

## Sound Propagation in Chemically Active Media\*

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(Received August 8, 1949)

A fluid containing chemically active ingredients in equilibrium may exhibit unique physical properties: the compressibility may depend on the rate of compression; similarly the specific heat may depend on the rate of temperature change. This rate dependence arises from the finite reaction rate of the chemical components. One phenomenon resulting from this behavior is the anomalous absorption and dispersion of sound. Expressions are given relating the chemical reaction rate, the equilibrium constant, and other chemical parameters, to the acoustical properties of the fluid. As an illustration of these relationships the unusual sound absorption in aqueous  $\text{MgSO}_4$  solution is discussed. Calculation shows that the partial compressibility associated with the ionization process is of the correct magnitude to explain the observed absorption.

### I. INTRODUCTION

A FLUID containing chemically active components may possess unusual physical properties which are not commonly encountered in ordinary fluids. One of these unique properties may be illustrated by the following experiment: Suppose a container is filled with a substance containing chemically active ingredients in equilibrium; the chemical reaction must be one whose equilibrium constant is pressure dependent. Means are provided for observing the instantaneous change in volume with pressure and hence of measuring the coefficient of compressibility. Such an experiment will yield the unusual result that the coefficient of compressibility depends on the *rate* of compression (or dilatation).

The explanation for this result is fairly obvious: the chemical reaction contributes in part to the volume change, but its contribution depends on how far the reaction has proceeded toward equilibrium and hence on the rate of compression. Furthermore, it is entirely possible for the compressibility measurement to be performed in a time too short for the chemical reaction to participate, in which case the measured compressibility will be only that of the reactants considered as inert. Hence, a chemically active fluid may be said to have two compressibilities: a static, or equilibrium compressibility, and a dynamic compressibility whose value depends on the compression rate and which approaches a limiting value at high rates of compression.

In an analogous manner a chemically active substance whose equilibrium is temperature dependent may possess dynamic and static specific heats. The static specific heat of the substance is measured after equilibrium is attained and is identified with the value obtained in conventional measurements. The dynamic specific heat will depend on the rate of change of temperature and will approach a limiting value at high rates of change. The difference between the limiting value and the static value is simply the partial specific heat of the chemical reaction.

An acoustic wave is a familiar example of a process in which rapid compressions and temperature changes

occur. In acoustics then, the distinction between the static and dynamic properties which exists in a chemically active medium may be expected to become extremely important. Long ago, Albert Einstein<sup>1</sup> interpreted the excessive sound absorption occurring in a partially dissociated gas such as nitrogen tetroxide, as a result of the dissociation reaction. It may also be expected that chemical reactions occurring in liquids might also influence the propagation of sound waves. Particularly interesting, are the possibilities for determining the reaction rates of rapid chemical processes from the study of acoustic behavior.

The ensuing sections deal with relationships between chemical and acoustic properties, which will be useful in studies of this kind. As an illustration of the application of these relationships, a calculation is made of the anomalous sound absorption in an aqueous  $\text{MgSO}_4$  solution which is compared with observation.

### II. PARTIAL COMPRESSIBILITY AND SPECIFIC HEAT OF A CHEMICALLY ACTIVE SUBSTANCE

#### A. Static Considerations

In order to obtain the dynamic compressibility and specific heats it is convenient to consider first static values. These may be obtained with the aid of the well-known thermodynamic relationships,<sup>2</sup>

$$(\partial \Delta F / \partial P)_T = \Delta V, \quad (1a)$$

$$(\partial \Delta F / \partial T)_P = -\Delta S. \quad (1b)$$

The first expression relates the isothermal change in free energy,  $\Delta F$ , to the molar volume change,  $\Delta V$ ; the second relates the isobaric change in free energy to the molar entropy change,  $\Delta S$ . From these two expressions the van't Hoff equation and its isothermal analog

$$(\partial \ln K / \partial T)_P = \Delta H / RT^2, \quad (2a)$$

$$(\partial \ln K / \partial P)_T = -\Delta V / RT \quad (2b)$$

<sup>1</sup> Albert Einstein, Sitz. Berliner Akad., 380 (1920).

<sup>2</sup> For example, see: Gilbert N. Lewis and Merle Randall, *Thermodynamics* (McGraw-Hill Book Company, Inc., New York, 1923).

