

estimated at  $3.20 \text{ \AA}$ ,  $e$  is  $6 \times 10^{-10}$  esu, the charge on the electron,  $E$  is the electric field in statvolts per centimeter  $= 300\epsilon$ . From this expression a value for the ionic velocity,  $v = 6.5 \times 10^{-5}$  cm/sec is calculated.

It has been assumed in the above arguments that the THF positive-ion radical was formed. However, it was not detected by EPR. The absence of a THF<sup>+</sup> spin signal may be explained by an argument presented by Eastman.<sup>16</sup> It should be noted that there is a large excess of THF neutral molecules over THF positive-ion radicals, and that holes are free to migrate from THF<sup>+</sup> to THF neutral species. A hole migration throughout the solution would be expected to lead to a broadening of the EPR signal so that it would become undetectable. Other similar cases of the observation of only a single radical have been reported.<sup>17</sup> The temperature dependence of the conductivity could give corroborating evidence for a hole migration process. Were the conductivity purely ionic, its change with change in temperature should be approximately as the change of the viscosity of the medium with changing temperature. If a hole migration process with a

<sup>16</sup> J. W. Eastman, G. M. Androes, and M. Calvin, *Nature* **193**, 1067 (1962).

<sup>17</sup> W. D. Phillips, J. C. Rowell, and S. I. Weissman, *J. Chem. Phys.* **33**, 626 (1960).

relatively high energy barrier is possible, a change in conductivity with a change in temperature greater than the change in viscosity is to be expected.

### SUMMARY

Evidence for the reversible photoinduced transfer of an electron from a THF donor molecule to a TCNE acceptor has been obtained from photo-EPR and photo-conductivity measurements. One of the radicals formed was identified from the hyperfine splitting of the EPR signal to be TCNE negative-ion radical. Calculations of the ionic velocities from EPR and conductivity data gave a reasonable agreement with values obtained from calculations based on Stokes' law. The THF positive-ion radical was not detected by EPR. A possible explanation for this is that the signal was broadened by exchange so that it became undetectable.

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## Collective-Coordinate Treatment of Electrolytes

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The configuration integral for an electrolyte in a continuous dielectric medium is calculated using the method of collective coordinates. The pair potential energy is taken to be Coulombic (with fixed dielectric constant) for all interionic distances outside some separation  $a$  and zero inside. This form permits handling the potential energy completely within the collective-coordinate framework, but has the disadvantage of limiting the concentration to which the treatment is applicable.

For low concentrations, the configurational partition function can be approximated to yield an analytic expression for the activity coefficient. For higher concentrations a numerical integration is used to calculate the mean molal activity coefficients for univalent salts in water at 25°C. The theoretical values obtained from the numerical integrations are within experimental error of the observed values up to molalities of 0.30 to 1.0, depending on the salt considered. As the concentration of the electrolyte goes to zero, the activity coefficient correctly tends to the Debye-Hückel limiting law.

### I. INTRODUCTION

ATTEMPTS to develop theories of the distribution of charges in fluids—electrolyte solutions or plasmas—have traditionally taken either of two points of departure. Historically, the first was a “statistical” model in which the charge distribution determines—and is determined by—the local electrostatic potential

through a statistical density introduced in the equation of continuity of the electric field. In the justly venerated Debye-Hückel<sup>1</sup> theory of electrolytes, the density of ions in the ionic atmosphere of a central ion was taken to be given by the Boltzmann factor, and led to the Poisson-Boltzmann equation—which, with deft intuitive insight, was immediately linearized. The replacement of the essentially classical Boltzmann density by the Fermi-Dirac quantum-statistical density, required for the treatment of electrons, led some three years

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<sup>1</sup> P. Debye and E. Hückel, *Physik. Z.* **24**, 185 (1923).

later to the equally celebrated Thomas<sup>2</sup>-Fermi<sup>3</sup> statistical theory of the atom. The enormous first steps achieved by these two elegantly simple theories have caused many followers to despair at the unlovely complication required to effect much improvement.

