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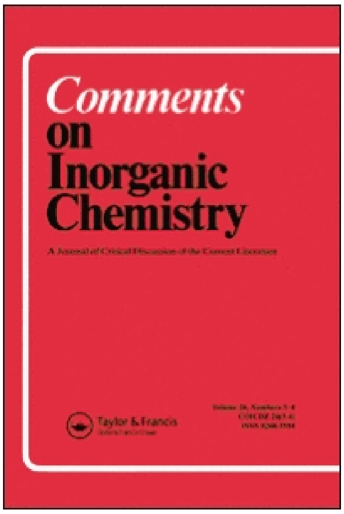

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Reactant Approach: The Spherical Shell Model for Molecular Juxtaposition

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Reactant Approach: The Spherical Shell Model for Molecular Juxtaposition

The use of a juxtaposition preequilibrium model is examined for a wide range of mechanisms. Particular attention is given to the effects of ionic strength both on equilibria and on electron transfer rates. A brief extension to gas phase reactions is noted.

INTRODUCTION

The occurrence of chemical reaction almost invariably implies reactant contact or juxtaposition. Thus, even unimolecular gas reactions exhibit low pressure bimolecularity. It is the purpose of this Comment to examine formulations and applications of a model for such juxtaposition, particularly from the viewpoint of the mechanisms of inorganic reactions in solution,[1] but with relevance to wider fields such as gas phase kinetics[2-4] and the problem of electrolyte interactions.[5] As may be anticipated, the analyses pivot on the choice of the critical range of distances of separation between reactants[6] (and additionally of orientations in many cases, though this important aspect is scarcely addressed here). A convenient classification of reactions based on separation criteria might be (i) gas phase electron transfers[7] (in favorable cases approaching ~10 Å, Table I); (ii) solution phase ion association processes[8-11] (2–10 Å, say—see next section); and finally, (iii) "covalent" reactions in which particular

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TABLE I

Experimental cross sections πb^2 for alkali–halogen reactions (Å^2)

	Cl_2	Br_2	I_2
Na	124	116	97
K	124	151	127
Rb	190	197	167
Cs	196	204	195

These follow approximately the simplified condition, reaction distance $b \approx e^2/(I_M - E_X)$, where I_M is the ionization potential of M and E_X is the electron affinity of the halogen molecule.

bonds need to be made and/or broken, such specificity appearing as a "contact" separation of say 1–4 Å, with little spread (only some few tenths of Å) about the critical separation. In this context, solution phase electron transfers might be expected to straddle all three classes, while corresponding substitutions will fall into the second, and perhaps more often, third categories.

THE JUXTAPOSITION EQUILIBRIUM OR PREEQUILIBRIUM

For noninteracting species A and B the probability of finding a B molecule at exactly some (appreciable) distance r from A is vanishingly small, as the occupancy by B of a zero-sized point at the distance r is being sought; such points form the surface of a sphere about A, the trace of the points still having zero volume. Hence, we consider occupancy of a small range of distances dr centered on the point(s) at r, Figure 1, which gives volume $4\pi r^2 dr$ to a spherical shell so formed about A. For the juxtaposition equillibrium $A + B \rightleftharpoons AB$, the equilibrium constant K_{jux} is obtained from consideration of the volume available to free B relative to that available to juxtaposed (paired) B, which is just the sum of all the spherical shells for the range of separations r within which B is deemed paired. This will extend from the least value r_{min} (which could be a hard-sphere contact distance a*) to an independently established or arbitrarily set out-

---

*The a employed here is the closest contact distance (implying hard spheres) for any two species, and should not be confused with the radii a in Born solvation models, or ionic radii in Marcus polarization theory. We use L for the Avogadro constant and note that factors of 1000, sometimes included to indicate a change from cm^3 to dm^3, are unnecessary: Purely physical equations do not imply particular units.

