THE DISSOCIATION OF STRONG ELECTROLYTES

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Received March 28, 1946

The difficulties of the classical theory of electrolytes with respect to strong electrolytes and various attempts at reconciling the theory with the experimental data are briefly reviewed. The theory of Debye and Hückel furnishes methods of separating the effects of interionic attraction and incomplete dissociation in dilute solutions of moderately strong electrolytes. The intrinsic limit of these methods is discussed. A clear distinction is made between molecules and interacting ions. A reliable, though not yet precise, method of determining the degree of dissociation of strong electrolytes is based on the intensity of Raman lines. The effect of incomplete dissociation on other properties like apparent molal volume, molal refractivity, extinction coefficient, heat of dilution, and heat capacity is ascertained. The molecular constitutions of nitric and perchloric acids are described. A few results are available for other substances.

I. INTRODUCTION

The problem of the dissociation of strong electrolytes is as old as the theory of Arrhenius (4). An address given by Arrhenius (5) in Chicago in 1912 presents a good deal of information on the birth of his theory. It is perhaps a little surprising to read that as early as in 1888 Planck, as well as van't Hoff, aired just one objection against the revolutionary theory: namely, that the dissociation constant was not constant (5, pages 361, 362).

At no time did there exist any real accord between the classical theory of electrolytes and the available experimental data on strong electrolytes. The success of Arrhenius' theory, however, was so overwhelming that its failure in *one* respect could be neglected at first. But the classical theory was still widely applied to strong electrolytes even when its failure in this field was generally recognized. This strange and unsatisfactory situation was due mainly to two causes: the lack of a better theory, and reluctance to adopt correct thermodynamic methods of handling imperfect solutions. The development of a consistent theory culminated in the theory of Debye and Hückel in 1923, at the same time that Lewis and Randall in their textbook presented their thermodynamic methods in a final form which soon was generally accepted.

Before 1923 the problem of strong electrolytes was frequently expressed in the following alternative: incomplete dissociation according to Arrhenius, or complete dissociation and an appreciable influence of interionic electrostatic forces. The simplification implied in this alternative was not unjustified. In a case like this it is, at first, an entirely sound attempt to explain the facts by means of one of two effects rather than by a superposition of both.

Today the numerous discussions of the classical problem are mainly of historical interest. A long and hard struggle between a well-established theory and

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discordant experimental facts always presents a fascinating and instructive picture. The retrospective observer notes the efforts to save the old theory, repeated again and again in ever new ways. He admires a number of clear and critical discussions of the data and inevitable conclusions. He enjoys the bold attempts to start from scratch with a new theory, attempts which at first are based on arbitrary and erroneous assumptions as well as on insufficient experimental data, and which gradually improve until success is achieved.

In the following three sections an attempt is made to outline this development, which came to a conclusion in 1923.

The problem of the dissociation of strong electrolytes was entirely changed by the theory of Debye and Hückel. The question could no longer be an alternative between incomplete dissociation and ionic interaction. The electrostatic effect was quantitatively established in the limit of low concentrations. Attempts at extending the theory to higher concentrations were partially successful but soon reached a barrier of insuperable difficulties. One of the principal problems still open was the delineation of the influences of electrostatic interaction and incomplete dissociation.

The later sections of this article review the development of this problem.

II. ATTEMPTS TO SAVE THE CLASSICAL THEORY

It will be convenient to list, for the special case of a binary electrolyte, the relationships which express the classical theory of electrolytes:

$$\bar{F}_i = F_i^0 + 2RT \ln (\alpha c) \tag{1}$$

$$\vartheta = 3.716(1 + \alpha)c \tag{2}$$

$$K_c = \alpha^2 c/(1 - \alpha) \tag{3}$$

$$\alpha = \Lambda/\Lambda_0 \tag{4}$$

($\bar{F}_i$ = partial molal free energy of the ions; α = degree of dissociation; c = concentration; ϑ = freezing-point depression of an aqueous solution; Λ = molal conductivity; Λ_0 = limit of Λ for $c = 0$.) Each of the first three relations expresses the assumption that the electrolyte forms an ideal solution. Only the relation of Arrhenius (equation 4), together with the data of Kohlrausch, could be expected to furnish values of high precision before the modern technique of determining electromotive forces (G. N. Lewis, A. A. Noyes) and freezing points (L. H. Adams, G. Scatchard) was inaugurated.

The experimental material of the earlier period has been reviewed and very clearly discussed by A. A. Noyes (101) and Noyes and Falk (103). While it is usually a difficult task to draw safe conclusions from complex data of low accuracy, two facts were early recognized: (*1*) the deviations between the degrees of dissociation, determined by different methods, are significant at unexpectedly low concentrations, and (*2*) the "dissociation constant" K_c (equation 3) is not a constant but changes rapidly with the concentration.

Very early, numerous suggestions were made to replace the mass-action law (equation 3) by some empirical formula (*cf.* 7, 134, 141, 145). Considering the thermodynamic connection of the first three equations, these formulas were apt to destroy the classical theory rather than save it, without furnishing any theoretically significant substitute.

No attempt to arrive at a more general theory could appear to be more logical and promising than that of Jahn (71) and Nernst (99). They abandoned the assumption of a perfect solution and developed the deviation of the partial molal free energy from equation 1 into a Taylor series with respect to c. Actually, this idea was not quite new. It had been suggested and applied to non-electrolytes with obvious success by Margules a few years before. What was the reason that a method as general as a development into a Taylor series could fail just for electrolytes? Today the reason can be easily understood. The Taylor development is restricted only by a single, very mild condition: A series extended to the n^{th} order requires the existence and finiteness of the first $n + 1$ derivatives in the whole range. But this condition is not satisfied by electrolyte solutions. Since Debye and Hückel demonstrated that the non-ideal part of the partial molal free energy of an electrolyte contains a $c^{\frac{1}{2}}$-term, no differential quotient with respect to c exists for $c = 0$. For this reason the development into a power series with respect to c could not be successful.

Many attempts were made to save the classical theory by assumptions regarding secondary disturbing effects like hydration and the formation of complex ions. These effects are undoubtedly important in certain cases. The idea that they are *generally* responsible for all deviations from the perfect solution, going back essentially to a suggestion of Dolezalek (34), has led to entirely arbitrary and unjustified conclusions. Attempts were also made to change equation 4 by introducing an arbitrary function of the viscosity of the solution (147).