Yet the Debye-Hückel theory fails magnificently at all but the lowest ionic concentrations. A few early attempts sought improvement in the retention of the full nonlinearized form of the Poisson-Boltzmann equation, until it was realized that this form is actually not self-consistent. Other modifications attempted to replace the continuous, constant dielectric medium by a more sophisticated representation of the solvent, again usually with only meager success. However, an improved model having a simplicity worthy of the elegance of the original Debye-Hückel treatment was given by Stokes and Robinson.<sup>4</sup> This model partitions the solvent molecules into two classes: those that constitute the strongly bound solvation sphere of the ion, and thus contribute to increasing both the effective ion size and the ionic concentration (by depleting the "free" solvent); and those outside these solvation spheres, which thus constitute the (depleted) Debye-Hückel continuous dielectric solvent. Unfortunately, the intuitive appeal and promise of this model were not entirely fulfilled: although the solvation parameters introduced could be chosen so as to fit the experimental data over a remarkably wide concentration range, their uncertain lineage—questionable in view of other unreformed delinquencies—revealed itself in terms of an unacceptable nonphysical behavior.

The second traditional point of departure, and nowadays the approach closer to conventional statistical mechanics, is the setting up and calculation by one means or another of the configuration integral. The intrepid attacks by Kirkwood and Poirier<sup>5</sup> and Mayer,<sup>6</sup> evaluating this integral in configuration coordinates, have established the essential correctness of the Debye-Hückel limiting form within the assumptions of the model. However, what approximation in the configuration-integral treatment would lead to the linearized Poisson-Boltzmann differential equation remains an open question.

Still aiming at the evaluation of the configuration integral, Bohm and Pines<sup>7</sup> more recently have introduced "collective coordinates" operating essentially in the momentum space conjugate to the configuration space. These have proven particularly useful in applications to plasmas, wherein one charge species (say, the electrons) can be treated as though constituting a uniform charge background, as opposed to discrete

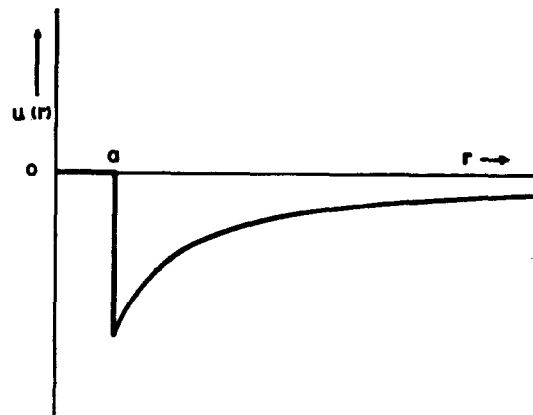


FIG. 1. Assumed Coulombic interionic pair potential energy for charges of unlike sign, with cutoff at Radius  $a$  [cf. Eq. (1)]. For charges of like sign, the assumed potential-energy curve is the mirror image in the  $r$  axis.

point charges. This treatment thus avoids the infinite attractive interactions between point charges of opposite signs. Unfortunately, in electrolyte solutions the charged species of both signs must be treated as discrete, and their finite sizes must be taken into account in order not to allow access to the very negative (Coulomb) energy regions inside the normal distance of closest approach. (The very positive energy regions at close distances between ions of the *same* sign are automatically excluded because of their low Boltzmann weighting, and no further exclusion is necessary at ordinary temperatures.)

The difficulty of handling a hard-sphere repulsive core has proved a major inhibition to the application of the Bohm-Pines treatment to electrolyte solutions. Edwards<sup>8</sup> sought to cope with this problem by treating the long-range part of the Coulombic interaction by collective coordinates and the short-range part by a kind of cluster-integral expansion. Unfortunately his treatment has not yet been carried to the point of numerical comparisons with experiment.

The present work also employs the Bohm-Pines approach, but differs from that of Edwards in the choice of potential function at close distances. The interionic potential used is shown in Fig. 1. In place of the more correct but unmanageable hard-sphere repulsive core, this potential merely goes to zero inside the distance  $a$  of closest approach. The superposition of the ions thus permitted causes an error (in the phase-space integral) which increases with increasing concentration, but at least avoids the negative infinity catastrophe of point ions. Moreover, this potential can be handled completely in the collective-coordinate framework.

## II. TOTAL POTENTIAL ENERGY

Using the interionic pair potential energy of Fig. 1, the total potential energy of the electrolyte for any set  $\{\mathbf{r}\} \equiv (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)$  of ion configuration co-

<sup>2</sup> L. H. Thomas, Proc. Cambridge Phil. Soc. **23**, 542 (1926).

