in the calculations. In his original theory van't Hoff had assumed that the relevant volume in the equation $PV = iRT$, when applied to solutions, is the volume of the *solution*. But chemists found that they obtain better agreement when they use the volume of the *solvent* present in the solution—that is, if they calculated concentrations in gram-molecules of solute per 1000 gm of water rather than per 1000 cc of solution.[269] They then suggested theoretical reasons why this should be a better basis for calculation. Armstrong was among those who used the problem as evidence of the incompetence of the ionists.[270]

The main English speaking opponents of the Ostwaldian theory employed conflicting conceptions of the nature of osmotic pressure and of the action of the semipermeable membrane in their arguments. It has already been pointed out that in 1891 Pickering had claimed that the very existence of osmotic pressure is an argument against the electrolyte dissociation theory. His belief that the membrane allowed only the smallest molecules to pass allowed him to infer that solute molecules must be highly hydrated in solution. Kahlenberg believed that the semipermeable membrane acted by

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[268] J. H. van't Hoff, *op. cit.* (note 263), p. 10. See also van't Hoff's comment in the *Report of the British Association* for 1890 (1891), p. 336, where he insisted that the kinetic interpretation of osmotic pressure was more intended to popularize than to prove the laws in question.

[269] H. N. Morse, *American Chemical Journal, 38* (1907), 175.

[270] See, for example, H. E. Armstrong, *Science Progress, 3* (1909), 651.

selective solubility, and that demonstration of this mechanism was an argument against van't Hoff's theory of solutions. Finally, Armstrong attributed osmotic effects to the action of the solute on the degree of association of the solvent, interpreting unexpectedly high osmotic pressure as evidence of a great effect on the depolymerization of water, not as evidence of dissociation of electrolytes. Thus *his* views on the origin of osmotic pressure also constituted an argument against the Ostwald school theory. As van't Hoff's original memoir allowed the Ostwaldians to claim different mechanisms of osmotic pressure as orthodox, chemists were not likely to reach an immediate consensus on the matter. By the time of the debate on osmotic pressure at the Faraday Society, scientists were generally aware of a great number of more or less acceptable possible mechanisms for osmotic pressure. None of these they could at that stage accept as basis for a convincing account of other features of electrolytes and solutions.[271]

By 1907 chemists had also understood—especially from the exchange between Kahlenberg and Whetham—that the thermodynamic treatment of solutions did not require any assumptions about a causal mechanism or the existence of a real example of a perfect semipermeable membrane.

We may see the discussion at the Faraday Society meeting of January 1907 as a record of reorientation: the main focus of the debate over the theory of solutions passed from the direct evaluation of van't Hoff's theory to new issues in which the opposing parties were drawn up in a new way. Some of the participants still expressed opposition to the Ostwald school theory, for they were not all of the same intellectual lineage, but such attitudes were no longer the main point of interest.

The Faraday Society Discussion of Hydrates in Solution, 1907

The second general discussion held by the Faraday Society in 1907 was that on hydrates in solution. It took place on 25 June with Pickering as chairman. Because Pickering took part in the discussion, the confrontation of the Ostwald school theory and the hydrate theory continued, but that was no longer the main object of the discussion. British chemists who were sympathetic to the theory of

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[271] A good idea of the openness of the issue is given a little later by A. Findlay in the last chapter of his monograph, *Osmotic Pressure* (London, 1913).

electrolytic dissociation now almost invariably acknowledged the importance of the hydration of ions. The main paper of the discussion, presented by W. R. Bousefield and T. M. Lowry,[272] dealt with the idea that it is the increase in hydration that stabilizes dissociated ions in solution. When Pickering resurrected his thermochemical arguments against the ionization theory, Bousefield dismissed his objection: "The criticism of the Chairman missed the point of the paper, which was not to prove the ionization theory, but, accepting the ionization theory, to show how one of its difficulties was removed."[273] Pickering also objected that the method by which Bousefield and Lowry had calculated the heats of formation of individual ions did not allow them to use their results as an argument for the independent existence of the ions in solution. They had only shown, he argued, that the heat of neutralization of acids and bases is constant, and they had used that result in the initial calculations. Pickering assumed that he was opposing an argument for the ionization theory and had failed to find any. But if one considers the calculation merely as an elaboration of the conceptual apparatus of the ionization theory, Pickering's criticism of circularity in the reasoning is not justified. In fact, Lowry claimed in his reply that he and Bousefield had shown that the additivity of the heats of formation holds for a wider range of electrolytes than strong acids and bases, so that they *had* gained further support for Arrhenius' theory.[274]

The participants at the meeting gave serious attention to Armstrong's idea that the properties of solutions should all be understood in terms of changes in *association.* G. Senter read a paper in which he criticized Armstrong's theory for its lack of quantitative explanations and for its failure in two cases to provide even correct qualitative explanations.[275] The participants of the meeting based the discussion on their concern to assimilate the known phenomena of hydration without having to abandon the successful explanations of the Ostwald school theory. British physical chemists of the early twentieth century generally knew more mathematics than those of two decades earlier, and they were more concerned to find quanti-

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[272] W. R. Bousefield and T. M. Lowry, "The Thermochemistry of Electrolytes in Relation to the Hydrate Theory of Ionisation," *Transactions of the Faraday Society, 3* (1907), 123-139.

[273] *Ibid.,* p. 161.

[274] *Ibid.,* p. 162.

[275] G. Senter, *Transactions of the Faraday Society, 3* (1907), 146-152.

tative explanations for their experimental observations. With such a requirement, the Ostwald school theory had no serious rival; the only satisfactory way of treating hydration effects was to start from that theory. Armstrong's warning against the distorting effects of undue emphasis on the quantitative aspects of theory carried decreasing weight with physical chemists. Although the chemical phenomena on which Armstrong had based his analogies were studied further, chemists were not interested in returning to his theoretical position. By the second decade of the twentieth century, the dissociation theory was in a state of rapid development anyway. Physical chemists made a succession of attempts to calculate the effects of ionic interaction, and they recognized the advantage of treating strong electrolytes as completely dissociated. Although Armstrong continued his opposition, there was no longer any real debate but rather a feeling that Armstrong was out of touch with the main issues of the field.