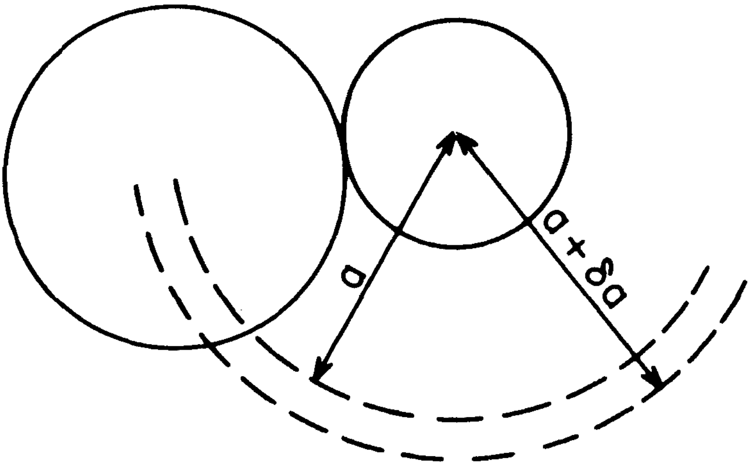

FIGURE 1 The origin of a and δa in the spherical shell model.

ermost value $r_{\max}$ (or d, in Prue's symbolism[8]) which encompasses all defined pairs; the range of r for such defined pairs is then $(d - r_{min}) = \delta a$. Then $K_{\text{jux}} = L \int_a^d 4\pi r^2 dr$ which for small δa becomes $4\pi La^2\delta a$. For a typically 4 Å and $\delta a = 0.1$ Å, K_{jux} even for noninteractive species is $\sim 0.01\ \text{M}^{-1}$, and if $\delta a = 1$ Å, K_{jux} is $0.1\ \text{M}^{-1}$, so observed values of such magnitude need careful interpretation.

For A and B which interact, with an interaction energy $w(r)$ at r the occupancy of each dr at r will be weighted by the Boltzmann exponential $\exp(-w(r)/k_B T)$, representing either enhancement or diminution when $w(r)$ is, respectively, attractive or repulsive. K_{jux}, including the weighting factor, now becomes

$$K_{\text{jux}} = L\int_a^d 4\pi r^2 \exp(-w(r)/k_B T) dr. \tag{1}$$

In case the exponential factor encompasses more than one B, it is more precise to write (now omitting the subscript) K as $L\int_a^d 4\pi r^2 \times g(r)dr$ where $g(r)$ is the pair distribution function by its definition excluding such adventitious triplets or higher aggregates, but we shall assume concentrations in general to be low enough to allow use of the exponential. Elegant examples of the treatment of appropriate models for $g(r)$ are given by Tembe *et al.*[9] The relation between hard-

TABLE II

Typical K values, $M^{2+}SO_4^{2-}$ in aqueous solution at 0 °C, with ionic strength corrections dependent on choice of distance $d = a_\gamma$

Chosen d/Å	Fitted K/dm^3 mol^{-1}		
(used in DH eq.)	$MgSO_4$	$CuSO_4$	$CoSO_4$
13.87	244	303	227
6.94	190	244	182
5.0	143	200	137
4.0	95	152	100
$-\Delta F_{\mathrm{hyd}}$/kcal mol^{-1}	455.5	498.7	479.5

For other solutes and solvents see Ref. 5. Free Energy of Hydration of M^{2+} appended [Chem. Rev. **65**, 467 (1965)].

sphere contact and continuous interaction potentials is such that the former best corresponds to the separation giving zero interaction potential.[6] The expressions for K with the Boltzman factor do not in general have simple algebraic forms except for some special cases:

(i) Bjerrum[10] used the coulombic cation–anion energy $z_A z_B e^2/Dr$ for $w(r)$ in a historic treatment of ion association, rather arbitrarily taking the minimum point in $r^2 g(r)$ given by $|z_A z_B e^2/2Dk_B T|$ as the upper limit d in Eq.(1). He presented K values for the resulting expression in terms of tabulated numerical integrals. For bibivalent electrolytes in water the minimum is at about 14 Å, which poses fierce problems about pair definition, especially for concentrated solutions when three (or more) ions might be included within this distance, and smaller d values, down to ~ 4 Å, fit thermodynamic data equally well (Table II).[11] Another way around the problem, which results in a decrease of d with concentration, is referred to below.