<sup>3</sup> E. Fermi, Z. Physik. **48**, 73 (1928).

<sup>4</sup> R. H. Stokes and R. A. Robinson, J. Am. Chem. Soc. **70**, 1870 (1948).

<sup>5</sup> J. G. Kirkwood and J. C. Poirier, J. Phys. Chem. **58**, 591 (1954).

<sup>6</sup> J. E. Mayer, J. Chem. Phys. **18**, 1426 (1950).

<sup>7</sup> D. Bohm and D. Pines, Phys. Rev. **85**, 338 (1952).

<sup>8</sup> S. F. Edwards, Phil. Mag. **4**, 1171 (1959).

ordinates takes the form

$$U\{\mathbf{r}\} = \frac{1}{2} \sum_{i,j} \frac{z_i z_j e^2}{\epsilon r_{ij}} \left[ 1 - \int_a \delta(\mathbf{r}_{ij} - \boldsymbol{\lambda}) d^3 \boldsymbol{\lambda} \right], \quad (1)$$

where  $z_i e$  is the charge on Ion  $i$ ,  $\epsilon$  is the dielectric constant,  $\mathbf{r}_{ij}$  is the vector distance from Ion  $i$  to Ion  $j$ , and the integral of the Dirac  $\delta$  function extends over the volume within the distance  $a$  of closest approach. For electrolyte solutions of sufficiently low concentration, clearly only a negligible error is introduced by augmenting the already-large configuration volume corresponding to zero potential by the small volume that should actually have been excluded by the finite sizes of the ions; i.e., those configurations which in this model correspond to interionic distances smaller than  $a$  constitute a negligible fraction of the whole.

The first step in expressing the configurational potential energy (1) in terms of collective coordinates consists in the Fourier expansion of  $1/r_{ij}$  and  $\delta(\mathbf{r}_{ij} - \boldsymbol{\lambda})/r_{ij}$ . The potential energy then becomes

$$U\{\mathbf{r}\} = \frac{1}{2} \sum_{i,j} \frac{z_i z_j e^2}{\epsilon V} \left[ \int \frac{d^3 \mathbf{r}_i}{r_{ij}} + 4\pi \sum_{\mathbf{k}} (k^2)^{-1} \exp(i\mathbf{k}\mathbf{r}_{ij}) \right] - \frac{1}{2} \sum_{i,j} \frac{z_i z_j e^2}{\epsilon V} \left[ \int_a \frac{d^3 \boldsymbol{\lambda}}{\lambda} + \sum_{\mathbf{k}} \exp(i\mathbf{k}\mathbf{r}_{ij}) \int_a \frac{1}{\lambda} \exp(-i\mathbf{k}\boldsymbol{\lambda}) d^3 \boldsymbol{\lambda} \right], \quad (2)$$

where  $V$  is the electrolyte volume and the primes on the summations indicate the exclusion of  $i=j$  and  $k=0$ , respectively; the leading term in each bracket corresponds to the  $k=0$  component. Performing the second integration over  $\boldsymbol{\lambda}$  and collecting terms now yields

$$U\{\mathbf{r}\} = \left( \frac{2\pi}{\epsilon V} \right) \sum_{i,j} z_i z_j e^2 \sum_{\mathbf{k}} \frac{\cos k a}{k^2} \exp(i\mathbf{k}\mathbf{r}_{ij}) + \frac{1}{2} \sum_{i,j} \frac{z_i z_j e^2}{\epsilon V} \left( \int \frac{d^3 \mathbf{r}_i}{r_{ij}} - \int \frac{d^3 \boldsymbol{\lambda}}{\lambda} \right). \quad (3)$$

The term containing  $\int d^3 \boldsymbol{\lambda}/\lambda$  is independent of the ionic configuration and thus may be absorbed into the reference zero of the potential energy. The term containing  $\int d^3 \mathbf{r}_i/r_{ij}$  is small in comparison with the remaining terms of the potential energy and is moreover insensitive to gross changes in the configuration. For these reasons the entire second term on the right-hand side of Eq. (3) is dropped hereafter.