\* This work represents one of the results of research carried out under contract with the Bureau of Ships, Navy Department.

are obtained, where  $\Delta H$  is the molal heat content, and  $K$  the equilibrium constant of the chemical reaction.

Compressibility is defined as  $-\partial V/V\partial P$ . This definition may also be written as

$$\beta_0' \equiv -(1/V)(\partial V/\partial \ln K)_T(\partial \ln K/\partial P)_T, \quad (3)$$

where  $\beta_0'$  will be defined as the static isothermal *partial* compressibility. It follows then from Eq. (2b) that

$$\beta_0' = (\partial V/\partial \ln K)\Delta V/VRT. \quad (4)$$

The partial compressibility can be reduced to a less general form depending on the nature of the chemical reaction: Consider the ideal reversible reaction  $A \rightleftharpoons B$ ; for example, a substance possessing two states (such a model has been proposed for both the shear and bulk viscosities of liquids). The equilibrium constant,  $K$ , is then,  $N/(1-N)$ , where  $N$  is the molal fraction in the excited state. From Eq. (4) we have for this case

$$\beta_0' = (dV/dN)(1-N)N\Delta V/VRT.$$

But  $\Delta V$  is by definition,  $dV/dN$ . Hence,

$$\beta_0' = (V/RT)(\Delta V/V)^2 N(1-N). \quad (5a)$$

Or, since  $\Delta F = -RT \ln K$ , the compressibility may also be written as

$$\beta_0' = (V/2RT)(\Delta V/V)^2 / (1 + \cosh \Delta F/RT). \quad (5b)$$

Another simple reaction is  $AB \rightleftharpoons A + B$ ; for example, a partially dissociated gas or liquid. In this case, ideally

$$\beta_0' = (V/RT)(\Delta V/V)^2 N(1-N)/(2-N). \quad (6)$$

Hence, the molar change in volume,  $\Delta V$ , and the free energy (or the equilibrium constant) serve to determine the value of the partial compressibility at any fixed temperature. For a maximum compressibility there exists an optimum degree of dissociation; complete dissociation ( $1-N \rightarrow 0$ ) and negligible dissociation ( $N \rightarrow 0$ ) would both be expected to exhibit small compressibilities.

In an analogous fashion a partial molal specific heat may be calculated for a chemically active substance. The molal specific heat is defined as

$$C_0' \equiv \Delta H \partial N / \partial T.$$

It follows from Eq. (2a) that

$$C_0' = [(\Delta H)^2/RT^2] dN/d \ln K. \quad (7)$$

For the two-state reaction,  $A \rightleftharpoons B$ ,

$$C_0' = [(\Delta H)^2/RT^2] N(1-N) = (\Delta H)^2/2RT^2 (1 + \cosh \Delta F/RT). \quad (8a)$$

Similarly, for the dissociation reaction,  $AB \rightleftharpoons A + B$ ,

$$C_0' = [(\Delta H)^2/RT^2] N(1-N)/(2-N), \quad (8b)$$

which completes the analogy.

## B. Kinetics of Compressibility and Specific Heat

It is convenient to begin kinetic considerations by once again referring to a specific reaction, for example  $AB \rightleftharpoons A + B$ . According to the law of mass action the recombination rate will be  $kN^2$ , and the dissociation rate,  $kK(1-N)$ , where  $k$  is the familiar reaction rate constant. At equilibrium it is clear that,

$$dN/dt = kN^2 - kK(1-N) = 0.$$

If the equilibrium of a reaction is only slightly perturbed, for example, by the application of a pressure change, it may easily be shown that the rate of return toward equilibrium is, to a first-order approximation:

$$d(\Delta N)/dt = \kappa(\Delta N - \Delta N_0),$$

where  $\Delta N_0$  represents the magnitude of the small perturbation; the newly introduced quantity,  $\kappa$ , will be defined as the *equilibrium* reaction rate. Although the form of the above equation holds for all chemical reactions the relationship between the conventional reaction rate,  $k$ , and the equilibrium reaction rate,  $\kappa$ , depends on the specific reaction. For example,  $\kappa = k(K+1)$  for the reaction  $A \rightleftharpoons B$ ;  $\kappa = k(2N+K)$  for the reaction  $AB \rightleftharpoons A + B$ .

If the applied perturbation,  $\Delta N_0$ , is a constant, the above gives as a solution

$$\Delta N = \Delta N_0 [1 - \exp(-\kappa t)].$$

Hence  $1/\kappa$  may be regarded as the time constant, or relaxation time, of the reaction in the vicinity of equilibrium.