Step by step the defense of the old theory had yielded ground. After about twenty-five years the conclusion was inevitable that the mass-action law, recognized as thermodynamically linked to the theory, was inconsistent with the experimental data. The last line of defense was the assumption that the mass-action law held only at very high dilution. This idea was proposed in two different ways.

Kraus and Bray (14, 78) succeeded in representing extensive data on non-aqueous and aqueous solutions by means of the equation:

$$B = K_c - Ac_i^h \tag{5}$$

In this empirical relation, K_c is defined by equation 3, c_i is the concentration of the ions, and A, B, and h are individual constants. The same function was proposed independently by MacDougall (88). A similar formula was suggested by Bates (*cf.* 148).

The exponent h was found to depend mainly on the solvent and to decrease with increasing dielectric constant. For aqueous solutions Kraus and Bray obtained values close to $h = 0.6$. Rosenstein (132) represented his colorimetric determinations of the dissociation constant of phenolphthalein in the presence of neutral salts by equation 5 with $h = \frac{1}{2}$. His formula, indeed, approximates the limiting law of Debye and Hückel at low ionic concentrations.

If the equation of Kraus and Bray holds with $h < 1$, differentiation of equation 5 furnishes the result:

$$\lim_{c=0} \frac{dK_c}{dc} = \infty \tag{6}$$

The classical law, therefore, can be said to hold only in a very restricted sense. Actually, Kraus and Bray found that the deviations expressed by the term Ac_i^h were appreciable down to concentrations below $c = 0.001$.

Washburn (148), too, assumed the validity of the classical theory as a limiting law and of equation 4, but he included in his assumption the relation

$$\lim_{c=0} \frac{dK_c}{dc} = 0 \tag{7}$$

This condition was used for the determination of Λ_0. The modern technique of the measurement of conductivity started from the work of Washburn and Weiland (148, 150), who obtained precise data for concentrations down to $c = 0.00002$.

But the result was not a very convincing confirmation of the assumption (58, 77a, 148). While the extrapolated value for potassium chloride at 25°C. was $K_c = 0.020 \pm 0.001$, the value $K_c = 0.0524$ was obtained for as low a concentration as $c = 0.001$. Again, the validity of the classical law appeared to be restricted to extreme dilution. It also may have been hard to understand that the dissociation constant of potassium chloride appeared to be about ten times smaller than that of an obviously weaker electrolyte like iodic acid (*cf.* table 1).

A footnote in Washburn's paper (page 151) furnishes the best explanation for all attempts to save the classical law: "The theoretical basis of the mass action law for a sufficiently dilute solution being almost purely thermodynamic in character, . . . ". This reasoning would have been perfectly correct, just as the method of Jahn and of Nernst, if the non-perfect part of the partial free energy of an electrolyte could be developed into a Taylor series with respect to the concentration.

III. CRITICAL DISCUSSIONS

van Laar appears to have been the first to call attention to the influence of electrostatic interaction on the thermodynamic properties (143).

A. A. Noyes, summarizing the results of a series of important experimental investigations (102), concluded that the ionization of strong electrolytes is essentially different from chemical processes, including the dissociation of weak electrolytes. His main reasons are: The degree of ionization of strong electrolytes depends on the valence type rather than on the chemical character, temperature is of little influence, the mass-action law is not satisfied, and the molar extinction coefficients are independent of the concentration.

Analyzing the various possible reasons of the anomalies of strong electrolytes, Wegscheider (149) pointed out that a test of the mass-action law in combination with equation 4 is fair only if Λ_0 is chosen so that a minimum variation of K_c is obtained. One cannot test equation 3 if Λ_0 is determined by an extrapolation inconsistent with equation 3. Washburn, in the work reported before, made use of this conclusion.

If the anomalies are due to electrostatic interaction and therefore depend on the valence type rather than on the chemical nature of the electrolyte, there should be a certain *ionic* concentration below which the classical laws should hold for uni-univalent electrolytes, weak or strong. This strict condition was stated by Wegscheider. He found from the data available for weak electrolytes that the limit is about $c = 0.03$. Washburn's later result that potassium chloride exhibits large deviations even at much lower concentrations might have been interpreted as final evidence of the failure of the classical theory.

The retrospective observer, of course, can easily put his finger on omissions and inconsistencies. But already in 1909 Lewis' paper, "The Use and Abuse of the Ionic Theory" (80), discussed the principal inconsistencies of the classical theory as it was applied to strong electrolytes. A few years later, Lewis developed correct and simple methods for treating the thermodynamic properties of electrolyte solutions (81). At the same time, he pointed out that the dependence of the transference number on the concentration immediately invalidated equation 4.

IV. ELECTROSTATIC INTERACTION AND COMPLETE DISSOCIATION

Malmström (94) proposed, in 1905, the first quantitative theory of the influence of electrostatic interaction between the ions on the free energy. While his paper was completely forgotten, similar ideas aroused considerable interest when proposed by Ghosh (54) thirteen years later.

Malmström's work was inconclusive because he still used equation 4 and because he did not assume complete dissociation of strong electrolytes. This bold step was undertaken a little later by Bjerrum (10) and Sutherland (142). Bjerrum drew the logical conclusion from the constancy of the extinction coefficients, previously pointed out by Noyes.

The application of the later theories of electrostatic interaction of Milner (95) and Hertz (68) and the first discussions of the theory of Debye and Hückel were based on the auxiliary assumption of complete dissociation.

V. MODERATELY STRONG ELECTROLYTES

The success of the theory of Debye and Hückel was correctly interpreted as proving the complete dissociation of strong electrolytes in dilute solution. As this conclusion was based on experimental facts and an approximately valid theory, it could never have axiomatic significance. "Complete dissociation" merely meant that electrostatic interaction, which according to the conclusive deductions of Debye and Hückel must be taken into account in any case, is sufficient to represent the data without an assumption of the existence of undissociated molecules.

In principle, of course, one has always to consider the influence of both interionic forces and incomplete dissociation. For the reasons advanced by Wegscheider, the interionic forces can be neglected or taken care of by minor corrections in the case of solutions of weak electrolytes, while the formation of molecules may be neglected for dilute solutions of strong electrolytes. This leaves an intermediate field, the moderately strong electrolytes, in which both effects are considerable even in dilute solutions.