### III. TRANSFORMATION TO COLLECTIVE COORDINATES

Following Bohm and Pines,<sup>7</sup> we now replace the individual-particle configurational coordinates by an equal number of collective coordinates  $\rho_{\mathbf{k}}$ . These collective coordinates are the Fourier amplitudes of the charge density  $\rho(\mathbf{r})$ :

$$\rho(\mathbf{r}) = \sum_i z_i e \delta(\mathbf{r} - \mathbf{r}_i) \equiv \sum_{\mathbf{k}} \rho_{\mathbf{k}} \exp(i\mathbf{k}\mathbf{r}), \quad (4)$$

where the (complex) Fourier amplitude  $\rho_{\mathbf{k}}$  is given by the transform

$$\rho_{\mathbf{k}} = (e/V) \sum_i z_i \exp(-i\mathbf{k}\mathbf{r}_i). \quad (5)$$

Although the two Fourier components defined by  $\mathbf{k}$  and  $-\mathbf{k}$  are distinct, their amplitudes (i.e., the corresponding collective coordinates) are not independent since from the definition (5) evidently  $\rho_{-\mathbf{k}} = \rho_{\mathbf{k}}^*$ —in any event a necessary condition to preserve the reality of the charge density. Thus in what follows, all sums and products over  $\mathbf{k}$  will be understood to extend over only *half* of the  $\mathbf{k}$  space in order to avoid redundant counting.

The quantity  $|\rho_{\mathbf{k}}|^2$ , which we employ in the expression for the potential energy, is

$$|\rho_{\mathbf{k}}|^2 = (e/V)^2 \sum_{i,j} z_i z_j \exp(i\mathbf{k}\mathbf{r}_{ij}) + N(z e/V)^2, \quad (6)$$

where  $N$  is the total number of ions in the system and  $z^2$  is the mean-square charge number:

$$z^2 = (1/N) \sum_i z_i^2. \quad (7)$$

Thus in collective coordinates the potential energy takes the form:

$$U\{\rho_{\mathbf{k}}\} = (4\pi/\epsilon V) \sum_{\mathbf{k}} (V^2 |\rho_{\mathbf{k}}|^2 - N z^2 e^2) (\cos k a) / k^2, \quad (8)$$

in which the contribution of the  $-\mathbf{k}$  components, although excluded from the summation, have been incorporated through a factor 2, since  $|\rho_{-\mathbf{k}}|^2 = |\rho_{\mathbf{k}}|^2$ .

### IV. CONFIGURATIONAL PARTITION FUNCTION

In order to effect the transformation of the configurational partition function  $Q_r$  from configuration to collective-coordinate space, we must evaluate the Jacobian  $J[\rho_{\mathbf{k}}]$ :

$$Q_r = \int \exp[-\beta U\{\mathbf{r}_i\}] \prod_i d^3 \mathbf{r}_i = \int \exp[-\beta U\{\rho_{\mathbf{k}}\}] J \left[ \frac{\mathbf{r}}{\rho} \right] \prod_{\mathbf{k}} d^2 \rho_{\mathbf{k}}. \quad (9)$$

To this end we employ the relation<sup>9</sup> between the probability distributions in configuration space and collective-coordinate space for a *randomly* distributed system of ions. Taking the probability  $P(\mathbf{r}_i) d^3 \mathbf{r}_i$  that Ion  $i$  have position  $\mathbf{r}_i$  within  $d^3 \mathbf{r}_i$  to be independent of the distribution of the other ions, the probability of any particular configuration may be written:

$$\prod_i P(\mathbf{r}_i) d^3 \mathbf{r}_i = \prod_{\mathbf{k}} P(\rho_{\mathbf{k}}) d^2 \rho_{\mathbf{k}}, \quad (10)$$

where the differential elements correspond in the two spaces. The probability density for the distribution of

<sup>9</sup> This method for obtaining the Jacobian through the use of the central limit theorem was suggested by R. Latter (private communication).