Any perturbation, produced in the chemical reaction by a sound wave, will vary periodically with time, for example, as  $\exp i\omega t$ . In this case the solution to the above equation gives for the amplitude of the perturbation

$$\Delta N = \Delta N_0 / (1 + i\omega/\kappa).$$

However,  $\Delta N$  is proportional to  $\Delta \ln K$ . Hence from Eq. (3) it follows for a periodic pressure variation, that

$$\beta' = \beta_0' / (1 + i\omega/\kappa), \quad (9a)$$

where  $\beta'$  is the *dynamic* isothermal partial compressibility. Similarly for a periodic temperature variation it follows from Eq. (6) that

$$C' = C_0' / (1 + i\omega/\kappa), \quad (9b)$$

where  $C'$  is the dynamic partial molal specific heat.

The complex character of the dynamic compressibility may be interpreted in terms of a phase lag between applied pressure and compression (or rarefaction). The real part of the dynamic compressibility is in phase with the pressure; the imaginary part lags the applied pressure by  $\pi/2$ . At low frequencies the magnitude of the real part predominates; at high frequencies the imaginary part is greater, diminishing toward zero with increasing frequency but less rapidly

than the real part. The above interpretation holds in a similar manner for the dynamic specific heat.

In the following section it will be shown how the complex character of the dynamic partial compressibility and dynamic partial specific heat results in the absorption of energy from an acoustic wave propagated through a medium.

### III. Sound Absorption and Chemical Reaction

That the existence of imaginary quantities in the expression for the specific heat or compressibility implies the dissipation of sound energy, can be simply shown as follows: A plane acoustic wave in an absorptive medium can be represented in the form

$$a = a_0 \exp[i\omega(t - x/c) - \alpha x],$$

where  $a$  is the amplitude of the sound wave at a distance  $x$ , and  $\alpha$  is the amplitude absorption coefficient. The expression may also be written in the form

$$a = a_0 \exp[i\omega(t - x/v)],$$

where  $1/v = 1/c + \alpha/i\omega$ . It is convenient to define the complex refractive index as  $c/v$ ; it follows then that the imaginary part of the square of the refractive index is  $-2i\alpha c/\omega$ . Hence, the imaginary part of the refractive index is associated with absorption of sound.

The complex refractive index for any medium may be calculated with the aid of the well-known relation.

$$v^2 = \gamma/\beta\rho, \quad (10)$$

where  $\gamma$  is the ratio of the specific heats and  $\rho$  is the

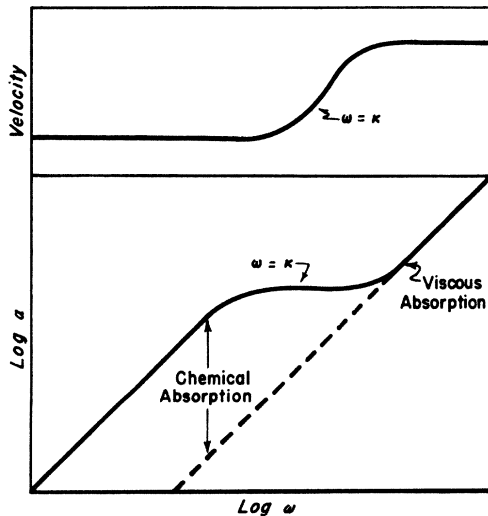


FIG. 1. These curves illustrate the dependence of sound absorption and velocity on frequency in a chemically active fluid. Except for the critical region ( $\omega \approx \kappa$ ) absorption is proportional to the square of the frequency and the velocity is independent of frequency. Increasing the equilibrium reaction rate,  $\kappa$ , decreases the magnitude of the chemical absorption (but not the velocity shift) as well as displaces the critical region to higher frequencies.