The methods for the calculation of the degrees of dissociation and the dissociation constant of a moderately strong electrolyte have been developed by Gross and Halpern (57), Sherrill and Noyes (138), and MacInnes (90). For a binary electrolyte, equations 3 and 4 are to be replaced by

$$K = \frac{(\alpha\beta_i)^2 c}{(1 - \alpha)\beta_u} = \frac{\gamma^2 c}{(1 - \alpha)\beta_u} \tag{8}$$

$$\alpha = \Lambda/\Lambda_e \tag{9}$$

where K denotes the thermodynamic dissociation constant, β_i and β_u the activity coefficients of the ions and the molecules, and $\gamma = \alpha\beta_i$ the stoichiometric activity coefficient. For low concentrations, β_i is determined by the limiting law of Debye and Hückel

$$\log \beta_i = - 0.505(\alpha c)^{\frac{1}{2}} \tag{10}$$

(aqueous solutions of a uni-univalent electrolyte at 25° C.), while $\beta_u = 1$. The quantity Λ_e represents the sum of the mobilities of the two ions. It is estimated under the assumption that Kohlrausch's law of independent migration is valid. For instance, it is assumed that for a solution of iodic acid of the concentration c and the ionic concentration αc, the quantity Λ_e is obtained from the molar conductivities of properly chosen strong electrolytes of the concentration αc by

$$\Lambda_e(c;\ \mathrm{HIO_3}) = \Lambda(\alpha c;\ \mathrm{HCl}) + \Lambda(\alpha c;\ \mathrm{NaIO_3}) - \Lambda(\alpha c;\ \mathrm{NaCl}) \tag{11}$$

Instead of using equations 9 and 11, Onsager (109) estimated dissociation constants from the deviations of conductivity data from the limiting law which he had derived. Similar methods were proposed and extensively used by Davies (6, 13, 27, 28, 29, 89, 97, 128, 129).

These methods permit the calculation of α either from Λ or from γ for low ionic concentrations αc. The dissociation constant K is calculated from equation 8. If a variation with the concentration indicates that the assumptions are not completely justified, the best value of K is obtained by extrapolation to $c = 0$. The calculation of α is carried out without difficulty by iterated approximation. Table 1 contains examples of dissociation constants obtained by these methods and by earlier classical calculations. The authors quoted are in many cases responsible only for the calculation, not for the experimental data. A few determinations by means of extinction coefficients are included for comparison; the method will be discussed later.

The methods for taking into account the interionic forces have greatly increased the accuracy of dissociation constants of weaker electrolytes. For acetic acid, for instance, Harned and Ehlers (67) derived $K = 1.754$ from electro-

TABLE 1

Dissociation constants of some moderately strong electrolytes

SUBSTANCE	K	TEMPERATURE	METHOD	YEAR	REFERENCE
		°C.			
TlCl	0.31	18	Conductivity	1927	Onsager (109)
	0.30	18	Conductivity	1927	Davies (29)
	0.23	25	E.M.F., solubility	1945	Garrett *et al.* (12, 52, 69)
HIO_3	0.262	0	Freezing point	1934	Abel, Redlich, and Hersch (2)
	0.19	18	Conductivity	1934	Abel, Redlich, and Hersch (2)
	0.18	25	Conductivity, freezing point	1903	Rothmund and Drucker (133)
	0.17	25	Conductivity	1927	Onsager (109)
	0.1686	25	Conductivity	1933	Fuoss and Kraus (51)
	0.163	25	Solubility	1939	Naidich and Ricci (98)
	0.167	25	Indicator	1944	Halban and Brüll (59a)
Trichloroacetic acid	0.217	20	Indicator	1944	Halban and Brüll (59a)
	0.232	25	Indicator	1944	Halban and Brüll (59a)
Tribenzylmethylammonium chloride	0.179	18	Conductivity	1912	Drucker (36)
Tribenzylmethylammonium bromide	0.139	18	Conductivity	1912	Drucker (36)
Picric acid	0.164	—	Distribution, freezing point	1903	Rothmund and Drucker (133)
Dichloroacetic acid	0.14	0	Freezing point	1930	Redlich and Rosenfeld (126)
$H_4P_2O_7$	0.14	18	Conductivity, distribution	1909	Abbott and Bray (1)
$PbCl^+$	0.064	25	Solubility	1901	von Ende (146)
	0.0775	25	Extinction	1931	Fromherz and Kun-Hou Lih (49)
	0.1	25	E.M.F.	1938	Güntelberg (59)
$PbBr^+$	0.071	25	Extinction	1931	Fromherz and Kun-Hou Lih (49)

TABLE 1—*Continued*

SUBSTANCE	K	TEMPERATURE °C.	METHOD	YEAR	REFERENCE
PbI^+	0.0345	25	Extinction	1931	Fromherz and Kun-Hou Lih (49)
H_2SO_4 in methanol	0.029	25	Conductivity	1943	Kanning *et al.* (73)
Nitroacetic acid	0.0208	18	Reaction rate	1943	Pedersen (110)
HSO_4^-	0.013		Conductivity	1903	Luther (85)
	0.03	25	Various	1910	Noyes and Stewart (104)
	0.015		Various	1911	Jellinek (72)
	0.013	25	Conductivity	1911	Drucker (35)
	0.017	18	E.M.F.	1920	Drucker (37)
	0.02		Colorimetric	1924	Kolthoff (76)
	0.030	25	E.M.F.	1926	Livingston (83)
	0.0115	25	Conductivity	1926	Sherrill and Noyes (138)
	0.0180	15	E.M.F.	1934	Hamer (62)
	0.0127	25			
	0.0084	40			
	0.0102	25	Conductivity	1940	Singleterry (140)
	0.01797	5	Colorimetric	1940	Young and Singleterry (140, 153b)
	0.01357	15			
	0.01015	25			
	0.00755	35			
	0.00558	45			
	0.00412	55			
H_2SO_3	0.012	25	Conductivity	1926	Sherrill and Noyes (138)
	0.0172	25	Conductivity	1941	Tartar (142a)
H_3PO_4; $H_3P_2O_7^-$	0.011	18	Conductivity, distribution	1909	Abbott and Bray (1)
H_3PO_4	0.0083	18	Conductivity	1926	Sherrill and Noyes (138)
$HSeO_4^-$	0.01	25	E.M.F.	1942	Gelbach and King (53)
o-Nitrobenzoic acid	0.0060	25	Conductivity	1926	MacInnes (90)
	0.006957	18	Conductivity	1933	Fink and Gross (44)
Chloroacetic acid	0.001396	25	Conductivity	1933	Saxton and Langer (135)

motive forces, while MacInnes and Shedlovsky (91, 92) found 1.753 from conductivities (25°C.; *cf.* also 135). The galvanic cells devised by Harned and other authors were especially efficient in eliminating the influence of electrostatic forces. Precise measurements of the dissociation of weak electrolytes have been reviewed by Harned and Owen (67a).