a given ion in configuration space is taken to be uniform and equal simply to the reciprocal of the system volume  $V$ :

$$P(\mathbf{r}_i) = 1/V. \quad (11)$$

The collective coordinate  $\rho_{\mathbf{k}}$  is a sum of two-dimensional vectors in the complex plane with a random distribution of angles. According to the central limit theorem, the probability function  $P(\rho_{\mathbf{k}})$  for the sum of  $n$  independent random variables tends towards a Gaussian distribution as  $n \rightarrow \infty$ . We therefore obtain for the (normalized) probability distribution function in collective coordinate space

$$P(\rho_{\mathbf{k}}) = (V^2/\pi N z^2 e^2) \exp(-|\rho_{\mathbf{k}}|^2 V^2/N z^2 e^2), \quad (12)$$

where the mean-square deviation of  $\rho_{\mathbf{k}}$  is evidently  $N z^2 e^2/V^2$ . Combining Eqs. (10)–(12) we find the Jacobian of the transformation  $J[\rho_{\mathbf{k}}]$  to be

$$J[\rho_{\mathbf{k}}] = V^N \prod_{\mathbf{k}} (V^2/\pi N z^2 e^2) \exp(-|\rho_{\mathbf{k}}|^2 V^2/N z^2 e^2). \quad (13)$$

We are now in a position to complete the transformation of the configurational partition function  $Q_r$  to collective coordinates. Combining Eqs. (8), (9), and (13), we obtain

$$Q_r = V^N \prod_{\mathbf{k}} \frac{V^2}{\pi N z^2 e^2} \exp\left[\frac{4\pi\beta N z^2 e^2 (\cos ka)}{\epsilon V k^2}\right] \times \int \exp\left\{\frac{-V^2}{N z^2 e^2} |\rho_{\mathbf{k}}|^2 \left[\frac{4\pi\beta N z^2 e^2 (\cos ka)}{\epsilon V k^2} + 1\right]\right\} \pi d|\rho_{\mathbf{k}}|^2. \quad (14)$$

Performing the indicated integration,

$$Q_r = V^N \prod_{\mathbf{k}} \left[ (\cos ka)/k^2 l^2 + 1 \right]^{-1} \exp[(\cos ka)/k^2 l^2], \quad (15)$$

where, as always, the product extends over only half of the  $\mathbf{k}$  space. The quantity  $l$  is the familiar Debye length,<sup>10</sup> defined by

$$l^2 \equiv \epsilon V / 4\pi\beta N z^2 e^2. \quad (16)$$

Taking the logarithm of Eq. (15) and converting sums to integrals yields

$$\ln\left(\frac{Q_r}{V^N}\right) = \int \frac{g(k) (\cos ka)}{k^2 l^2} dk - \int g(k) \ln\left[\frac{(\cos ka)}{k^2 l^2} + 1\right] dk, \quad (17)$$

where  $g(k)$ , the degeneracy of  $\rho_{\mathbf{k}}$ , is given by just half the full degeneracy of states in  $\mathbf{k}$  space:

$$g(k) = V k^2 / (2\pi)^2. \quad (18)$$

Since the number of degrees of freedom is  $3N$ , we must cut off the  $k$  spectrum at some maximum value

<sup>10</sup> If we express the thermal energy  $1/\beta$  in terms of the characteristic interionic potential energy  $z^2 e^2/b\epsilon$ , i.e.,  $\beta' = \beta z^2 e^2/\epsilon b$ , where  $b$  is the radius of the (spherical) volume per ion,  $4\pi b^3/3 \equiv V/N$ , the expression for the Debye length assumes the simple and perspicuous form,

$$(b/l)^2 = 3\beta'. \quad (16')$$

$\bar{k}$  such that

$$3N = \int_0^{\bar{k}} g(k) dk = \frac{V \bar{k}^3}{12\pi^2}. \quad (19)$$

Now defining the new dimensionless variable  $\eta \equiv kl$  and carrying through the integrations of Eq. (17) on the interval  $0 \rightarrow \bar{\eta} \equiv \bar{k}l$ , we obtain finally for the configurational partition function the expression,

$$\ln\left(\frac{Q_r}{V^N}\right) = \left(\frac{V}{4\pi^2 l^2 a}\right) \sin\left(\frac{\bar{\eta} a}{l}\right) - \left(\frac{V}{4\pi^2 l^2}\right) \int_0^{\bar{\eta}} \eta^2 \ln\left[\left(\frac{1}{\eta^2}\right) \cos\left(\frac{\eta a}{l}\right) + 1\right] d\eta. \quad (20)$$