Methodological Discussion of the Issues Raised by Pickering's Career

Pickering's remarks in the discussion at the Faraday Society in 1907 were his last direct contribution to the debate on the theory of solutions. They show how out of touch he had become with the subject. His experimental work on solutions had ceased in the mid 1890's; an accident forced a change of career and Pickering devoted himself to fruitgrowing and horticultural research.[276] There is no sign that Pickering recanted his views on the theory of solution. His contribution to the 1907 Faraday Society is that of a dedicated opponent of the Ostwald school theory. His last theoretical paper (on residual affinity)[277] did not contain an explicit discussion of the Ostwald school theory, but in the course of an explanation of heats of neutralization in terms of affinity he claimed that one thermochemical effect that his explanation could account for could not be accounted for by the dissociation hypothesis.[278]

Pickering's career reminds us that there are several ways in which a scientific idea can come to dominate an area of science. Its proponents may succeed in converting its opponents to the new idea but

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[276] The factors involved in the change are discussed in Pickering's biography, T. M. Lowry and J. Russell, *op. cit.* (note 48).

[277] P. S. U. Pickering, *Proceedings of the Royal Society, A93* (1917), 533–549.

[278] *Ibid.*, pp. 547–548.

they may also come to dominate the field if their opponents withdraw without changing their views. The appearance of greater unanimity is thus restored to the field by default.

The history of Pickering's opposition to the Ostwald school theory reflects the difference in methodological attitudes between the Ostwald school and its British opposition on the use of quantitative methods in chemistry. In many ways, the Ostwald school was positivistically inclined: for its members, even approximate mathematical laws were a triumph for science. They held that science should build upon the quantitative laws that were first established in limited domains. But for Pickering, as for Armstrong, the wide-ranging experience of the chemist provided a far better basis for a full understanding of the phenomena of solution than the hypotheses erected on approximate regularities holding over limited domains. He formulated this methodological issue quite clearly in 1890:

> No one can doubt the mathematical correctness of the conclusions which Arrhenius, van't Hoff, Ostwald and others draw from the premises with which they start in their arguments respecting osmotic pressure, nor can we doubt the value of connecting numerous actions with one and the same cause, or that there are a large number of instances in which the observed facts are in substantial agreement with their conclusions. But we may, I think, legitimately doubt whether the premises of the argument are sound, whether the conclusions harmonize as well as they should with the experimental data, whether the theory is more than a mathematical exercise, or more than a convenient working hypothesis of a rough character, instead of being, as its supporters maintain, an hypothesis established so firmly that we may build upon it a physical theory of solution.[279]

A few months later Ramsay responded to Pickering's criticism of the dissociation theory.

> Professor Ramsay agreed with Mr. Pickering that many difficulties still remained to be solved before accepting the theories of Arrhenius and van't Hoff in their entirety. He thought, however, that a theory whatever its nature, could not be regarded as an absolute explanation of phenomena, but merely as a mental picture, whereby phenomena familiar to our senses could be con-

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[279] P. S. U. Pickering, *Philosophical Magazine* [5], *29* (1890), 490.

> ceived of as analogous to those which do not directly appeal to our senses. It might well be possible that the analogy was a defective one; we "explain" many phenomena by the "atomic theory" but have a very limited conception of an "atom"; and the analogy between dilute solutions and gases must also be accepted as merely provisional—as a means of connecting together a great number of phenomena which would otherwise remain isolated facts. By all means let us draw attention to seeming discrepancies; to explain them may involve modification of the theory; but till we have a better one, let us accept one which correlates a large number of phenomena which have not otherwise been united under any other scheme.[280]

In retrospect, it can be understood why Pickering remained unconvinced by the arguments of the Ostwald school, and it can also be seen why his ideas persuaded so few people. His arguments were not as muddled as they were sometimes said to be. But the telling arguments were always presented side by side with misunderstandings and personal idiosyncracies which enabled his opponents to sidestep the difficult questions and answer only those that suited them. His opponents were probably not conscious of this feature of their response, for it is much easier to comment only on those features of a criticism that one is prepared to answer. It is really only in sympathetic historical retrospect that Pickering's work can be fully appreciated.

H. E. Armstrong's Later Research Program

By 1906 Armstrong had set up a systematic research program on the theory of solutions, involving many of his students. The program had three main lines, yielding three series of papers.[281] In his research papers Armstrong was less concerned to show that the dissociation theory was unsatisfactory (though he liked it as little as ever) than to prove that his alternative ideas could effectively guide research. In referring to the dissociation hypothesis in one paper in 1906 he wrote: "It is neither desirable to dwell on the inherent improbability of the conception nor to enter into any discussion of the hypothesis, beyond saying that it is difficult to discover any argument of which it is the unavoidable consequence among the reasons

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[280] W. Ramsay, *Proceedings of the Chemical Society, 6* (1890), 172.

[281] A bibliography of these papers is contained in J. V. Eyre, *Henry Edward Armstrong* (London, 1958).

put forward in support of its acceptance, as these are inconclusive when not based on uncertain premises; my object is to consider an alternative explanation."[282]

One of the most fruitful topics Armstrong found for the development of his alternative conception was hydrolysis. The dissociationists had suggested that hydrolysis is due to the presence of the free hydrogen ion and will occur at a rate dependent on its concentration. Some of the papers in the studies of the Armstrong school on enzymes were related to the work on hydrolysis. The hydrolytic actions of enzymes are very specific. Their action can only be explained, Armstrong argued, by assuming that the key stage of hydrolysis is an association of the substance hydrolyzed, the enzyme, and water. Hydrolysis certainly cannot be explained by assuming that the same active substance (the hydrogen ion) is liberated by all hydrolytic agents. In a long series of papers, "Processes Operative in Solutions," the arguments about the specificity of hydrolysis reactions were extended to inorganic substances. For example, some acids have an increased hydrolytic activity in the presence of their metallic salts, although by the dissociation theory this should depress the formation of the hydrogen ion.

In his series of papers, "The Origin of Osmotic Effects," Armstrong and his students developed a similar case for osmotic phenomena. The work extended the idea developed earlier that the main osmotic effect is produced by the solvent, and the solute merely affects its degree of polymerization.