In the group of moderately strong electrolytes the second dissociation of sulfuric acid has been studied most frequently. This case illustrates the progress which has been made in this field. The discrepancies between the results of the earlier authors are due to the uncertainty of the theoretical basis, but the recent results of Young and his coworkers (140, 153b) are reliable within the much narrower limits of experimental error and hardly affected by any uncertainty of interpretation (*cf.* also 67a). Young (153a) also showed that an apparent deviation of the heat of dilution from the theory of Debye and Hückel was due to the incomplete dissociation of the hydrosulfate ion.

But the range covered by conclusions from thermodynamic properties and conductivities has hardly been increased. Iodic acid furnishes a characteristic example. While the recent determinations are more precise and based on a much stronger theory, the classical result of Rothmund and Drucker had furnished a good approximation (*cf.* table 1).

It can be demonstrated, indeed, that the dissociation constant of iodic acid is already close to the upper limit of the range to which the methods discussed in this section can be applied.

These methods are invariably based on the assumption that the influence of the interionic forces can be predicted without recourse to experimental data for the individual case. To discuss this assumption, one has to start from a more general relationship than equation 10, for instance:

$$\log \beta_i = -0.505(\alpha c)^{\frac{1}{2}} + B\alpha c + \cdots \qquad (12)$$

While the individual constant B shows certain regularities, no theory has been developed which safely predicts the value of B.

With the approximation of $1 - \alpha = \beta_i^2 c/K$, following from equation 8 for small values of $1 - \alpha$ and c, the stoichiometric activity coefficient can be represented by

$$\ln \gamma = \ln \alpha + \ln \beta_i = -\beta_i^2 c/K - 2.303[0.505(\alpha c)^{\frac{1}{2}} - B\alpha c] \qquad (13)$$

Within the approximation desired in this case, β_i and α in the coefficients of c may be replaced by unity, so that

$$1/K = 2.303B - [2.303 \cdot 0.505(\alpha c)^{\frac{1}{2}} + \ln \gamma]/c \qquad (14)$$

However accurately the experimental quantity γ may be known, the dissociation constant can be derived from equation 14 only if the absolute value of the unknown coefficient B may be expected to be small compared with $1/2.303K$.

From the extensive survey of Prentiss and Scatchard (111) it can be concluded that for hydrochloric acid roughly $B = 1$, and that values of about this amount occur quite frequently. The basic assumption does not hold, therefore, for values of K larger or even close to $\frac{1}{2}$.

In the place of equation 10, more elaborate relationships have been used, which are likely to give somewhat better values for β_i. But the uncertainty in β_i is not so much reduced that the order of magnitude of the estimated limit of K is changed.

The situation is similar with respect to the methods which use Λ instead of γ for the determination of the dissociation constant.

For these reasons, calculations of dissociation constants of moderately strong electrolytes should always be critically examined. A cautious statement, incidentally made by this author (126) in 1930, that the freezing points of thallous nitrate solutions can be represented by (Debye's limiting law and) a dissociation constant $K = 0.80$, has no significance in spite of Nernst's (100) assertion that this salt is obviously not completely dissociated. The same is true for numerous dissociation constants calculated by Davies.

The upper limit for the derivation of dissociation constants from activity coefficients or conductivities is much lower for polyvalent electrolytes, owing to the lower range of validity of the limiting laws. For instance, even a dissociation constant as low as $K = 0.0045$ ascribed to zinc sulfate (27) is highly questionable (20, 21). The same is true for other similar cases.

The transference number, successfully used in early and recent times for the investigation of complex ions (see, for instance, 67a, 86, 140a), has been repeatedly used as a source of information regarding incomplete dissociation. However, the limitations applying to the conductivity are valid also for the transference number (*cf.* 46, 87).

While the promotion of our knowledge of dissociation was one of the great successes of the theory of Debye and Hückel, there still remained a large class of electrolytes of which no more could be said but that no evidence was available of the existence of undissociated molecules in dilute solutions.

VI. ION PAIR AND MOLECULE

Before we can proceed in reporting the various attempts made in recent times to investigate the dissociation of strong electrolytes, the concept of the undissociated molecule is to be discussed briefly. In the historical development of our problem some doubt has arisen as to whether or not a sharp distinction can and should be made between molecules in the traditional meaning and ions which are kept close together by strong electrostatic forces.

An early paper of A. A. Noyes (102), discussed in a preceding section, may perhaps be interpreted as suggesting that electrostatic attraction produces molecules of a particular character.

Bjerrum (11), in 1926, went a step farther. He noticed that, according to the theory of Debye and Hückel, under certain conditions an appreciable fraction of the ions must be very close to ions of the opposite sign, forming "ion pairs." Treating this association of ions to pairs formally like the formation of molecules, he developed an efficient approximation method for calculating the influence of the electric forces on the activity coefficient at moderate concentrations. This method was repeatedly used by other authors,—in an elaborate method by Scatchard and Epstein (135a) and by Fuoss (50) for non-aqueous solutions. Indeed, the electric forces acting in solutions of low dielectric constant are so great that a large fraction of the ions must be kept together quite firmly by Coulomb forces.

From another viewpoint Fajans (40, 42, 43) arrived at somewhat similar conclusions. He observed that the interaction manifested in the dependence of the molar refraction on the concentration furnishes proof of contact between ions and of the mutual deformation of their electronic systems. According to Fajans, pairs of rigid undeformed ions represent the extreme case of the ideal ionic bond. The variation of the molar refraction constitutes a measure of the deformation and, in general, of the approach to the non-polar bond type. All intermediate stages between these extreme types exist.

The old concept of the undissociated molecule obviously can be maintained only if a criterion exists which permits one to draw a natural and reasonably sharp line between molecules and interacting ions. This criterion must be theoretically significant and experimentally realizable.