## V. MEAN ION ACTIVITY COEFFICIENT

Since both the ion-solvent interaction and the momentum-space integral part of the canonical partition function  $Q$  are taken to be, respectively, identical in the real and ideal (i.e., uncharged, indicated by asterisk) solutions at equal concentration  $c$ , we may write for the excess Helmholtz free energy,

$$\beta(A - A^*) = -\ln(Q/Q^*) = \ln(Q_r/Q_r^*) = -\ln(Q_r/V^N), \quad (21)$$

in which the ideal configurational partition function,  $Q_r^* = V^N$ , has been substituted. Denoting the chemical potential of a "molecule" of the salt by  $\mu$ , the total number of salt "molecules" by  $M$ , and their activity by  $\alpha$ , we find

$$\beta(\mu - \mu^*) = \left\{ \partial[\beta(A - A^*)] / \partial M \right\}_{\beta, V} = \ln(\alpha/c) = \nu \ln \gamma_{\pm}, \quad (22)$$

where  $\gamma_{\pm}$  is the mean ion activity coefficient and  $\nu$  is the number of ions into which the salt "molecule" dissociates. Since the total number of ions is  $N = \nu M$ , we obtain from Eqs. (21) and (22),

$$\ln \gamma_{\pm} = - \left[ \frac{\partial \ln(Q_r/V^N)}{\partial N} \right]_{\beta, V} = \left(\frac{9}{\bar{\eta}^3}\right) \int_0^{\bar{\eta}} \frac{\cos(\eta a/l) d\eta}{(1/\eta^2) \cos(\eta a/l) + 1} + 3 \ln \left[ \left(\frac{1}{\bar{\eta}^2}\right) \cos\left(\frac{\bar{\eta} a}{l}\right) + 1 \right] - \left(\frac{9l}{\bar{\eta}^3 a}\right) \sin\left(\frac{\bar{\eta} a}{l}\right) - \left(\frac{3}{\bar{\eta}^2}\right) \cos\left(\frac{\bar{\eta} a}{l}\right). \quad (23)$$

It is easy to show that as the concentration goes to zero (i.e.,  $\bar{\eta} \rightarrow \infty$ ,  $\bar{\eta}/l \rightarrow 0$ ), Eq. (23) correctly approaches the Debye-Hückel limiting law.

## VI. COMPARISON WITH EXPERIMENT

Mean molal activity coefficients were calculated by a numerical integration of Eq. (23) for a number of

TABLE I. Comparison of theoretical mean molal activity coefficients at 25°C in water [Eq. (23)] with experiment<sup>a,b</sup> (*a* values given at head of "Theoret." columns are in angstrom units).

Molality	NaCl		KCl		RbCl		CsCl		NaBr		KBr	
	Theoret.	Exptl.	Theoret.	Exptl.	Theoret.	Exptl.	Theoret.	Exptl.	Theoret.	Exptl.	Theoret.	Exptl.
	3.90		3.25		3.00		2.50		4.20		3.50	
0.001	0.967	0.966	0.966	0.965	0.966		0.966		0.967	0.966	0.966	0.965
0.002	0.954	0.953	0.953	0.952	0.953		0.953		0.954	0.955	0.953	0.952
0.005	0.930	0.929	0.929	0.927	0.929	0.93	0.928	0.92	0.930	0.934	0.929	0.927
0.01	0.905	0.904	0.903	0.901	0.903	0.90	0.902	0.90	0.905	0.914	0.904	0.903
0.02	0.873	0.875	0.871		0.870		0.868	0.86	0.875	0.887	0.871	0.872
0.05	0.823	0.823	0.816	0.815	0.813		0.808	0.79	0.825	0.844	0.818	0.822
0.1	0.779	0.778	0.767	0.769	0.762	0.764	0.753	0.755	0.784	0.781	0.771	0.771
0.2	0.734	0.734	0.716	0.717	0.708	0.709	0.692	0.693	0.739	0.739	0.722	0.721
0.3	0.704	0.710	0.685	0.687	0.675	0.675	0.655	0.653	0.708	0.717	0.691	0.692
0.5	0.654	0.682	0.642	0.650	0.633	0.634	0.609	0.604	0.651	0.695	0.646	0.657
0.7	0.607	0.668	0.607	0.626	0.600	0.607	0.579	0.573	0.597	0.687	0.606	0.637
1.0	0.538	0.658	0.557	0.605	0.557	0.583	0.545	0.543	0.523	0.687	0.548	0.617
1.5	0.437	0.659	0.478	0.585	0.487	0.559	0.498	0.514	0.420	0.704	0.458	0.601
2.0							0.454	0.495				
2.5							0.411	0.485				
3.0							0.368	0.480				

