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GILBERT N. LEWIS AND THE THERMODYNAMICS OF STRONG ELECTROLYTES

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Introduction

For this paper I have chosen to focus in detail on the final period of Lewis' thermodynamic research before the publication of his remarkable book (1) which had such great influence. His emphasis in this period was on the peculiar properties of strong electrolytes. In view of my recent research in this area, it was of particular interest to examine the original papers of all of the leading investigators of that period and to note how various concepts were developed. But before proceeding to the detailed discussion of strong electrolytes, I wish to make a few remarks about my personal relationship with Lewis, and at somewhat greater length, to review the general nature of Lewis' contributions to chemical thermodynamics.

I had the good fortune to know Gilbert Lewis very well even though I never collaborated with him in a research project or publication. His influence though his leadership in seminars was very great, but in addition I had many personal discussions of scientific questions with him. He liked to talk with someone who maintained an independent viewpoint and I was willing, even as a very junior member of the department, to defend a viewpoint even if it differed from his. He had an enthusiastic interest in a wide variety of topics and a remarkable capacity to focus on the key questions. The chemical applications of quantum theory were still in their exploratory stages and our discussions often fell somewhere in that area. Although there were still very interesting questions in thermodynamics

and especially in statistical thermodynamics, Lewis showed only limited interest in this area in the last decade of his life. He encouraged me to carry on my research and was pleased by the results obtained. But after the publication of his great book with Randall (1) in 1923, his personal interest in thermodynamics was no longer intense. Thermodynamics continued, however, to be a major area of research at Berkeley with support and encouragement by Lewis but under the immediate leadership of Giauque, Latimer, Hildebrand and others.

Classical thermodynamics (i.e., excluding the third law) was well established by 1900 when Lewis entered the field. Even the extension of the basic laws to systems of variable composition, primarily by Gibbs in 1876-78 (2), had occurred two decades earlier. But chemists were using thermodynamics only in very limited areas and often inexactly even then.

Lewis (3,4) proposed new quantities, fugacity and activity, which were closely related to the familiar quantities pressure and concentration yet precisely defined in a manner to allow exact calculations. He also measured and encouraged others to measure the free energies of the most important chemical substances. Thus he brought into existence an extensive and accurate data base for the use of thermodynamics in chemistry.

Although the equations of Gibbs utilizing the chemical potential are exact, most of the practical working equations in use in 1900 involved approximations of ideality for gases and solutions. If the properties of a gas, for example, are accurately known, one can relate the gas pressure to the chemical potential without use of the perfect gas law. However, the equations now seem different and more complex. By his definition in 1901 of fugacity, Lewis obtained exact relationships of fugacities which had the same form as the familiar approximate equations

in terms of pressures. Thus one can use the same form of equation in all cases with substitution of pressures as an approximation or of fugacities if the highest accuracy is required.

The situation for solutions is somewhat more complex than for gases but the relationships are essentially the same. Solubility products, ionization quotients, etc., retain their form but become exact relationships when activities are used.

As the third law of thermodynamics began to emerge, Lewis saw its importance to chemists. In his 1917 paper with Gibson (5) this was explained and implemented insofar as data then allowed. But of the greatest importance was the encouragement Lewis gave to Giauque, Latimer, and others to develop at Berkeley the low temperature facilities and to apply the third law to a variety of important substances. The simultaneous development of statistical thermodynamics by Giauque was a natural result of this program.

It is hardly possible to exaggerate the enormous influence of the thermodynamics book of Lewis and Randall. Lewis wrote it in a style easily readable and conveying enthusiasm and excitement yet at the same time precise and accurate. Not only were the important working equations derived from basic principles, but also a body of numerical values were assembled concerning the most important substances. Published in 1923 it was still in print and widely used in 1952 when the publisher persuaded Professor Brewer and me to undertake a revision. We left almost untouched the masterful presentation of Lewis of the basic ideas but added chapters on recent developments. The material on selected values for particular substances was, of course, completely replaced. We are pleased that our efforts gave renewed life to Lewis' presentation of the general concepts

of thermodynamics. The revised edition is healthy after over twenty years and now nearly sixty years after the first edition was published.