A criterion of this kind is the vibration spectrum. In addition, the vibration spectrum affords an opportunity to maintain in a precise way the traditional idea of the molecule as a mechanical unit. In the days of the kinetic theory of gases this primary property of the molecule was so far beyond any doubt that it hardly was even discussed.

As a mechanical unit, a molecule or an ion possesses three translational degrees of freedom. The dissociation of a molecule does not change the total number of degrees of freedom, which is just three times the number of atoms. But it is accompanied by a change of three other modes of motion into translations. Also, the number of rotational degrees of freedom changes. It increases by three unless atomic or linear ions are involved. These special cases are easily examined one by one, the result being that on dissociation in any case at least one (type HCl) and at most six (type NH_4NO_3) modes of vibration change into translational or rotational motions.

The change of the number of vibrations, of course, need not be the only characteristic difference between the spectra of the molecule and the ions. It is especially the change of symmetry which causes characteristic and predictable changes in the vibration spectrum.

Very extensive experimental evidence supports the conclusion that the vibration spectrum is indeed a characteristic property of a molecule or ion. The environment influences the vibration frequency and the width of a spectral line, but the general type of the spectrum and the number of lines depend only on the nature of the molecule or ion.

Frequently, but not necessarily, the Raman spectrum presents sufficient information to enable one to distinguish between the molecule and the ions. However, in a case like solutions of sodium chloride the absence of a Raman line corresponding to the sodium–chlorine vibration cannot be taken for final evidence of complete dissociation, since the intensity of Raman lines correlated with polar bonds is always low.

On the other hand, the fact that the intensity of the nitrate lines in the Raman spectra of alkali nitrates is proportional to the concentration (116, 123, 139) furnishes sufficient proof of complete dissociation. The validity of this conclusion, of course, is restricted by the limits of experimental errors, which may amount to 5 per cent or even more. But the significance of this restriction need not be overestimated. Actually it applies only to the highest concentrations, i.e., to almost saturated solutions, since the fraction of undissociated molecules in any case must decrease with decreasing concentration.

These two examples illustrate the fact that each case must be discussed individually. But there can be no doubt that the question of dissociation can be solved in any case in which complete knowledge of the vibration spectrum is available.

It need hardly be pointed out that ion pairs are not molecules according to the suggested definition (123).

No logical objections are to be raised against a more extended definition of the term "molecule," which also includes ion pairs and interacting ions. In this case, however, a new term would be required for the traditional concept of the molecule. No advantage can be seen in abandoning the strictly definable meaning of an old idea and using the old term for a concept which cannot be sharply limited and does not require a separate term at all.

The statement that the proposed narrower definition of the molecule furnishes a strict distinction between molecule and ions is to be taken with a grain of salt. The average lifetime of a molecule as a mechanical unit may conceivably be of the order of magnitude of a vibration period. Experimentally this borderline case would be characterized by an anomalous width of a vibration line. No safe evidence of the existence of a case of this kind is available. The existence of borderline cases would not impair the usefulness of the concept.

VII. STRONG ELECTROLYTES

As mentioned in the preceding section, there is no reason to assume undissociated molecules even in concentrated solutions of some salts, such as the alkali nitrates. Many years ago, Bray (15) demonstrated that fused salts are dissociated to a high degree (*cf.* also 82), and later van Laar (144) and Gross (56) concluded that they are completely dissociated.

Never could there be any doubt, however, that concentrated solutions of some strong electrolytes contain a large fraction of undissociated molecules. The low conductivity of the absolute acids and the high amount of the heat of mixing and of the volume contraction on dilution furnish sufficient evidence. In addition, a reaction like

$$HClO_4 + H_2O = H_3O^+ + ClO_4^-$$

is necessarily incomplete if the molal ratio exceeds 1:1. Direct proof was furnished by the discovery of the Raman spectra of undissociated nitric acid (17, 74, 114, 151) and of other strong acids.

Various attempts at estimating dissociation constants or degrees of dissociation of strong acids (16, 38, 45, 60, 63, 100, 136, 137, 152, 154) were entirely unsuccessful. Obviously this failure was due to the direct or indirect introduction of the laws of the perfect solution. Two methods, however, appear to approximate the order of magnitude: Wynne-Jones (153) extrapolated the dissociation constants of non-aqueous solutions as a linear function of the reciprocal values of the dielectric constant, and Kossiakoff and Harker (77) based an estimate on the constitution of the molecule.

The classical methods failed because they were based on properties which are influenced too much by the environment of the ions and the molecules, and also because these properties are not sufficiently distinct for ions and molecules. Safe quantitative results for the degree of dissociation of a strong electrolyte could be expected only from a property which is highly characteristic of a particular ion or molecule, and at the same time is not seriously affected by its environment. Apparently only some optical properties and the magnetic susceptibility satisfy these requirements. Since A. A. Noyes's early remark (101), it has been realized by Lewis (80), Bjerrum (10), and Hantzsch (64) that the absorption of light promised to furnish a clue to the problem of dissociation. Likewise, the intensity of Raman lines furnishes quantitative and unambiguous information.

Precise refractivity measurements have been used by Fajans as a powerful tool to elucidate the mutual influence of ions. It was to be expected that the much coarser effect of dissociation is conspicuous also in the refractivity. This is confirmed by the example of nitric acid, discussed in a later section. The refractivity is less useful for a primary determination of the extent of dissociation, since in general all components of a solution contribute appreciably to its value. Okazaki's measurements and review of older data (106) indicate a similar situation for the rotation of the plane of polarization in a magnetic field.

The magnetic susceptibility may be expected to furnish unambiguous quantitative information regarding the dissociation of some strong electrolytes (*cf.* 46).

VIII. ABSORPTION OF LIGHT

In many cases frequencies can be found for which the extinction coefficient of one of the ions is much larger than that of the molecule, or *vice versa.* In these cases the extinction coefficient is sufficiently specific.

The influence exerted on the extinction coefficients by the components of the solution was carefully examined by Halban and Eisenbrand (60). Their data and the results of Fromherz and coworkers (32, 33, 48, 49) show clearly that this influence, while definitely exceeding the limits of experimental error, is considerably smaller than the changes which frequently are produced by dissociation. The extensive and accurate measurements of these authors demonstrate that a quantitative determination of degrees of dissociation and dissociation constants of strong electrolytes can be based on extinction coefficients.