Molality	RbBr		CsBr		NaNO <sub>3</sub>		KNO <sub>3</sub>		RbNO <sub>3</sub>		CsNO <sub>3</sub>	
	Theoret.	Exptl.	Theoret.	Exptl.	Theoret.	Exptl.	Theoret.	Exptl.	Theoret.	Exptl.	Theoret.	Exptl.
	3.00		2.50		2.75		1.20		1.10		1.00	
0.001	0.966		0.966		0.966	0.966	0.966		0.966		0.966	
0.002	0.953		0.953		0.953	0.953	0.953		0.953		0.953	
0.005	0.929		0.928	0.93	0.929	0.93	0.928		0.928		0.928	
0.01	0.903		0.903	0.90	0.903	0.90	0.901		0.901		0.901	
0.02	0.869		0.868	0.86	0.869	0.87	0.865		0.864		0.864	
0.05	0.813		0.808	0.79	0.811	0.82	0.799		0.799		0.798	
0.1	0.762	0.763	0.752	0.754	0.758	0.758	0.735	0.733	0.734	0.730	0.732	0.729
0.2	0.707	0.706	0.691	0.692	0.700	0.702	0.657	0.659	0.654	0.656	0.652	0.651
0.3	0.674	0.674	0.653	0.652	0.666	0.664	0.606	0.607	0.602	0.603	0.599	0.598
0.5	0.631	0.634	0.606	0.603	0.623	0.615	0.537	0.542	0.532	0.534	0.527	0.526
0.7	0.598	0.606	0.575	0.570	0.593	0.583	0.491	0.494	0.484	0.484	0.477	0.475
1.0	0.554	0.579	0.538	0.537	0.555	0.548	0.443	0.441	0.434	0.429	0.425	0.419
1.5	0.484	0.552	0.488	0.504	0.497	0.509	0.390	0.378	0.378	0.365	0.366	0.354
2.0			0.442	0.486	0.440	0.481	0.354	0.327	0.341	0.319	0.326	
2.5			0.403	0.474	0.386	0.457	0.328	0.293	0.313	0.284	0.296	
3.0			0.357	0.468			0.307	0.266	0.291	0.256	0.273	

<sup>a</sup> Reference 11.<sup>b</sup> Reference 12.

values of the "distance-of-closest-approach" parameter *a* and a range of concentrations. From these calculations the value of *a* was selected for each salt so as to reproduce the experimental activity coefficient over the widest possible concentration range. The chosen *a* values and the resulting theoretical activity coefficients are given in Table I, along with the accepted experimental activity coefficients.<sup>11,12</sup>

The calculated values are seen to be within the experimental errors of the measured values up to concentrations of 0.3 to 1.0*M*, depending on the salt considered. It is noteworthy that the activity coefficients

<sup>11</sup> H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolyte Solutions* (Reinhold Publishing Corporation, New York, 1950), 2nd ed., p. 562. The empirical relation on p. 252 was used to convert the concentration in Eq. (23) from molarity to molality for use in the subsequent experimental comparisons.

<sup>12</sup> W. M. Latimer, *Oxidation Potentials*, (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1952), 2nd ed., p. 354.

for NaCl obtained by Poirier<sup>13</sup> using Mayer's<sup>6</sup> theory are in excellent agreement with those from the present calculations. The agreement of both with experiment for NaCl is found to be very good up to 0.4*M*. In addition, the distance of closest approach which gives the best experimental fit for NaCl is in both cases equal to 3.9 Å. The fact that this value exceeds the sum of the crystal ionic radii is generally attributed to hydration. However, it would be dangerous to place great credence in the physical interpretation of the *a* parameter: although for the alkali nitrates the agreement with experiment extends into a higher concentration range than for NaCl, the value of *a* is for these salts less than the sum of the crystal ionic radii. Clearly, as in previous treatments, the parameter *a* does not represent simply the distance of closest approach. In

<sup>13</sup> J. C. Poirier, *J. Chem. Phys.* **21**, 972 (1953).

fact it would be surprising if its value, chosen to give the best experimental fit, did not compensate for other imperfections of the theory.