Since Gibbs died in 1903, not long after Lewis' first paper in 1899, it is not obvious whether they became personally acquainted, and I am sorry that I never asked Lewis about Gibbs. But Dr. E. W. Hughes did ask and thoughtfully gave others a report on the reply which I summarize. Hughes said that the question brought a happy smile and that Lewis said that he had stopped over at New Haven on one of his many journeys between his home in New York City and Harvard while he was still a graduate student. Although completely unknown to Gibbs, he was warmly welcomed. Gibbs professed to be rather lonely at Yale where there were few, if any, others actively interested in his work. Lewis repeatedly suggested that he should not impose further on the time of the great man but Gibbs kept him engaged in conversation all afternoon. Thus it is clear that Lewis did have at least one long and friendly conversation with Gibbs.

Strong Electrolytes: a Puzzle

In the years just before and after 1900 a number of widely accepted natural laws were found to fail in explaining the now more accurately measured properties of real systems. The formulation of quantum theory and relativity in response to two of these situations is well-known. The behavior of dilute solutions of strong electrolytes constituted another situation of this type, although in this case it was resolved by an improved application of established basic physical principles rather than a change in those principles.

The behavior of weak electrolytes, where the fraction ionized changed greatly with concentration, was explained satisfactorily by mass-action

equilibrium-constant relationships in terms of concentrations, i.e., the Ostwald dilution law as it was then commonly called. We now know that this was only an approximation, but there was no clear discrepancy at the level of accuracy then available. For electrolytes such as NaCl or HCl, however, which were largely dissociated even at high concentration, there were two serious failures. First, the fraction associated could be determined from either conductance or freezing-point-depression measurements and the results differed substantially, by roughly a factor of two. Second, and even more serious, was the failure of this fraction of association on either basis to be explained by the mass-action equilibrium expression. Apparent equilibrium constants for dissociation varied by more than a factor of ten for simple 1-1 electrolytes such as KCl between 0.001 and 0.1 molal. And Lewis pointed out as an extreme case $K_4Fe(CN)_6$ where the apparent dissociation K varied from 0.7 at 0.0005 M to 842000 at 0.4 M, a change of five orders of magnitude.

This failure of the widely accepted principles incorporated in the Ostwald dilution law was so surprising, that for a decade or more the efforts of physical chemists were directed toward experiments of increased accuracy with the purpose of deciding whether this anomaly was really true, but without any effort to offer an explanation. One of the last papers of this type is that by Flügel (6) in 1912 working in Nernst's institute in Berlin. In the 1913 edition of Nernst's "Theoretische Chemie" (7) he acknowledged that this difficulty existed for strongly dissociated salts and acids, but he presented no discussion of possible explanations. By this time others, including Lewis, had already accepted the existence of the anomaly and were discussing the direction in which an explanation might be found. Some of these early proposals were

ill chosen, however. Thus in 1912 Lewis proposed that possibly the mobility of ions increased somewhat with increase in concentration which is, of course, opposite to the truth as it eventually developed. Lewis promptly abandoned this idea, although the data he assembled at the time was useful in later work.

The simple idea that dilute, strong electrolytes were, for practical purposes, fully dissociated, is attributed first to Sutherland whose reasons were not very convincing. But others supported this concept with better evidence and by 1920 it was widely accepted.

Strong Electrolytes: the Answer

In this paper I shall not examine the work of this earlier period in detail, rather I shall concentrate on the period just after the first World War, during which Lewis served as chemical staff officer to General Pershing in France. By that time Lewis was also very active in his theoretical work on the nature of the chemical bond which led to his book, "Valence and the Structures of Atoms and Molecules". Nevertheless, Lewis and his associates played a major role in the resolution of the "strong electrolyte anomaly" during the period 1919-1921. While Debye and Hückel (8), in their masterful paper of 1923, are properly credited with the quantitative theoretical explanation, we shall see that many of the quantitative relationships, as well as the concepts, had been established earlier by Lewis and associates and by Bronsted.

In 1919 Lewis and Linhart (9) presented their treatment of the best freezing point data then available. They adopted the empirical equation which can be restated in more familiar symbols as

$$1 - \phi \cong j = \beta m^{\alpha} \qquad (1)$$

where ϕ is the osmotic coefficient, m is the molality, which is equivalent to the molar concentration for very dilute solutions, and α and β are empirical parameters. The function j is defined by the equation

$$j = 1 - \theta/\nu\lambda m \qquad (2)$$

where θ is the freezing point depression, ν the number of ions in a formula unit, and λ is the molal lowering of the freezing point at infinite dilution which in turn is given by the heat of fusion of water, the temperature, etc. Except for a small correction which becomes negligible in the very dilute range, $j = 1 - \phi$.