The Armstrong school published papers until about 1915. Armstrong remained as polemical as ever, but his active research in science diminished after his chemistry department was progressively shut down in 1911-1913.

Armstrong's Last Polemical Writings and a Methodological Discussion of the Issues Raised by his Career

Armstrong's later polemical remarks are of special interest to the present historical study because, as he perceived that the debate was not going as he wished, he described its course in sociological terms, using in particular the metaphors of fashion and religious dogma. He is thus a valuable source of insight into the interpenetration of the methodology and the sociology of scientific practice. Of course,

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[282] H. E. Armstrong, *Proceedings of the Royal Society, A78* (1906), 264.

Armstrong was far from impartial in his representation of the conflict. He was frustrated by his opponents' failure to follow his conception of rational scientific discourse. This led him to note a social dimension in the historical choice between rival scientific ideas. Although he believed that science should resolve disagreements by open and fair argumentation, he described how the Leipzig school resisted criticism very much as Kuhn describes the maintenance of orthodoxy in normal science.

Armstrong compared the methods by which the new school had come to prominence with the nonrational social processes he considered to be at work in women's fashion and the transmission of religious dogma. His fiery polemics put the case more strongly than could any paraphrase.[283] The metaphor of fashion was used to indicate the degeneration of the discipline.

> After all, we scientific workers (or should it not rather be said we workers in science? Because, although evil communications corrupt good manners, the work of science has not, as a necessary consequence, the establishment in the worker of a scientific habit of mind), like women, are the victims of fashion: at one time we wear dissociated ions, at another electrons, and we are always loath to don rational clothing; some fixed belief we must have manufactured for us: we are high or low church, of this or that degree of nonconformity, according to the school in which we are brought up—but the agnostic is always rare among us and of late the critic has been taboo.[284]

In another context, Armstrong discussed the importance of fashion in the scientific education system. "Of late years, in science, as in ordinary life, fashion has ruled the day and there has been a tendency to adopt extremes. 'Authority', exercised through textbooks and fostered by our examination system, dictated the fashion. Students of chemistry all the world over have been led to profess their belief in the doctrine of electrolytic ionic dissociation, much for the

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[283] The most interesting polemical documents of Armstrong's later career are "The Thirst of Salted Water," *Science Progress, 3* (1909), 638-656, a polemical continuation of the ideas set out in simple form in "A Dream of Fair Hydrone," *Science Progress, 3* (1909), 484-499; and "Ionomania in Extremis," *Chemistry and Industry, 14* (1936), 916-917.

[284] H. E. Armstrong, *Science Progress, 3* (1909), 643.

same reason that they have turned up their trousers, not because the practice is rational but because it is conventional. . . ."[285]

Armstrong also described the state of the field by the metaphor of religious dogma. In a polemical letter published late in his life, he made clear his attitude to all forms of dogma. "More than seventy years ago, I not only cast religious dogma aside but also asserted my spiritual freedom when I walked out of church because I could not listen to the nonsense talked from the pulpit. . . . Most so-called physical chemistry is just religious dogma—faith with no works."[286] The decline of rationality in chemistry Armstrong attributed to the replacement of rational discussion by dogma.

> It is difficult to avoid the conclusion that we have offended against all the old canons of practice by which former workers were guided. They disputed, often vigorously and violently—they held the strongest opinions; but as a rule they were careful to balance arguments and to allow arguments to be balanced.
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> The modern method is not even to present the case of the opponent—the student is not allowed the choice of alternatives, he is rarely, if ever, informed that there are alternatives. Prof. J- simply asserts: "This is the truth; believe it you must and shall." Of such kind has been the Leipzig message from the beginning. The spirit of intolerance is abroad among us. If we are not almost back to the days of the Inquisition, we are at least as dogmatic as are the adherents of any religious persuasion. All this in the name of science and of scientific method, of the discipline upon which we are placing so much hope of future enlightenment of society.[287]

He used the same metaphor of religious dogma to espress one of his main worries—corruption of young scientists by Ostwaldian physical chemists. "All the major channels of communication and most of the minor are secured by the high priests of the cult: they command the almost universal obedience of student youth; and now their technical jargon confronts us everywhere."[288] Any benefits in the productiveness of the Ostwaldian dogma could not outweigh the cost to the discipline. "It will be held by some, perhaps even by many, that even

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[285] H. E. Armstrong, "Graham Memorial Lecture," *Science Progress, 6* (1912), 606.

[286] H. E. Armstrong, *Chemistry and Industry, 14* (1936), 917.

[287] H. E. Armstrong, *Science Progress, 3* (1909), 655.

[288] *Ibid.*, p. 656.

if my indictment be true, it matters little nevertheless that a visionary scheme has been advanced—or even that it should have been forced into use for a time. It has inspired workers. But at what expense has victory been gained—if indeed there be true victory of any kind? What nature of example is it that we have set? To what extent are almost all sources of information available to the youthful mind polluted for years to come?"[289] Armstrong was certainly stressing a widely recognized problem. I have already noted a number of scientists who criticized the Ostwald school for omitting reference to their critics in textbook expositions of their theories. But when scientific education is closely tied to the research frontiers, it is perhaps inevitable that the special needs and practices of such teaching dictate the selection of material. The Ostwald school theory was well suited to the needs of the lecturer, and the mainly critical ideas of Armstrong were less suitable for textbook presentation than the positive ideas of the Ostwald school.[290]

Armstrong disapproved of the distinguishing feature of the work of the Ostwald school; namely, the use of mathematical and especially thermodynamic reasoning. He insisted that such standards were inadequate for chemistry.

> As a chemist and a friend of the poor molecules, I feel that the aspersion of immorality should not be allowed to rest upon them

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[289] *Ibid.*, p. 655.

[290] This was made especially clear by A. Smithells in a review of J. W. Walker, *Introduction to Physical Chemistry* (London, 1899). After noting that Walker had failed to give the full case against the Ostwald school theory of solution, Smithells went on to point out the difficulty of stating the opposition's case explicitly:

> The theory of ionic dissociation has been applied to explain and co-ordinate a very large number of chemical facts, and has thrown light on matter that was previously dark. The contention of the objectors appears to be mainly that this light is illusory. The present writer is far from claiming judicial functions in the matter; but he ventures to think that the opposition to the dissociation theory would be more respected, both here and on the Continent, if it were of a more positive character, and if a more tangible alternative theory could be presented than the one which is assailed. The history of science shows plainly enough that a comprehensive theory with some weak points will hold its ground until a not less comprehensive theory with fewer weak points makes its appearance. It is probably on this ground that Professor Walker takes his stand in freely imparting the doctrines of electrolytic dissociation to elementary students of physical chemistry.