density. The compressibility,  $\beta$ , is the dynamic compressibility of the medium as a whole. However, published values for the compressibilities of materials are invariably static compressibilities. The static compressibility,  $\beta_0$ , is related to  $\beta$  by

$$\beta = \beta_0 - \beta_0' + \beta_0'/(1 + i\omega/\kappa). \quad (11)$$

Analogously,

$$C_P = C_0 - C_0' + C_0'/(1 + i\omega/\kappa), \quad (12a)$$

$$C_V = C_0 - \Delta - C_0' + C_0'/(1 + i\omega/\kappa), \quad (12b)$$

where  $\Delta$  is  $C_P - C_V$ . Hence, the square of the refractive index is given by

$$(c/v)^2 = \frac{C_0}{C_0 - \Delta} \cdot \frac{C_0 - \Delta - C_0' + C_0'/(1 + i\omega/\kappa)}{C_0 - C_0' + C_0'/(1 + i\omega/\kappa)} \cdot \frac{\beta_0 - \beta_0' - \beta_0'/(1 + i\omega/\kappa)}{\beta_0}. \quad (13)$$

Collecting imaginary terms it is found approximately that,

$$2\alpha = \left[ \frac{C_0' \Delta}{C_0^2} + \frac{\beta_0'}{\beta_0} \right] \frac{\omega^2 \kappa}{c(\omega^2 + \kappa^2)}. \quad (14)$$

The first term in this equation results from temperature-induced changes in the chemical reaction; the second term is associated with the effect of pressure on the reaction. At low frequencies, ( $\kappa \gg \omega$ ), absorption is proportional to the square of the frequency; in the critical region, ( $\kappa = \omega$ ), absorption increases much less rapidly with frequency; at extremely high frequencies absorption is independent of frequency provided other dissipative processes are absent. Actually the dissipation resulting from the viscosity of the medium cannot be neglected at high frequencies which again results in a square dependence on frequency in this region. These relationships between chemical absorption, viscous dissipation, and frequency are summarized in Fig. 1.

The real part of the refractive index is also frequency dependent; expressed in another way, dispersion of the velocity of sound may be exhibited by a chemically active fluid. The real part of the refractive index is approximately

$$(c/v)^2 = 1 + 2\alpha\kappa c/\omega^2. \quad (15)$$

Hence, the sound velocity in a chemical medium is constant at low frequencies, and increases in the critical region becoming constant again at higher frequencies as illustrated in Fig. 1. Clearly, data on velocity dispersion will yield the same kind of chemical information as can be derived from sound absorption data. However, the total change in velocity is usually an extremely small fraction and may not easily be observed. Particularly difficult would be the elimination of velocity variations resulting from uncontrolled temperature changes in the medium.

In the following section a calculation is made illustrating the utilization of absorption data to obtain the partial molar compressibility and chemical reaction rate of a chemical reaction.

#### IV. ILLUSTRATION OF SOUND ABSORPTION RESULTING FROM A CHEMICAL REACTION

It was found recently<sup>3</sup> that the absorption of sound in sea water behaves in an anomalous fashion. The quantity  $2\alpha/\omega^2$  was observed to be constant at frequencies up to 100 kc and to decrease by a factor of 50 becoming constant again at frequencies above 1000 kc. Significantly, this effect was not found in fresh water although the absorption of sea water and fresh water are practically identical at frequencies above 1000 kc. Obviously the anomalous absorption could be attributed to a process involving one of the dissolved substances in the ocean.

Sufficient measurements were made to establish the frequency dependence of the absorption in the ocean in the form

$$2\alpha/\omega^2 = A\kappa/(\kappa^2 + \omega^2) + B. \quad (16)$$

It will be noted that this frequency dependence is identical with that predicted by Eq. (14). From this identity,

$$A \equiv C_0'(C_P - C_V)/cC_0^2 + \beta_0'/\beta_0c$$

obtains. The coefficient  $A$  was found to be  $2.9 \times 10^{-10}$  sec./cm; the reaction rate,  $\kappa$ , of the process responsible for the absorption, was  $0.9 \times 10^6$ /sec.

Recently, Robert W. Leonard<sup>4</sup> was able to repeat these sea water measurements in the laboratory. By synthesizing artificial sea water he was able to show that  $\text{MgSO}_4$  was the dissolved substance in sea water which was chiefly responsible for the absorption anomaly. It was found that a pure  $\text{MgSO}_4$  solution having the same molal concentration (0.02 mole/liter) as is found in the ocean, gave somewhat higher absorption than the synthesized sea water which also included  $\text{NaCl}$ ,  $\text{MgCl}_2$ , and  $\text{CaSO}_4$ . It appears from Leonard's data that the quantity  $A$  for the  $\text{MgSO}_4$  solution is  $10^{-9}$  sec./cm and  $\kappa$  is  $1.5 \times 10^6$ /sec.