We now know that equation (1) does represent the correct limiting expression with $\alpha = 1/2$ and β given by the expression of Debye and Hückel which involves only the charges on the ions as well as solvent properties, T, etc. Thus for 1-1 electrolytes in water β depends on the temperature but not on the particular solute of that charge type, i.e., it is the same for NaCl, KCl, HCl, HNO_3, etc.

Lewis and Linhart plotted log j vs log m and found curves which became essentially straight lines below 0.02 M with the slope determining α, and the intercept β. Their calculations were slightly revised and extended by Lewis and Randall in 1921 (10) with the results shown in Table I. In their 1921 paper Lewis and Randall drew the conclusion that α was 1/2, within experimental error, for all 1-1 electrolytes.

Table 1. Parameters for equation (1) from Lewis and Linhart with revisions and extensions by Lewis and Randall

	α	β
NaCl	0.535	.329
KCl	.535	.329
KNO_3	.565	.427
$NaIO_3$	(.500)	.417
KIO_3	(.500)	.417

The data for KNO_3 are shown in figure 1 with lines drawn for α values of 1/2 and 1/3. The agreement with 1/2 is excellent, although the best fit corresponds to a slightly larger value as shown in Table 1. The exponent of 1/3 arises from lattice-type theories which were then current and still are re-proposed from time to time although there is now overwhelming evidence, both theoretical and experimental, in favor of the exponent 1/2.

While the number of examples in Table I is not large, there were also data from electrochemical cells for HCl and from solubility measurements for TlCl in mixtures with several salts and acids. These experiments were related to the activity coefficient rather than the osmotic coefficient, but the two coefficients are related by thermodynamics which yields

$$\ln \gamma_{\pm} = -\left(\frac{\alpha+1}{\alpha}\right) \beta m^{\alpha} \qquad (3)$$

Interpretation of the electrochemical cell data for HCl is complicated by the fact that the standard potential for the cell must also be determined by extrapolation to infinite dilution. Lewis encouraged his student Linhart (11) to extend the measurements of the cell Pt, $H_2 | HCl(m) | AgCl,Ag$ to lower concentration and Linhart devised several improvements in electrode formulation and cell design which are unsurpassed even today. Accurate potentials were obtained to 0.000242 M and a somewhat doubtful point even at 0.000136 M. From these high dilutions the extrapolation to infinite dilution is unambiguous as is shown in Figure 2 taken from Linhart's paper (11). Curve I and the right hand ordinate scale give E' (= E + 0.1183 log m) which extrapolates to E°. We need not be concerned with curves II and III. With this value of E° established, the data at slightly higher molality fit equation (3) with $\alpha = 1/2$.

Solubility measurements for TlCl in mixtures with KNO_3, KCl, HCl, and $TlNO_3$ were also carefully analyzed and indicated that $\ln \gamma_{\pm}$(TlCl) depended on the one-half power of the total molality of 1-1 electrolyte.

At this point let us examine the work of others and especially Bronsted before returning to another very important result of Lewis. It is interesting that Bronsted, working in Copenhagen, published most of his papers of this period in the Journal of the American Chemical Society (12). This indicates clearly his evaluation of the quality and leadership of American research in this field. In addition to some excellent experimental results, Bronsted's first major theoretical contribution was the recognition that the ordinary interparticle forces existing in nonelectrolytes as well as electrolytes would yield a linear term in concentration for either the osmotic or activity coefficient. This term would be specific to the particular electrolyte; he stated it as "the principle of specific interaction of ions." Bronsted's second major contribution was his conclusion that the special "electrostatic" term should not be specific to individual electrolytes but should depend only on the electrical charges. Thus in 1922 Bronsted (12) wrote

$$1 - \phi = f(c) + B_i c \tag{4}$$

where f(c) is a universal function and B_i a coefficient specific to the salt considered. (Bronsted used the symbol β which is here changed to B to avoid confusion with Lewis and Linhart's β). Bronsted went on to show that a probable expression for the universal function was

$$f(c) = \beta\ c^{\frac{1}{2}} \tag{5}$$

with β about 0.32 for 1-1 electrolytes at 0°C. He acknowledges the earlier choice of ½ for the exponent by Lewis and Randall. But Bronsted's

contribution is very important because his inclusion of the linear term made it possible to fit the best experimental data with a universal value of β rather than one which varied slightly from solute to solute.