Unfortunately, the available data are not quite sufficient for definite conclusions in this respect. The substances investigated by Fromherz either reveal no incomplete dissociation at all, like the halides of the alkali and alkaline earth metals, or are electrolytes of moderate strength (*cf.* table 1). The measurements on nitric acid and calcium nitrate by Halban and Eisenbrand do not furnish sufficient information on dilute solutions.

Dalmon's measurements (22) on nitric acid and the results of Freed and his coworkers (45a, 45b, 46a) for europium nitrate will be discussed later.

IX. RAMAN SPECTRA

For the reasons discussed in a preceding section, Raman spectra yield the most direct and conclusive evidence. As mentioned before, several authors (18, 114, 139) realized that the intensity of a Raman line is proportional to the concentration of the corresponding molecule or ion. But their attempts to determine the constant factor relating intensity and concentration were obviously unsuccessful.

According to a suggestion made by Redlich and Rosenfeld (127) in 1937, the true ionic concentration is determined by comparison with the solution of a completely dissociated electrolyte containing the same ion. Thus, to find the concentration αc of the ions in nitric acid of concentration c, one prepares a solution of sodium nitrate of such strength that the intensity of the Raman lines of the nitrate ion is equal for both solutions. Since sodium nitrate is practically completely dissociated, its stoichiometric concentration is equal to its ionic concentration or equal to αc. This method has been used by N. R. Rao (115, 116, 118, 120), Redlich and Bigeleisen (123), and Redlich, Holt and Bigeleisen (124).

The method not only eliminates the apparatus factor relating intensity and concentration but also has the technical advantage that only lines of equal intensity are to be compared. Still the experimental difficulties are considerable, owing to the fact that the Raman lines are broader in the presence of the acid molecules.

So far only the photographic method has been used. But owing to the peculiar relationship between light intensity and blackening, the photographic plate is a poor tool for integrating intensities distributed in different ways. In addition, owing to the comparatively low intensity, a considerable distortion of the distribution by the finite widths of the slits of the spectrograph and microphotometer can hardly be avoided. Even with an elaborate method of comparing intensities (124) the limits of error are still large. Important progress can be expected from the use of the photoelectric method, for which suitable equipment has been developed in recent years (112, 113).

The special results reported in the following sections are based primarily on the method of comparing the intensities of the Raman lines.

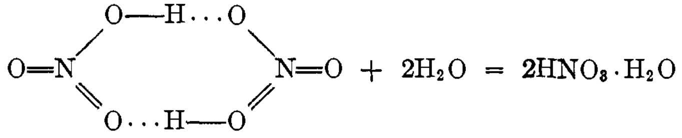
X. NITRIC ACID

The degrees of dissociation found by N. R. Rao (116) and by Redlich and Bigeleisen (123) are in good agreement. The latter authors derived the value $K = 21 \pm 4$ for the thermodynamic dissociation constant defined by equation 8.

This value agrees sufficiently well with Wynne-Jones' estimate $K = 40$ (153), with the value $\log K = 0.1$ of Kossiakoff and Harker (77), and with the value $K = 9$ derived by the author (122) from the extinction coefficients of Halban and Eisenbrand (60). It is just compatible with the lower limit derived by Halban and Seiler (61) by an indicator method.

The question of the molecular constitution of nitric acid has been the subject of many discussions. Today sufficient experimental data are available for a fairly detailed and reliable description.

Chédin (19) concluded from the Raman spectrum that the absolute acid contains a few per cent of nitrogen pentoxide, as already suspected by Halban and Eisenbrand (60). Dalmon and Freymann (24, *cf.* also 23) found evidence of hydrogen bonds in their infrared spectra. According to their spectra, addition of water results in depolymerization, which perhaps may be symbolized, as suggested by Hantzsch (64, 65), by the equation:



However, the existence of the dimer and the hydrate as definite molecules in the solution has not been directly proven.

TABLE 2

Degree of dissociation (α) of nitric acid (approximately 25°C.)

c	0.1	1	2	3	4	6	8	10	12	14
α	0.997	0.978	0.95	0.90	0.85	0.72	0.56	0.42	0.28	0.16

According to the infrared spectra, this reaction is practically complete at the composition corresponding to $HNO_3 \cdot H_2O$ ($c = 18$). At this concentration not more than a few per cent of the acid are dissociated (table 2). Dissociation takes place mainly on dilution from $c = 14$ to $c = 4$. The degree of dissociation for lower concentrations is best obtained by graphical extrapolation of log ($K\beta_u$) (123) and by means of equation 8. The approximate values recorded in table 2 for higher concentrations are taken from a smooth curve.

This picture of the molecular constitution of nitric acid, while not particularly precise in detail, is directly based on experimental facts. It is somewhat simpler than expected by earlier authors. The brilliant ideas which Hantzsch suggested on an experimentally and theoretically insufficient basis find a striking confirmation in some respects, while they fail entirely in other respects.

The dependence of many properties on the concentration has often been connected with the dissociation of strong electrolytes. Strangely enough, the attention was usually concentrated on dilute solutions, where the effect of dissociation is entirely negligible (*cf.* 100). Actually, several properties of nitric acid solutions change greatly just in the range between $c = 4$ and $c = 14$. These variations can be safely, and even in a crudely quantitative way, correlated with the dissociation. They are more or less clearly distinct from the variations which are due to other causes,—namely, depolymerization and hydration, responsible mainly at concentrations higher than $c = 18$, and ionic interaction, conspicuous in the dilute range. The electrostatic effects are always much smaller than the effects due to chemical changes.

The apparent molal volume, Φ, and the molal refraction, R, measured by Fajans and coworkers (*39, 41, 75, 84*), and the extinction coefficient, ϵ, at 3180 Å., determined by Dalmon (22), are plotted as functions of $1 - \alpha$ in figure 1.