A. Smithells, *Nature, 62* (1900), 77.

> forever unless the evidence be really condemnatory beyond question. In any case, it is important that we should discover the true nature of the crime committed in solution; to cloak the inquiry by restricting it to thermodynamic reasoning—a favorite manoeuvre of the mathematically minded—is akin to using court influence in abrogation of full and complete investigation; such a course may satisfy the physicist but is repulsive to the chemist, who, although able, perhaps to imagine the existence of a frictionless piston, yet desires, in the first place to get nearer to a knowledge of what happens to the real tangible piston of practice.[291]

By 1909 Armstrong had read a comment by Helmholtz suggesting that chemists following van't Hoff and Ostwald and working on experiments on solutions cannot adequately appreciate thermodynamic laws, which can be grasped in their abstract form only by rigidly trained mathematicians.[292] Armstrong referred to this comment with approval and accepted Helmholtz' implication that Ostwald and his supporters were not physicists. Armstrong went on to say: "The fact which Helmholtz did not sufficiently appreciate was that the men who were taking the liberties he deprecated were not chemists, at least in feeling—that they were men who had thrown chemistry to the winds and were proceeding on hypothetical let-it-be-granted principles. The physico-chemical school, in fact, has never been a school of chemists."[293] By 1936, Armstrong admitted that he was dealing with chemists (though of a special kind); the same criticism took a new form.

> The fact is, there has been a split of chemistry into two schools since the intrusion of the Arrhenic faith, rather it should be said, the addition of a new class of worker into our profession—people without knowledge of the laboratory arts and with sufficient mathematics at their command to be led astray by curvilinear agreements; without the ability to criticise, still less of giving any chemical interpretation.
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> The fact is, the physical chemists never use their eyes and are most lamentably lacking in chemical culture. It is essential to cast

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[291] H. E. Armstrong, *Nature, 74* (1906), 77.

[292] Helmholtz made the comment in a letter in 1891. It was quoted by L. Königsberger in *Hermann von Helmholtz,* 3 vols. (Braunschweig, 1902–1903), which had recently appeared in a slightly abbreviated English translation (Oxford, 1906). See p. 340.

[293] H. E. Armstrong, *Science Progress, 3* (1909), 648.

> out from our midst, root and branch, this physical element and return to our laboratories.[294]

The critics of the Ostwald school did not share a unified position. It is of interest, therefore, to quote Armstrong's retrospective view of the relation between his own ideas and those of other opponents of the Ostwald school. Of Pickering he wrote: "My work has so often been referred to in conjunction with that of Pickering on the determination of the composition of hydrates in solution that it is desirable to point out that the questions considered by us were often of a very different character. I always believed in the existence of hydrates but I was in search of something more—of a process, in fact, to account for the reciprocal character of the effect which solute and solvent exercised; one which at the same time would make it possible also to explain the effects produced by non-electrolytes."[295] He had a more positive view of his relationship with FitzGerald. FitzGerald had regularly deferred to Armstrong's chemical judgment, and Armstrong was encouraged by the support of such an eminent physicist and quoted him to lend respectability to his own position. "But what has weighed more than almost any other consideration with me has been the absolute and uncompromising attitude of objection to the hypothesis taken by FitzGerald at British Association meetings and especially in his Helmholtz Memorial Lecture. He alone appeared to me always to understand the situation, and to appreciate the difficulties."[296]

Our study of Armstrong's ideas and arguments is now complete. His position changed very little throughout his long career, though its relationship to the prevailing attitudes of the field was radically transformed. His ideas were presented in positive and negative forms in alternate decades, and his own theory never progressed beyond an increasingly unfashionable kind of qualitative speculation. Thus, his influence on theory was primarily as a stimulant to sharpening the ideas of his opponents. However, he did represent a viable alternative approach to *experimental* physical chemistry. Many of his students were faithful to that approach throughout their careers. There continued to be room for laboratory-oriented non-mathematical physical chemists, and those Armstrong influenced are hard to

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[294] H. E. Armstrong, *Chemistry and Industry, 14* (1936), 917.

[295] H. E. Armstrong, *Science Progress, 3* (1909), 652.

[296] *Ibid.,* p. 651.

identify by their publications alone, unless they indulged in chemical speculation or in historical review. But because there is a direct line of intellectual influence from Armstrong to succeeding generations, it is impossible to say that the Ostwald school reached universal dominance in physical chemistry.

8. THE RELATIONSHIP OF THE DEBATE TO LATER DEVELOPMENTS IN PHYSICAL CHEMISTRY

In the early decades of the twentieth century the new specialty of physical chemistry flourished. The theory of solutions, which had been so important in the institutionalization of the field during the 1880's and 1890's, was displaced by new problem areas from its position as the most fashionable interest of the discipline. In part the shift occurred because physical chemists began to exploit twentieth-century developments in physics, and in part it was a natural outcome of the debate. As a result of the intensive study of electrolytes and solutions triggered by the debate, physical chemists had exploited the most productive topics and had either settled or postponed the divisive issues. As the topic of solutions became less fashionable, the unresolved problems lost their urgency. The theory of electrolyte solutions continued to develop, but the changes were due as much to the influence of related developments in physics as to the impetus from research in the problem area itself. Conceptions of atomic and molecular structure were undergoing rapid change in the first decades of the century, leading to new ideas about the relationship between chemical and electrical forces. The concept of a charged ion increasingly became central to chemical theory. In such a context, the development of the theory of electrolyte solutions could only be seen as a natural extension of Arrhenius' original theory, for the original debate had been most strongly polarized on the question of the existence of charged dissociated ions. Although later theories of electrolysis made full use of ions, some of Arrhenius' other original postulates were abandoned. For example, Arrhenius had explained the properties of solutions in terms of an equilibrium between ions and undissociated solute molecules. The later theories treated strong electrolytes as being *completely* dissociated, the interaction between an ion and its "atmosphere" of oppositely charged ions being the primary factor in the deviation of ions from completely independent behavior.[297] Further modifications of the theory took some account of solute-solvent interaction.