Among other investigators of that period, I will mention only Harned who continued work on electrolytes for many years and later, with Owen, wrote the comprehensive monograph, "The Physical Chemistry of Electrolyte Solutions." In a 1920 paper (13) he reported excellent measurements on several types of electrochemical cells and in interpretation used the equation (which in our symbols becomes)

$$\log \gamma_{\pm} = -\beta c^{\alpha} + Bc. \tag{6}$$

This equation is of the same general form as Bronsted's. With three freely adjustable parameters, Harned easily fitted his data. But the relatively small variation of β and α among several solutes undoubtedly encouraged Lewis and Randall in their choice of ½ as the universal value of α and Bronsted in his further choice of a universal value of β.

The Ionic Strength

The most remarkable contribution of the 1921 paper of Lewis and Randall (10) was the formulation of ionic strength as the quantity determining activity and osmotic coefficients in mixed electrolyte of various valence types. They define the ionic strength as

$$I = \tfrac{1}{2} \sum m_i z_i^2 \tag{7}$$

where m_i is the molality and z_i the charge in protonic units for the ith species of ions and the sum covers all ions present. With the factor ½, I becomes equal to m for a single 1-1 electrolyte. Thus $I^{\frac{1}{2}}$ can replace $m^{\frac{1}{2}}$ (or $c^{\frac{1}{2}}$) in various equations and they become applicable to mixed electrolytes including ions of various charges. The first evidence cited

in support of this concept was the solubility of TlCl in $BaCl_2$, Tl_2SO_4, and K_2SO_4. On the ionic strength basis these data were concordant with those already mentioned for TlCl solubility in other 1-1 electrolytes. Solubility data for $Ba(IO_3)_2$, $CaSO_4$, and $La(IO_3)_3$ in mixed electrolytes of various valence types were also successfully treated with ionic strength as the variable controlling the activity coefficient in very dilute solutions.

This combination of concentration multiplied by the square of the charge is, of course, the function which gives the concentration dependence in the theory of Debye and Hückel (8). But it was unambiguously identified and applied empirically two years earlier by Lewis.

It is not my purpose to review in any detail the derivations of purely theoretical equations for dilute electrolyte properties. It should be noted that Milner in 1912 (14) made a very significant attempt and that certain aspects of his results are nearly correct. But his analysis was so complex and his approximations were so difficult to evaluate that his work received only very limited attention. It clearly had more influence on Bronsted than on Lewis.

In contrast, the 1923 paper of Debye and Hückel (8) essentially solved this theoretical problem. By a remarkable choice of approximations, they obtained a simple final equation which retained all of the essential features for the limit of low concentration and a qualitatively correct indication of the behavior at somewhat higher concentration. Many further investigations were required to prove that the limiting law of Debye and Hückel was theoretically exact. But the simplicity of the result encouraged its rapid acceptance as a guide to the extrapolation of experimental data to infinite dilution.

For comparison with the earlier equations of Bronsted and of Lewis and Randall, the Debye and Hückel equation for the osmotic coefficient of a pure electrolyte may be expanded with the first two terms as follows:

$$1 - \phi = \beta c^{\frac{1}{2}} - B_i c + \ldots \tag{8}$$

This is exactly the 1922 formula of Bronsted, but Debye and Hückel give a theoretical expression for the coefficient α in terms of the charges on the ions, the dielectric constant of water, the temperature and basic physical constants.

For the mean activity coefficient of a salt in a mixed electrolyte the leading term in the Debye-Hückel result may be expressed as

$$\ln \gamma_{\pm} = -A|z_+ z_-|I^{\frac{1}{2}} \tag{9}$$

where I is the ionic strength as defined by Lewis and Randall. Again there is a theoretical value for the parameter A and the further dependence on charge type is given by the factor $|z_+ z_-|$. But the dependence on the concentrations and charges of the various ions present is given by the quantity discovered by Lewis and Randall two years earlier.

Although Debye and Hückel in their original paper make comparisons with experimental freezing point data, they do not recognize or comment on the interpretative papers of Lewis and of Bronsted. In a later paper, Debye (15) does recognize the 1921 paper of Lewis and Randall and the fact that their "ionic strength" is exactly the function of charges and concentrations which appears in the Debye-Hückel theory. Surprisingly, Debye still does not recognize in his 1924 paper the very significant 1922 papers of Bronsted.