The chemical reaction in  $\text{MgSO}_4$  solution responsible for this sound absorption is one of several normally present; as a group these are termed ionization. The nature of the particular reaction is uncertain, for ionization processes in solution are complicated and not well understood. For the present purpose identification of the reaction is not required and in subsequent discussions it will be referred to simply as an ionization process.

The partial specific heat of the solution may be obtained directly from the temperature dependence of the

heat of dilution eliminating the need for evaluating Eq. (8b). Such observations have been made by Plake<sup>5</sup> for  $\text{MgSO}_4$  at two temperatures,  $20^\circ$  and  $10^\circ\text{C}$ . These data give only an approximate value for  $C_0'$  but the accuracy is adequate. Plake's heat of dilution data yields  $1.2 \times 10^{-3}$  cal./g/ $^\circ\text{C}$  for  $C_0'$ . Using  $(C_P - C_V)$  equal to  $6 \times 10^{-3}$ , and  $C_0 = 1$  and  $c = 1.5 \times 10^5$  the first term of  $A$  is found to be  $4.5 \times 10^{-11}$  sec./cm. It is clear that the partial molal specific heat of  $\text{MgSO}_4$  can only account for about 5 percent of the observed absorption. This conclusion is substantiated by a few observations on the temperature dependence of the absorption. The specific heat term in Eq. (14) is proportional to  $(C_P - C_V)$  which diminishes rapidly with decreasing temperature and vanishes in the neighborhood of a few degrees centigrade. However, these measurements of absorption show no such marked sensitivity to the temperature.

Inasmuch as the first term of Eq. (14) is not adequate to explain the absorption, the effect of the compressibility term will now be considered. Compressibilities of dilute solutions have been investigated with the aid of sound velocity measurements using Eq. (10). The results of these measurements can be expressed in terms of the quantity  $\phi$  which is defined as

$$\phi \equiv (\beta_S - \beta_0)/m,$$

where  $\beta_0$  and  $\beta_S$  refer to the compressibility of the solution and of the solvent and  $m$  is the molar concentration of the solute. Bachem<sup>6</sup> determined  $\phi$  for  $\text{MgSO}_4$  over a range of concentrations and found the approximate empirical relationship,

$$\phi = \phi_0 - 35 \times 10^{-7} m^{\frac{1}{2}}. \quad (17)$$

The empirical relationship above does not give explicitly the partial compressibility arising from the ionization process. This portion of the compressibility may be distinguished from the whole with the aid of Eq. (6). Reinterpreting Eq. (6) for ideal ionic dissociation in solution, it predicts that the partial molal compressibility arising from the ionization reaction should approach 0 with negligible concentration; furthermore, this compressibility may be expected to increase approximately as the square root of the concentration for dilute solutions. Hence it seems reasonable that the second term of Eq. (17) represents the partial molal compressibility associated with ionization; the first term  $\phi_0$  represents the partial molal compressibility of the completely ionized solute. It follows that for  $\text{MgSO}_4$ ,

$$\beta_0' = -35 \times 10^{-7} m^{\frac{1}{2}}.$$

It is to be noted that the sign of  $\beta_0'$  is negative although  $\phi$  is positive; the molal compressibility of a solution is decreased by the addition of a solute, but increasing the concentration lessens the effect.

<sup>3</sup> Leonard Liebermann, J. Acous. Soc. Am. **20**, 868 (1948).

<sup>4</sup> Leonard, Combs, and Skidmore, J. Acous. Soc. Am. **21**, 63 (1949). Dr. Leonard has kindly made available the data which was shown on a slide at the thirty-sixth meeting of the Acoustical Society of America in Cleveland, Ohio (November 4-6, 1948).

<sup>5</sup> Ewald Plake, Zeits. f. Physik Chemie **A162**, 257 (1932).

<sup>6</sup> Ch. Bachem, Zeits. f. Physik **101**, 541 (1936).

The partial dynamic compressibility calculated from the above with a concentration of 0.02 mole/liter yields for  $A$ ,  $1.3 \times 10^{-9}$ . Hence the magnitude of  $A$  calculated by means of the dynamic compressibility, is in good agreement with the value obtained from the observed sound absorption in  $\text{MgSO}_4$ . Clearly the partial compressibility of the  $\text{MgSO}_4$  ionization reaction is of the correct magnitude to explain this unique sound absorption.