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## Ionization of Atoms by Collision with Excited Atoms

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Ionization of atoms by collisional transfer of electronic excitation energy,  $A^*+B\rightarrow A+B^++e$ , is considered theoretically. A formula for the cross section is derived for the case where the transition  $A\rightarrow A^*$  is optically allowed and the excitation energy of  $A^*$  is larger than the ionization potential of B, and is applied to several examples where  $A^*$  is He ( $2^1P$ ).

### 1. INTRODUCTION

MANY theoretical studies have been carried out on electronic excitation energy transfer between gaseous atoms. Most of them deal with excitation transfer between discrete levels of two atoms,<sup>1-6</sup> i.e.,  $A^*+B\rightarrow A+B^*$ , where A, B and  $A^*$ ,  $B^*$  represent atoms in the ground states and excited states, respectively. Only a few studies have been done for the case where B is excited to a continuum state, namely, where B is ionized.<sup>7</sup> It is the latter process that we discuss in the present paper.

The process  $A^*+B\rightarrow A+B^*$  at thermal velocity has a cross section extremely large compared with the gas-kinetic cross section, if the excitation energies of  $A^*$  and  $B^*$  are close enough (the resonance condition), and if transitions  $A\rightarrow A^*$  and  $B\rightarrow B^*$  are optically allowed. This result leads us to expect a large cross section for the ionization of an atom by collisional excitation transfer,  $A^*+B\rightarrow A+B^++e$ , when the transition  $A\rightarrow A^*$  is optically allowed and when the excitation energy of

$A^*$  is larger than the ionization potential of B, so that final states satisfying the resonance condition are available.<sup>8</sup> In Sec. 2, a general formulation of the theory for this type of excitation transfer in a slow collision is given. Numerical values of the cross sections for thermal collisions of He ( $2^1P$ ) with several kinds of atoms and molecules are calculated in Sec. 3.

### 2. FORMULATION OF THE THEORY

Neglecting the effect of the interatomic force on the relative motion, let Atom B in the ground state be located at the origin of a fixed coordinate system and let Atom A in an excited state travel with constant speed  $v$  parallel to and at a distance  $R_0$  (impact parameter) from the  $x$  axis. The initial electronic state of the entire system is designated by the product of the eigenfunctions of the two atoms,  $\phi_{A^*}(\mathbf{r}_a)\phi_B(\mathbf{r}_b)$ . The electronic wavefunction of the final state, in which Atom A is found in the ground state and Atom B is excited to a continuum state, is given by  $\phi_A(\mathbf{r}_a)\phi_{B^++e}(\mathbf{r}_b)$ . In general these initial and final states are degenerate. We specify a set of quantum numbers  $m$  and designate the wavefunctions of the initial and final states as  $\varphi_m$  and  $\psi_{B,m}$ . In the present case, where the ground states of Atoms A and B are assumed to have zero angular

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<sup>1</sup> H. Kallmann and F. London, *Z. Physik. Chem.* **2**, 207 (1929).

<sup>2</sup> O. K. Rice, *Phys. Rev.* **38**, 1943 (1931).

<sup>3</sup> A. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, London, 1934).

<sup>4</sup> R. A. Buckingham and A. Dalgarno, *Proc. Roy. Soc. (London)* **A213**, 506 (1952).

<sup>5</sup> D. R. Bates, *Discussions Faraday Soc.* **33**, 7 (1962).

<sup>6</sup> M. Mori, T. Watanabe, and K. Katsuura, *J. Phys. Soc. Japan* **19**, 380 (1964).

<sup>7</sup> E. E. Ferguson, *Phys. Rev.* **128**, 210 (1962).

<sup>8</sup> (a) Even when the transition  $A\rightarrow A^*$  is optically forbidden, namely,  $A^*$  is metastable, the cross section for the ionization is still usually large (comparable to the geometrical cross section), if the excitation energy of  $A^*$  is larger than the ionization potential of B. This process is important in the Penning effect because of the long lifetime of the metastable atom, and a lot of experimental studies have been done on this process; (b) M. A. Biondi, *Phys. Rev.* **88**, 660 (1952); (c) W. P. Jesse and J. Sadauskis, *Phys. Rev.* **100**, 1755 (1955).