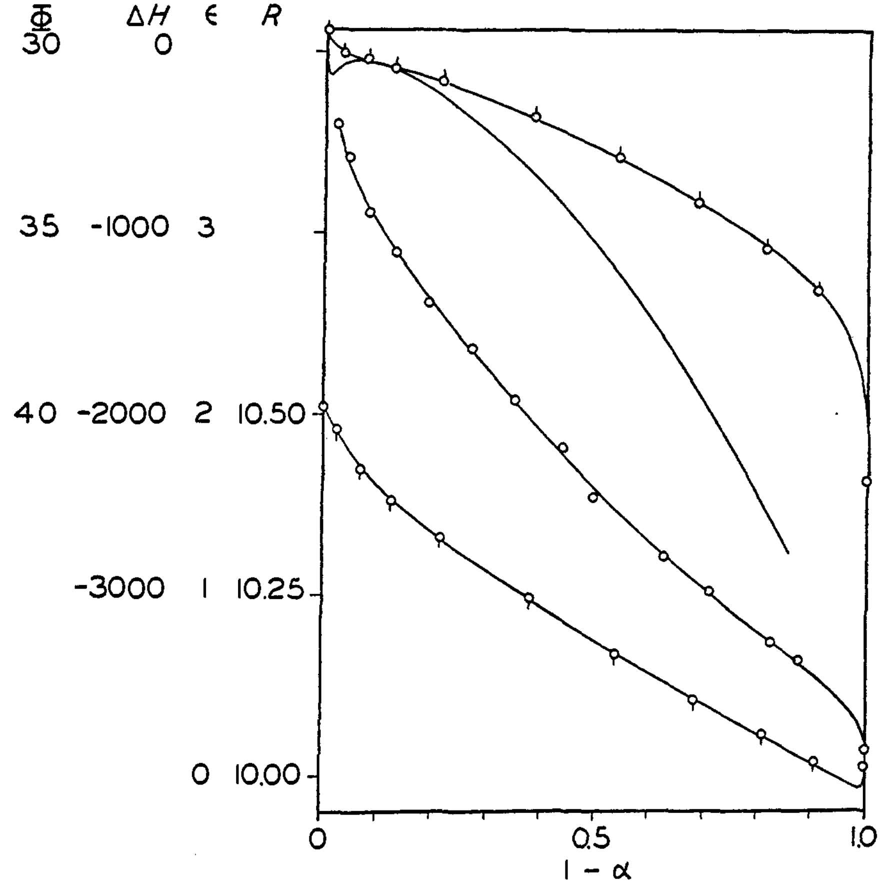


FIG. 1. Nitric acid. ȯ, apparent molal volume (Φ); ΔH, heat content per mole HNO_3; O, extinction coefficient (ϵ); ♀, molal refraction (R) as function of the degree of dissociation.

In a diagram like this any colligative property $g = g_i\alpha + g_u(1 - \alpha)$ is represented by a straight line. Actually, the three curves are fairly flat in the middle portion. This indicates that the variation in this range is mainly due to dissociation. It is quite possible that the remaining curvature is partly due to errors in the degree of dissociation. Crude values of the refractivities, extinction coefficients, and molal volumes of the ions and the molecule can be read from the diagram.

The integral heat of dilution, $-\Delta H$ (9, 70, 127), can hardly be considered a colligative property. From the slope of the curve in figure 1 one may estimate that the heat of dissociation will be in the range of about 2000 to 5000 calories per mole. This means that the heat of dilution of the absolute acid, 7440 calories, includes a considerable amount for depolymerization and hydration.

This estimate can be compared with a similarly crude value which may be derived from N. R. Rao's measurements (120) of the degrees of dissociation at higher temperatures (table 3). For each of the two lower concentrations the two temperature intervals furnish approximately equal values for

$$\frac{\mathrm{d}}{\mathrm{d}T} \ln \frac{\alpha^2}{1 - \alpha} = \frac{\mathrm{H}_i - \mathrm{H}_u}{RT^2} - \frac{\mathrm{d}}{\mathrm{d}T} \ln \frac{c\beta_i^2}{\beta_u} \tag{13}$$

where the molal heat contents of the ions and the molecule are denoted by H_i and H_u. Neglecting the last term in equation 13, one obtains $\mathrm{H}_u - \mathrm{H}_i = 2400$ and 4500 for $c = 10.5$ and 12.58. The two temperature intervals do not furnish consistent values for $c = 14.50$.

Another check of the order of magnitude can be carried out by means of Miščenko's data for the specific heat (96), which agree well with unpublished measurements by Rosenfeld (131). In the concentration range, which is most affected by the change of dissociation, the specific heat can be approximated by

TABLE 3

Degree of dissociation of nitric acid at higher temperatures

c	10.5	12.58	14.50
30°C	0.352	0.212	0.114
60°C	0.300	0.155	0.095
90°C	0.226	0.105	0.032

$$c_p = (1 - p)c_0 + p[\alpha c_i + (1 - \alpha)c_u + (\mathrm{H}_i - \mathrm{H}_u)\mathrm{d}\alpha/\mathrm{d}T] \tag{14}$$

where p denotes the grams of nitric acid dissolved in 1 g. of the solution, and c_0, c_i, and c_u the specific heats of water, the ions, and the molecule, respectively. The quantity $\mathrm{d}\alpha/\mathrm{d}T$ is eliminated by means of equation 13, the last term again being neglected. Denoting the molal weight of HNO_3 by M, one obtains:

$$c_p = c_0 + p\left[c_i - c_0 + (c_u - c_i)(1 - \alpha) + \frac{\mathrm{H}_i - \mathrm{H}_u}{\mathrm{M}RT}\cdot\frac{\alpha(1 - \alpha)}{2 - \alpha}\right] \tag{15}$$

Table 4 contains Miščenko's values for 21.07°C. and the values calculated with $c_0 = 0.9983$, $c_i = -0.115$, $c_u = 0.435$, and $\mathrm{H}_i - \mathrm{H}_u = 3300$. The agreement, while quite satisfactory, is not very significant, as three arbitrary coefficients have been introduced. But it may be noted that the values of c_i and c_u are reasonable, and that the value of $\mathrm{H}_i - \mathrm{H}_u$ agrees with the two preceding estimates.

This interpretation of the variation of all these properties is undoubtedly very crude, but it furnishes a consistent and fairly simple picture.

XI. NITRATES

According to numerous measurements the Raman spectrum of aqueous solutions of all nitrates contains a moderately strong line at about 720 cm.$^{-1}$ (*cf.* 93). In the spectrum of concentrated solutions of polyvalent nitrates an additional line appears, the frequency of which is about 20 cm.$^{-1}$ higher. The interpretation of this line as due to an intermediate ion such as $CaNO_3^+$ etc. has been discussed, though not generally accepted, by several authors (25, 26, 55, 79, 107, 108, 130).