#### V. ABSORPTION PROCESSES IN SOLUTIONS

The preceding discussion relating sound absorption and chemical reaction has been chiefly phenomenological, with little concern for the nature of the molecular processes which produce these acoustic effects. Possibly a few pertinent facts and relationships which are summarized below may well be significant as a basis for a molecular description of sound absorption in solutions.

One of the several possible ionic interactions present in ionization has been treated theoretically by Debye and Falkenhagen<sup>7</sup> in their theory of electrical conductivity in solutions. In this theory the normal interaction between the solute and solvent ions in solution is assumed to be perturbed by the application of an external electric field; this perturbation between ion and solvent, of course, proceeds with a specific reaction rate. Hence, application of an alternating electric field results in a dependence of conductivity on the field frequency in a manner exactly analogous to the preceding acoustic treatment. It has already been pointed out that  $\text{MgSO}_4$  absorption data lead to a reaction rate for one of the reactions associated with the ionization process, namely,  $\kappa = 1.5 \times 10^8/\text{sec}$ . The value of  $\kappa$  from the frequency dependence of electrical conductivity for  $\text{MgSO}_4$  is of the approximate order of magnitude which suggests a possible similarity meriting further study.

As pointed out previously, the partial compressibility and the partial specific heat have been found empirically for most salts to vary approximately as the  $\frac{3}{2}$  power of the concentration of the solute. The reaction rate,  $\kappa$ , may also depend on the concentration as can be inferred from the earlier discussion of reaction kinetics. For a dissociation reaction, which seems reasonable in

this case,  $\kappa$  is approximately proportional to the concentration.\*\* Hence, sound absorption in solution may be predicted to vary as the square root of the solute concentration. Interestingly, the Debye-Falkenhagen theory predicts the same dependence of conductivity on the concentration.

It may be expected that other salts possessing compressibility properties similar to  $\text{MgSO}_4$  would also exhibit similar acoustic properties. Salts which exhibit similar compressibilities are  $\text{CdSO}_4$ ,  $\text{CuSO}_4$ ,  $\text{MnSO}_4$ , and  $\text{ZnSO}_4$ ;  $\text{Na}_3\text{PO}_4$  exhibits a somewhat greater compressibility. Provided their reaction rates are nearly identical to  $\text{MgSO}_4$ , which is a likely possibility, these salts may be expected to be acoustically similar. Univalent salts such as  $\text{NaCl}$  uniformly exhibit a smaller partial compressibility and would be expected to be less active acoustically. In spite of this it is somewhat surprising that the 25-fold increase in concentration of  $\text{NaCl}$  over  $\text{MgSO}_4$  found in sea water does not compensate for the lower partial compressibility of the former and produce comparable sound absorption. Further, the quantity,  $A$ , for  $\text{NaCl}$  is 40 times greater than for  $\text{MgSO}_4$ . Clearly in order to explain the lack of absorption of the former the reaction rate must also be considerably greater; at least 200 times greater than that of  $\text{MgSO}_4$  to produce a negligibly small absorption. This conclusion regarding the greater reaction rate in  $\text{NaCl}$  is in agreement with chemical expectations: The increase in  $\kappa$  resulting from the greater concentration of the  $\text{NaCl}$  is 25; the increase arising from the difference in ionization constants is nearly 10, which leads to a reaction rate similar to that deduced above.

Finally it deserves mention that the unique compressibility properties exhibited by a  $\text{MgSO}_4$  solution bear a close resemblance to that property of pure liquids known as the dilatational (compressional) viscosity.<sup>8</sup> Actually, there exists at present no experiment by which these two properties, dilatational viscosity, and partial compressibility associated with a chemical reaction, could be distinguished. Quite likely the distinction is purely a formal one requiring some theoretical clarification but in no way excluding these chemical reactions from the class of mechanically dissipative processes known as viscous forces.

<sup>7</sup> Peter Debye and Hans Falkenhagen, *Physik. Zeits.* **29**, 121, 401 (1928). Also see<sup>6</sup> Hans Falkenhagen, *Electrolytes* (Clarendon Press, Oxford, 1934), pp. 181-192.

\*\* For the two state reaction,  $A \rightleftharpoons B$ , the equilibrium reaction rate,  $\kappa$  is independent of the concentration.

<sup>8</sup> Leonard Liebermann, *Phys. Rev.* **75**, 1415 (1949).