Van't Hoff's theory of solution became a subordinate part of the general problem area of the application of thermodynamical methods to chemistry. More powerful mathematical methods (stemming in particular from the initially unappreciated work of J. W. Gibbs) displaced the simple reasoning of van't Hoff and other early popularizers of the field. The analogy between ideal gases and dilute solutions and the early thermodynamic treatment of osmotic processes were inevitably evaluated in terms of the more sophisticated theory. As such van't Hoff's work appeared as a rather useful special case of the general relationships, and the ideas that had helped him to develop his theory and which were not reflected in the fuller treatment, were ignored. Except for those who, like Armstrong, could not follow or appreciate abstract thermodynamical reasoning, physical chemists generally agreed that understanding in the field had progressed from, but had not undermined, van't Hoff's work.

It is easy to conclude, therefore, that the main development of physical science has vindicated the claims of the Ostwald school theory. But although the issues of the debate are no longer alive, our obvious preference for one side is largely to be explained by the historical accident of unexpected discoveries in other fields and by the way physical chemistry became institutionalized, rather than by some logical criterion of which theory best survived exposure to experimental test. The increased importance of ions in chemical theory was a consequence of the new understanding of the atom; few physical chemists played a pioneering role in these developments, perhaps because Ostwald so strongly opposed atomism. Also the rapid rise of the new discipline of physical chemistry had as much to do with the favorable conditions for its growth in Germany and America as it had with the productiveness of its central ideas. The growth of the discipline reflects the larger number of chemists with mathematical and physical training. Moreover, because of their training, such scientists were far more interested in building on quantitative regularities over limited ranges of phenomena than in employing qualitative chemical speculations that linked a rich variety of chemical phenomena but were not amenable to quantitative

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[297] For the later history of the theory of strong electrolytes, see H. Wolfenden, *op. cit.* (note 194).

treatment. They would have preferred the Ostwald school theory and its direct successors.

9. CONCLUSION

A General View of the Nature and Significance of the Debates

The manner in which the debates over the theory of solution arose suggests one particular mechanism for generating dissent in science.

Many of the influences encouraging conformity in scientific work are most active during the period of training and the scientist's early career. If there is any geographical variation in conceptions of the problem field of a science, the scientists who have been trained at a particular institution will tend to acquire the local variant. The main influences on such local views do not come uniformly from the work of the whole international scientific community, but mainly from local work or, for peripheral regions, from work done at the centers of scientific excellence that are recognized locally. Under conditions in which international communication is imperfect distinct patterns of scientific influence can emerge or be perpetuated. Thus, if Frenchmen cite Frenchmen most often, while Scandinavians, Germans, and Austrians cite Germans, there is a tendency towards regional stratification, so that the main ideas of a science are carried forward in parallel but quasi-independent channels of influence. Such parallel streams often correspond closely to one another (this is one source of simultaneous independent discovery by people in different countries), but the conceptual, linguistic, political, or geographical barriers to communication also allow significant divergences. So do individual genius, quirk of personality, or local circumstances. For example, distinctive scientific approaches may emerge under favorable institutional conditions, without immediately being diffused internationally. When different local scientific variations do come into contact, the exposure of scientifically significant differences may generate dissent. An analogous situation may occur when scientists working in different but related problem areas lack adequate means of communication.

The debates over the theory of solutions are an example of disagreement between national groups of scientists who developed different solutions for the same problems. In countries in which science was not strongly dominated by German science, chemists developed chemical theories of the nature of solutions. In Germany, organic chemists dominated, and only a few chemists, mostly Bunsen's associates and students, worked on topics in physical chemistry. Arrhenius, van't Hoff, and Ostwald developed the key ideas on solution in countries that took their scientific orientation from German science, but in which chemistry was not as completely dominated by the most fashionable themes of organic chemistry as in Germany. The new ideas on solution were more closely linked to conceptions of theoretical physics than to the chemical theories of solution chemists favored in Britain, France, and Russia (Mendeleef). When Ostwald moved from Riga to Leipzig in 1887, he was able to build up a new school of physical chemistry rapidly because there was so little *active* opposition from German chemists, and because his approach was in harmony with German thermodynamic theory. Ostwald's laboratory dominated the new field and was able to attract a community of students from all nations. Ostwald aggressively sought to establish his new approach (with the help of Arrhenius and other supporters)[298] and by his manner increased the intensity of the confrontation with the English. The initial reactions of research scientists in England were critical. The first to be won over, Ramsay, may have been converted so readily because he was more interested in quantitative results than in understanding the processes involved in solution.[299] After chemists recognized the extent of the divergence of views between the two sides, the Ostwald school were invited to the British Association meeting in 1890. The people on the two sides gained quite different impressions of the outcome of this meeting. Ostwald said several times that he thought that his side had done well. The English, however, continued to hold to their earlier arguments.

The debate over the nature of solutions was intense and prolonged. One factor contributing to its intensity may have been the crucial importance of theory in physical chemistry at that time. It was not difficult to gather data on the physical properties of solutions (though it was harder to do it well). What was in short supply

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[298] See, for example, the comment by Arrhenius, *Journal of the American Chemical Society, 34* (1912), 363.

[299] The discussion by Travers, *op. cit.* (note 70), suggests that Ramsay's initial understanding was rather superficial; his inclination to regard scientific theories primarily as provisional tools for representing quantitative regularities is illustrated by the comment cited in note 280 above.

was an adequate theoretical treatment of the data. There was no theory that provided an adequate explanation of all the data available. Rival theoretical approaches treated different ranges of data in different ways with varying precision, and each of the two sides naturally paid greater attention to the kinds of data it could treat by its methods. While Ostwald's approach gave a quantitative treatment of infinitely dilute solutions, the English chemists sought a mainly qualitative treatment of solutions of all strengths. The disagreement between the Ostwald school and the English chemists over theoretical orthodoxy raised so many other points of disagreement that the arguments of one side often seemed circular to its opponents.