Bauer, Magat, and Da Silveira (8) tested this interpretation by comparing the intensities of the two lines with the intensity of the strong nitrate line at 1050 cm.$^{-1}$ in solutions of calcium nitrate and of mixed solutions of calcium nitrate with calcium chloride and lithium nitrate. The results did not agree with what was qualitatively expected according to the mass-action law. However, Bauer, Magat, and Da Silveira undoubtedly overestimated the applicability of the photographic method of measurement of intensity. The two lines in question are so close that they can hardly be sufficiently resolved in a determination of intensities, and the line at 1050 cm.$^{-1}$ is so much stronger that it cannot be used as a reference. In fact, unpublished results of Mr. I. I. Friedman (47) on solutions of calcium nitrate and chloride are qualitatively in perfect agreement with the mass-action law.

TABLE 4

Specific heat of nitric acid at 21.07°C.

p	c_p (OBSERVED)	c_p (CALCULATED)	p	c_p (OBSERVED)	c_p (CALCULATED)
0	0.9983		0.35	0.7371	0.7344
0.06	0.9286	0.9336	0.40	0.7175	0.716
0.10	0.8861	0.8932	0.45	0.6992	0.701
0.15	0.8426	0.8474	0.50	0.6815	0.683
0.20	0.8063	0.8097	0.55	0.6622	0.665
0.25	0.7790	0.7791	0.60	0.6415	0.647
0.30	0.7576	0.7535	0.65	0.6190	0.625

A similar split into a doublet has been observed with regard to the diffuse lines at 1350 cm.$^{-1}$ (all nitrates) and 1450 cm.$^{-1}$ (only polyvalent nitrates). Both lines, however, appear also in Friedman's spectra of sodium nitrate and lithium nitrate, the relative intensity of the higher frequency being greater in solutions of polyvalent nitrates. These results have not yet been explained.

Similar though less extensive evidence is available for many bivalent and trivalent nitrates.

The results of Freed and coworkers (45a, 45b, 46a) present, as far as this reviewer can see, unambiguous evidence for the incomplete dissociation of europium nitrate. Europium salts are exceptional in having sharp absorption lines in the blue region of the spectrum. Freed found four absorption lines with nitrate solutions at $c = 0.0007$, identical with lines of europium chloride in solutions up to $c = 1.5$. However, between $c = 0.01$ and $c = 1.5$, three lines were found for the nitrate, at least one of which is clearly different from the chloride lines. In the middle range,—namely, between 0.001 and 0.01,—superposition of both spectra was found.

This is precisely the behavior to be expected if $Eu(NO_3)^{++}$ is a weak electrolyte. While a closer examination of the thermodynamic properties is desirable, there is no reason to expect any results inconsistent with the theory of Debye and Hückel, since appreciable deviations from the limiting laws must be anticipated for a trivalent electrolyte even in the range from 0.001 to 0.01 with or without complete dissociation.

XII. PERCHLORIC ACID

A comparison of the results obtained for nitric acid and perchloric acid reveals the wide differences which exist within the group of strong electrolytes. The degrees of dissociation from Raman data (124) substantiate the assumption of earlier authors, especially of Hantzsch and Weissberger (66), that this acid is considerably stronger than nitric acid. While some of the figures of table 5 may be in error by as much as 10 per cent, some characteristic differences are quite obvious. The maximum ionic concentration of nitric acid amounts to 4.5 gram-ions per liter (at $c = 7.5$), that of perchloric acid to 10.3 (at $c = 12$). At the composition of the monohydrate, nitric acid is practically undissociated; the degree of dissociation of perchloric acid is about 0.55 ($c = 14.7$). At high concentrations the dissociation of perchloric acid appears to approach completeness with respect to the reaction:

TABLE 5

Dissociation of perchloric acid

PER CENT	c (25°C.)	αc (53°C.)
60	9.1	8.9
70	10.9	10.1
	12.0	10.3
84.8	14.7	8.1
	16.0	5.6

$$HClO_4 + H_2O = ClO_4^- + H_3O^+$$

The dissociation increases considerably with decreasing temperature. This is in accord with the large heat of mixing.

The available experimental data do not indicate any molecular species other than the ions and the undissociated acid. The dissociation constant could not be calculated, because the activity coefficients are known only in the range of practically complete dissociation.

N. R. Rao (121) found an appreciable change of the intensity of the line at 930 cm.$^{-1}$ when he compared spectra of perchloric acid in the range between $c = 5$ and $c = 10$ obtained with exposures inversely proportional to the concentration. The actual change of dissociation in this range amounts at most to a few per cent at room temperature and is undoubtedly far below the limits of perceptibility in this method. The apparent change in intensity illustrates the well-known fact that misinterpretation of photographic intensities can be avoided only by a careful technique.

XIII. OTHER SUBSTANCES

Sulfuric acid was investigated by N. R. Rao (115) by comparison with ammonium sulfate and potassium hydrosulfate. Rao's table of his results contains several inconsistencies, and this author has not been able to derive satisfactory figures. De Béthune and Kimball (30) attempted to locate one error and calculated concentrations of the hydrosulfate ion.

Ochs, Guéron, and Magat (105) found a diffuse Raman line at 2630 cm.$^{-1}$ in hydrochloric acid above $c = 9$. At this concentration, therefore, an appreciable fraction of undissociated molecules must be present.

A few measurements on iodic acid were made by N. R. Rao (118). The same author (117) also found that dissociation decreases with increasing temperature, a fact which can be immediately derived from the positive sign of the heat of mixing. Rao also found (119), obviously by a misinterpretation, some qualitative contradiction to the expected common-ion effect.

XIV. CONCLUSIONS

So far only the measurement of the intensities of Raman lines has furnished unambiguous quantitative results. But extinction coefficients and magnetic susceptibilities are also so characteristic of the molecular state that independent results may well be expected.

Various properties like refraction, volume, heat content, and heat capacity indicate the influence of dissociation clearly enough. Since they are less specific they can, however, hardly furnish primary quantitative information.

In the interpretation of Raman spectra it should be always borne in mind that the absence of a characteristic spectrum is not a conclusive proof of the absence of a molecule. The specific intensities of Raman lines are so widely different that complete dissociation can be demonstrated only by the determination of the intensities of the lines of the ions.

At present only a small amount of information on the dissociation of strong electrolytes is available. Moreover, the accuracy of the data is low. But there is little reason to doubt that more extensive and more accurate information can be obtained, and that coördinated examination of various properties will furnish opportunities to check the results. One of the old problems of physical chemistry appears to be on the way toward solution.

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