In conclusion, I want to emphasize my appreciation of Gilbert N. Lewis as a remarkably able scientist and leader and inspirer of other scientists. This particular vignette may also help remind later generations of the great contributions of Lewis to the nearly complete understanding and empirical representation of the peculiar behavior of strong electrolytes prior to the theory of Debye and Hückel.

The support of the Department of Energy, Office of Basic Energy Sciences, through Contract No. DE-AC03-76SF00098 is gratefully acknowledged.

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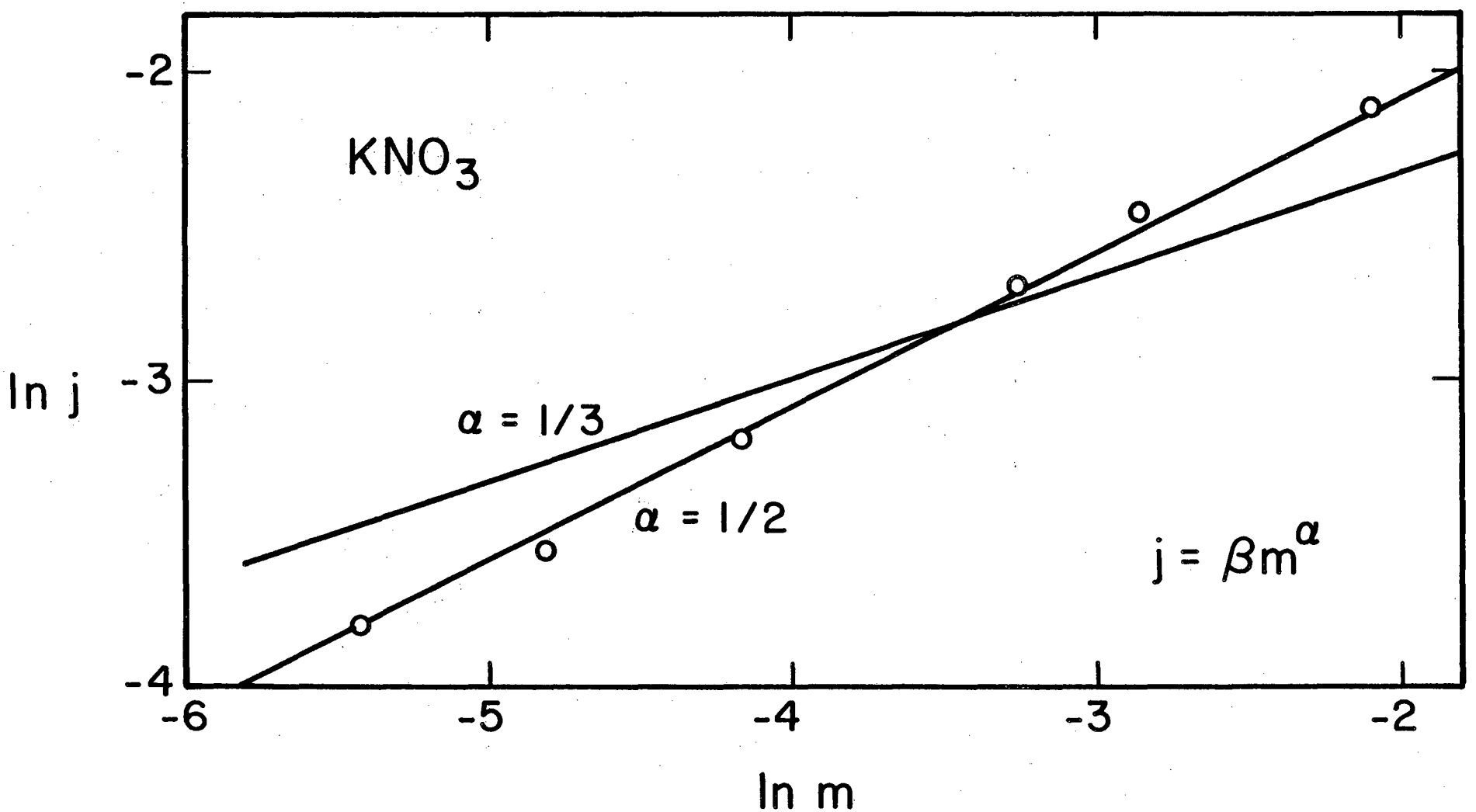
Figure Captions

Figure 1. Tests of 1/2 and 1/3 for the exponent α with the freezing point data for KNO_3.