By the late 1890's the two sides understood each other better. This did not prevent further debate; for example, the exchange in *Nature* in 1896–1897. Except for Armstrong's polemics, the exchanges were more constructive. However, the differences between the two sides were not to be settled by rational exchange; the outcome was determined by indirect factors. By the 1900's, it was clear that the original opposition to the Ostwald school had failed to develop alternative theories very far. The Ostwald school program of extending quantitative treatment from infinite dilution to more concentrated solutions and then to non-aqueous solutions had some success, but also limitations, which were exposed by Kahlenberg. There were fewer difficulties about the experimental aspects of the Ostwald program. But Armstrong, too, was able to guide experimental research in topics devised under the stimulus of his prejudice against ions and his belief that chemical change involved association rather than dissociation. Thus the experimental work of each side could proceed, even though it was largely unappreciated by the other. As time went on, the debate over the theory of solutions became less central to the field without having produced a generally accepted resolution. Although the theories of van't Hoff and Arrhenius had been the spearhead of the new specialty of physical chemistry disseminated by the Ostwald school, the new science was not restricted to the study of solutions, and other topics such as the study of chemical affinity and reaction rates gained greater prominence as productive methods were applied to them. New problem areas emerged, particularly with the study of radioactivity and atomic structure, and later with the rise of quantum theory. As later theoretical treatments assumed that strong electrolytes were completely ionized in solution, theoretical discussion moved away from the issues of the older debate. The final exchanges in the debate, therefore, had little urgency for anyone except for people like Armstrong and Kahlenberg, who had committed a significant proportion of their careers and reputations to the debate. Others could afford to ignore it if they wished.

The rational procedures employed in the debate can be said to have failed, for they did not lead to a general consensus about its outcome. Those who were not directly involved tended to accept simplified versions of what happened, if they thought about the issue at all. Since the training of young physical chemists had come to be dominated by teachers and textbook authors descended directly from the Ostwald school, most later physical chemists accepted judgments about the outcome of the debate from that perspective. As far as the views of the participants of the debate are concerned, the following four judgments, as well as intermediate positions, may be clearly identified from the available retrospects. Each is illustrated by a quotation.

1. The Ostwaldian theory prevailed in the face of intense opposition.

> It is not at all surprising that the chemists who had been thinking of reactions in terms of atoms during a long lifetime should have hesitated to welcome the new conception with open arms. Yet the evidence produced for this theory by Arrhenius was so varied and quantitative, that the new theory soon had many adherents. It quickly acquired the support of Ostwald and van't Hoff, and this gave it the stamp of authority.
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> The objections which were at first offered to the theory were of two kinds; those based on a lack of familiarity with the theory itself, and with the phenomena with which it was meant to deal, and these are of no interest to us, or to any one else.
>
> Then there came the objections which were based upon an intelligent desire to get at the truth. When chemists began to think of chemical phenomena in terms of the new theory, they encountered real difficulties, partly on account of the newness of the theory itself. The theory was called upon to prove itself, as it should be able to do. This kind of thoughtful, conservative criticism is always most useful in science. It is an antidote for extreme radicalism, which is hurtful in science as in everything else. The result has been that during the past quarter of a century, about every rational objection has been offered to the theory of electrolytic dissociation that could be thought of. Facts have been cited,

> which, taken at their face value, seemed distinctly at variance with the theory. When these supposed facts have been tested by careful experimental work, they have in practically every case been found to be in error. The theory has met the unusually large number of objections unflinchingly; and it stands today as one of the cornerstones of the modern developments in chemistry. All things considered, it is certainly one of the most important generalizations that has been reached in chemistry, certainly since the discovery of the law of conservation of mass and the law of conservation of energy.[300]

2. The opponents of the Ostwald school theory were triumphant in that their major claims and criticisms were vindicated.

> But in 1887 Arrhenius put forward the view of electrolytic *dissociation* which was in complete contrast to this view [that of H. E. Armstrong on the importance of the solvent and of *association*], in that the influence of the solvent was entirely ignored, it being supposed that mere dissolution caused a stable salt to tumble apart in complete defiance of the laws of chemical affinity and chemical attraction. It is therefore hardly to be wondered that Henry Armstrong, having already realised the vital importance of the solvent in electrolysis, refused to be carried away by the hypothesis in which its essential functions were completely overlooked. His opposition to the crude expositions of the German physical chemists in their early enthusiasm for the new theory was based on considered judgement, arrived at before the theory was promulgated, and was too well founded to be swept away by the current of popular approbation.[301]

3. A compromise was reached in which the best points of each side were retained and the defects eliminated. The difference between the two theories became no more than that of complementary working hypotheses, each guiding a different kind of approach.

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[300] Jones, *op. cit.* (note 128), pp. 121–123. Jones's perspective has been influential among later historians of chemistry. For example, A. J. Ihde writes: "Perhaps the most comprehensive account of the rise of physical chemistry is Harry C. Jones' *A New Era in Chemistry.*" *The Development of Modern Chemistry* (New York, 1964), p. 809. A similar historical evaluation to Jones's is given by Arrhenius, *op. cit.* (note 298).

[301] Eyre, *op. cit.* (note 28), pp. 220–221.

> It is surely now time that all the irrelevant and intemperate things that have been said and written by the supporters of the osmotic pressure and electrolytic dissociation theories on the one hand, and by those of the hydrate theory on the other, should be forgotten. Far from being irreconcilable, the theories are complementary, and workers may, each according to his proclivity, pursue a useful course in following either.[302]

4. The Ostwaldian theory continued to dominate, but it inspired chemists with an increasing sense of crisis as its limitations became more conspicuous.

> Both [the ionic theory and the phlogiston theory] postulated the existence of an entity which no one could succeed in isolating: phlogiston in one case and the dissolved ion in the other. Both neglected facts which they could not explain, though these facts might well be vital. Both wore an attractive air of simplicity which vanished on closer inspection. And both had to be twisted and contorted into all kinds of queer shapes to meet the needs of the moment. . . . The ionic theory appears to occupy very much the position which was held by the phlogiston theory immediately before the work of Lavoisier: many chemists are enthusiastic about it, and the majority are content to follow their lead, but the air is heavy with portents and revolutionary changes may be at hand.[303]

We see, then, that a degree of consensus was restored to the field not because chemists reached a rational resolution of their scientific disagreements, but because the main issues of the field were replaced by new central concerns. The remaining differences in opinion about the issues of the debate were not crucial to the research practice of the younger physical chemists. Was the debate of little consequence then? It is difficult to assess the overall impact of any internal development in a science that is also substantially affected by external factors. However, it is clear that the debate did have a significant impact. In general, the impact of a scientific debate cannot be judged solely by the overt outcome, by whether or not everyone agrees that one side has won or that a compromise has been reached. The typical direct effect of a debate is that the opinions of the opposing sides converge, either because those holding extreme opinions change their

[302] J. Walker, *Report of the British Association* for 1911 (1912), p. 356.
[303] E. J. Holmyard, *The Great Chemists* (London, 1928), p. 121.

minds or because they come to be ignored in the science. But the indirect effects of debate can also be substantial. At the least, the debate may produce a shift in the line between generally agreed upon facts and controversial conjectures, and the polarization of viewpoints brought about by the debate may assist in the perpetuation of the heterogeneity of the intellectual lineage of the field. Critical discussion may also, however, expose and put under pressure assumptions of underlying technique, inference, methodology, and philosophical method, so that they have to be more clearly stated and thought out. In the absence of a challenge, the supporters of a theory may only exploit its strongest points and not look very hard at its limits. But even in a debate in which "rational" processes appear to have failed, theorists may be stimulated to tackle problem areas that emerged not through the internal development of their respective theories, but in the course of the debate. If a theory can handle such areas better than its rival, that may add to its plausibility and recruiting power, and thus increase its subsequent influence in the field. A scientific field develops most rapidly in its focal areas, the themes or problem areas which attract most interest and attention. The temporary effect of a debate is to make the points of contention into focal issues. Some of the lines of research which are so stimulated may be successful, that is, they may lead to the formulation and solution of a productive sequence of research problems. If, however, even after continued research, those who are not heavily committed to one of the sides in a dispute decide that science in its current state is unlikely to settle the points at issue, then the debate may have a negative effect as research interest swings away from its issues. The belief that it is "time to get on with something worthwhile now," especially when expressed by younger members of the field, may encourage a new direction of development of the field. Thus, even the most inconclusive of debates may be of historical importance.

Several aspects of the indirect effects of debate that I have discussed are illustrated by the influence on physical chemistry of the debate over the theory of solution. However, it is difficult to demonstrate the precise significance of these effects through historical documentation. It is clearly the case, for example, that the debate forced attention upon a range of controversial issues, revealing which of them were suitable for further research and which were not yet amenable to scientific study. Thus, the debate helped to redirect lines of investigation within the general problem area. But it must be conceded that the part played by the debate was not crucial to the most prominent subsequent developments in the science. In an ideal version of internally generated scientific change, experimental investigation and theoretical representation go hand in hand, each stimulating and drawing upon the other. But in practice—and physical chemistry around the turn of the century is no exception—there are many theoretical developments that are insufficiently linked to experimental work, and there are many experimental studies that remain theoretically problematic because there is no single, well-attested way of making their unexpected results fully accord with theory. The debate over the theory of solution did influence theoretical studies and experimental studies, but it did not produce the ideal situation in which key developments of theory and experiment are closely linked. For example, the debate brought to the fore the study of the interaction between solvent and solute, which had not been a prominent part of the original Ostwaldian theory. Lines of investigation can be traced from the nineteenth century critics of the Ostwald school theory to constructive studies in the twentieth century. Thus, an effect of the debate was to keep solvation as an important problem, even though it was not a simple consequence of the thermodynamic treatment of the Ostwald school or an application of a successful experimental technique. In the first half of the twentieth century, there were continuing attempts to invoke solvation as an explanation of residual discrepancies between theory and experiment in the study of other phenomena of solution. These were not fully satisfactory, as the extent of hydration of the dissolved species varied with the solution property it was related to. The attempts continued, because many chemists accepted the idea that there is considerable solvent-solute interaction in aqueous solutions. The issue added little to the achievements of physical chemistry, but it added to the number of open problems in the field that investigators could take up with some hope of success.

A second problem that became prominent through the debate was that of non-aqueous solutions. Kahlenberg pointed out the early difficulties chemists encountered when they applied the Ostwald school program to non-aqueous solutions. The study of non-aqueous solutions remained an important area for empirical study, but theory lagged far behind experiment in the early part of the century. Even such theoretical suggestions as could be made (such as the relation between dissociation in a solvent and its dielectric constant) had a very limited applicability and gave only limited insight.

The Usefulness of the Concept of Dissent in the Historical Study of Scientific Change

The present study is intended to provide not merely a historical account of a particular scientific debate but also sharper definitions and richer descriptive categories to be applied to the study of other debates. The historical development of science has been rich in controversy, which is well worth examination. If historical attention is directed primarily to the development of individuals or of specific ideas, social interactions tend to be less studied and less understood; by focussing on social processes such as debate, the historian can gain a more balanced understanding of the nature of scientific activity. Studying cases of scientific debate can reveal the underlying assumptions of scientific practice. When debate is triggered by or feeds on implicit differences of fundamental assumptions or values, these can be made explicit as they come to the participants' attention. For example, the significance for the practice of science of differing extra-scientific commitments can be more readily examined as these commitments are revealed in controversy.[304] Useful insights into the social processes of science can sometimes be gained from the scientists themselves in a debate. Social mechanisms of scientific change are not normally considered by the participants of a scientific debate, but they may be if the scientists find that their aims are frustrated during a controversy.[305] The historical study of dissent and debate is especially interesting in the development of general theories of scientific change, in ways that the present study has attempted to illustrate, and which are discussed in more general terms in the remainder of this concluding section.

Even the most general treatments of the nature of scientific change can benefit from the study of dissent. One view of scientific change holds that science proceeds steadily in an atmosphere of general agreement. Another view holds that science generates the best account of natural phenomena by developing and successively eliminating alternatives. The latter view, which separates the creative

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[304] This was an important theme emerging in a meeting of historians and sociologists of science sponsored by the Science Studies Unit at the University of Edinburgh in September, 1974.