Figure 2. Curve I in this figure, taken from Linhart (11), shows the approach of $E' = E + 0.1183 \ln m$ to $E°$ as m approaches zero.



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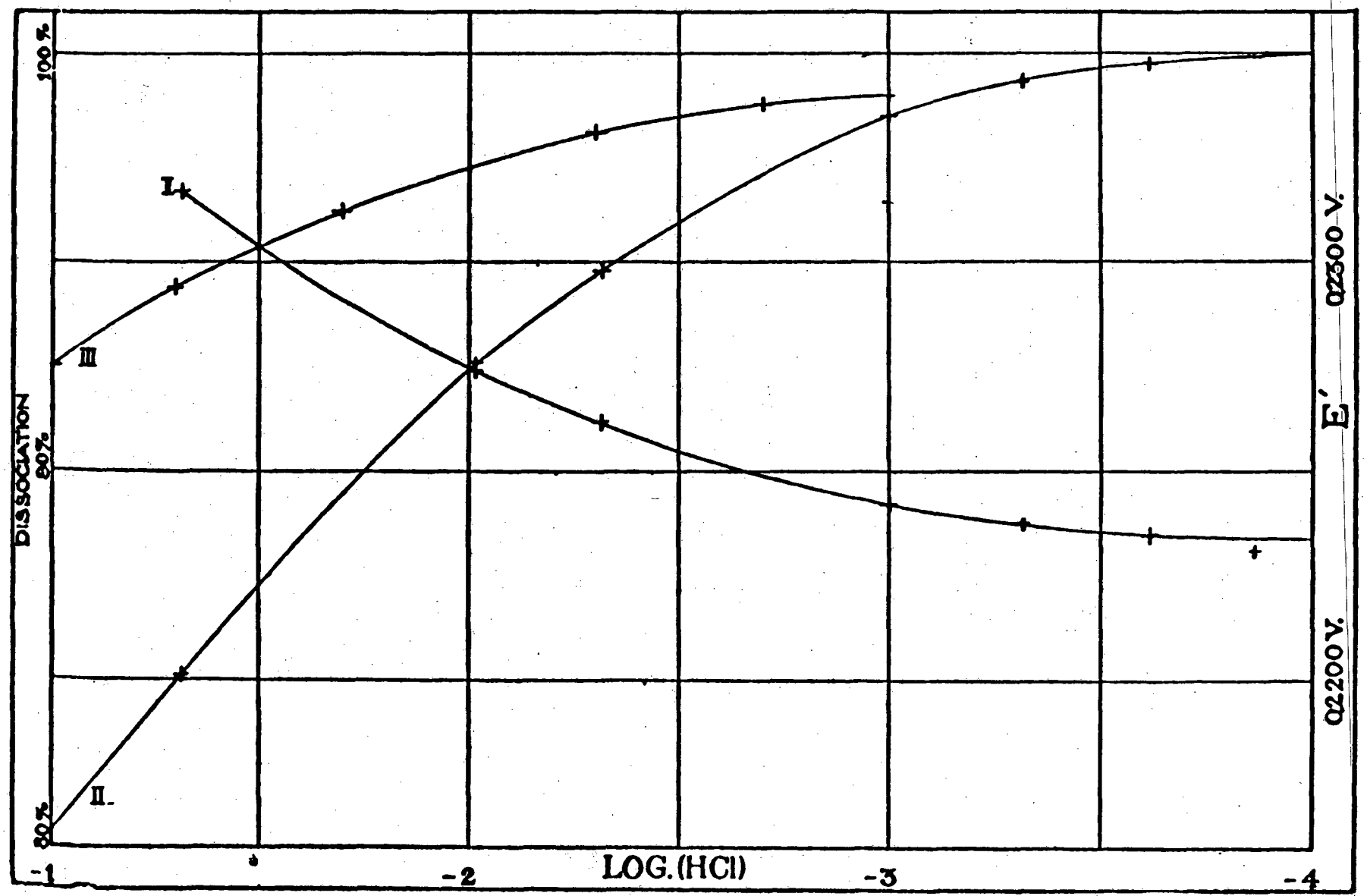

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