[305] The comments of H. E. Armstrong in the present study illustrate this point.

and critical phases, especially if new ideas require a major investment of creative effort before they can be exposed to critical assessment, will gain depth by studies of the social processes of criticism and dissent. Since both of these general kinds of views have been held by historians,[306] it would be of interest to compare them in connection with a study of the prevalence and character of dissent in science. In recent discussions in the philosophy of science stemming from the exchange between T. S. Kuhn and K. R. Popper,[307] very different roles have been given to debate. A historical investigation of its character and prevalence might produce the insights required to clarify its role in scientific change. Popper suggests that dissent is a widespread phenomenon in scientific change, that scientists actively seek to falsify and to overthrow other scientists' theories. The attempt to falsify theories must be in part a social process for the obvious psychological reason that it is a lot easier to try to overthrow the other man's theory than it is to criticize one's own while there is still some hope that it might be developed further. Kuhn, on the other hand, sees a large proportion of scientific activity conducted within the harmonious consensus of "normal" science. In the first edition of his *The Structure of Scientific Revolutions,* Kuhn suggested that debates in mature science that involved more than individual acrimony—for example, those over priority—were limited to the revolutionary episodes of a whole science in crisis. But although, as Kuhn stressed, the methods of training in science encourage relatively uncritical conformity in normal science, there are other parallel factors that encourage dissent. Kuhn's later discussions[308] suggest that his analysis should be applied to smaller groups of scientists. His arguments still apply to the nature of the consensus within paradigm-sharing communities, but because of the small size

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[306] The first view has often been held by scientists who took an extreme empiricist view of science. The latter view is clearly illustrated in E. G. Boring, "The Psychology of Controversy," *History, Psychology and Science: Selected Papers* (New York, 1963), 67–84, and in M. Polanyi, "Passion and Controversy in Science," *Bulletin of Atomic Scientists, 13* (1957), 114–119.

[307] See in particular, *Criticism and the Growth of Knowledge,* ed. I. Lakatos and A. Musgrave (Cambridge, 1970).

[308] See in particular, T. S. Kuhn, postscript to the second edition of *The Structure of Scientific Revolutions* (Chicago, 1970); "Logic of Discovery or Psychology of Research?" and "Reflections on my Critics" in *Criticism and the Growth of Knowledge,* pp. 1–23, 231–278; and "Second Thoughts on Paradigms," in *The Structure of Scientific Theories,* ed. F. Suppe (Urbana, 1974), pp. 459–482.

of these communities they are now more dependent on external resources and stimuli in their work. There is therefore greater room for minor conflicts between social groups, particularly if they are geographically separated or tackle different but overlapping ranges of problems. The subject of the present study may be regarded as an example of controversies at an intermediate level between major revolutions and conflicts between individuals. Further studies of controversies at the intermediate level should be informative about the social and intellectual mechanisms underlying scientific change.

The historical study of scientific controversies can illuminate another methodological interest in the role of dissent in scientific change. Two extreme patterns of dissent may be distinguished. The first is a rational pattern in which consensus is achieved by rational exchange over an isolated disagreement. This version of debate is acceptable to most traditional philosophies of science. It is the ideal of H. E. Armstrong in the present study. At the other extreme is the account of incommensurable viewpoints developed by P. K. Feyerabend and Kuhn.[309] This account applies best to theories or paradigms which are so different in their fundamental structure and in the methodological values presupposed that every concept employed in them is affected. Every observational situation is construed differently from the two theoretical orientations, because the descriptive and explanatory terms employed are not linked in the same way to the rest of their respective system, even though some words may be common to both systems. If two scientific viewpoints are regarded as incommensurable in this way, it becomes difficult, if not impossible, to make logical comparisons between particular statements or sets of statements when they are extracted from their original theoretical context. Even comparisons of whole systems become difficult, except in the most intuitive way, especially if the range of phenomena covered and the kind of knowledge claimed by each are not identical. Hence, logical relations of inclusion and contradiction must be replaced by such metaphors as gestalt switch or translating between languages of radically different cultures. If the major confrontations of ideas in scientific change are best described as incommensurable in this way, it might be thought that debate can only be a *symptom* of scientific change, revealing the deep divisions between the two sides. Rational

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[309] For a recent statement of Feyerabend's position on incommensurability see his book, *Against Method* (London, 1975). For Kuhn see "Reflections on my Critics" in *Criticism and the Growth of Knowledge.*

processes would be so ineffective in them that arguments merely harden attitudes rather than modify them.

The clearest examples of incommensurability in science come from cases in which the two sides confront each other in the philosopher's mind. When the philosopher considers incommensurability in terms of static confrontation, he tends to crystallize the thought of each side into a more precise and rigorously logical structure than was employed, or at least agreed upon, by the practitioners themselves. The philosopher then discusses incommensurability in terms of the difficulty of relating the logical structures in a noncontroversial way. But the total thought of an actual science while it is developing is a combination of explicit semi-formal structures of argument set in a context of informal and flexible assumption and conjecture, which is being articulated in the course of further work. When the formal parts of a scientific approach are compared, they do not appear incommensurable; rather, they seem to agree, to contradict, or to relate to different issues. It is only when the *total* problem-solving orientations are reconstructed that the nature and range of incommensurability becomes apparent. We can learn more about science if, instead of making static confrontations of crystallizations of systems of belief, we study the confrontation of opposing approaches in actual historical situations. The historical study will lead us to analyze the processes involved in confrontation and the manner in which debate changes the situation. As the present study illustrates, even though the *initial* confrontation appears incommensurable, the two sides soon came to understand one another more fully, though they continued to disagree. Although methods of rational persuasion had very limited effect, the two sides came to be separated less by misunderstanding than by contrasting commitments. What incommensurability remained stemmed from the tendency of each side to see the gaps and latent tensions in the informal aspects of the opposing position as basic defects or falsifications, and the corresponding features of its own position as research puzzles already implicitly solved and to be spelled out fully in further research.

The examination of historical cases of debate can aid us in assessing the extent to which dissent plays a part in scientific change. It can also show to what extent the different scientific beliefs are selected and transformed by rational discussion, by the indirect effects of confrontation, or by mechanisms in which contrasting beliefs are developed independently, their relative fortunes not being affected by confrontation at all.