(ii) If $(d - a) = \delta a$ is taken to be small, then the average of $w(r)$ may be taken as a constant value $w(a)$ giving the simple expression[12]

$$K = 4\pi L a^2 \delta a \exp(-w(a)/k_B T). \qquad (2)$$

If $w(r)$ is coulombic, its r^{-1} dependence comprises the most slowly varying in the hierarchy of r dependences, and the approximation of constancy for $w(a)$ is most acceptable, especially if there are separate criteria for assigning δa, as arise in the case of electron transfer reactions referred to below.

(iii) Since Fuoss first proposed it for ion association,[13] a form

$$K^{\mathrm{F}} = \frac{4}{3}\pi La^3 \exp(-w(a)/k_{\mathrm{B}}T) \qquad (3)$$

with $w(a) = z_A z_B e^2/aD$, has had remarkably wide currency doubtless owing to its beguilingly simple dependence on but a single parameter a. A similar form, in a ratio of forward and reverse diffusive rate constants, appears in Eigen's treatment.[14] Thus, besides coulombic association Eq.(3) has been used for substitution processes,[15] electron transfer processes[16,17] and in a model for chelation[18] (where, however, the effects of its use cancel; another form involving $4\pi Ll^3/3$, where l is the length of a chelating ligand, is free of the objections below).

Eigen[19] has quoted ion-association rate constant expressions for diffusion-controlled forward and reverse rates, k_f and k_r, which in the original paper employ only a volume Δv within which a second ion is deemed juxtaposed (i.e., undergoing reaction); in a later publication[14] only by implication does the detailed expression for k_r give the ratio $k_f/k_r = K^{\mathrm{F}}$. The volume $4\pi a^3/3$ in k_f/k_r should be replaced by $4\pi a^2\delta a$ if occupancy of a spherical shell is the criterion for reaction, and indeed such a diffusion formulation[6] is well known for nonionic reactants. The volume Δv is open to no end of examination, but in the present context it represents solely the juxtaposition shell; Eigen originally gave it as a volume for $r \to a$, not $r = a$, and the same arguments apply to the detailed diffusive processes as to equilibrium juxtaposition. Detailed derivation of diffusive rate constants is given by North.[6]

Despite insistence[20] that K^{F} represents hard spheres in contact, the equilibrium derivation[13] involves free penetration by point sized B of a sphere of radius a about A. While perhaps applicable to association of M^+ and solvated electron e_s^- in some conceivable special cases (where e^- is delocalized over M^+ with a solution-phase "ionization potential" fortuitously given by e^2/aD, a representing the outermost distance for existence of free e_s^-) such an application was clearly never intended.[21] Nor presumably was the formulation which we write $L\exp(-w(a)/k_{\mathrm{B}}T)\int_0^a 4\pi r^2 dr$, rightly deemed peculiar.[22] However, K^{F} can be rescued by noting that δa is only a minor fraction of a (e.g., $a \approx 3$ Å, $\delta a \approx 1$ Å is a frequent envisagement in ion association), then assuming that $\delta a = a/3$ precisely. Furthermore, $\delta a \approx 1$ Å has been suggested[12] as being representative of the extra void space, introduced by inserting spherical solute molecules into solvent molecules, through which a constant $w(a)$ might operate. However, Justice[23] notes that observed values of log K plotted against $1/D$ for a variety of solvents commonly have a curvature largely accounted for by Bjerrum-like formulations involving integration, but in clear contradiction of the linearity required by log K^F. Provided that the arbitrariness of and severe approximation in K^F are recognized, use can nevertheless be found for this form in semiquantitative applications. But if precise inferences of dependences of experimental quantities on a are to be made[17] a more stringent basis is clearly required. The Eigen formulation implies an "excluded volume" in the occupancy of Δv by the pair species.

When experimental K values are fed into Eq.(1), the inferred a values will be expected to equal or exceed the sum of crystal radii; if such a are considerably smaller, extra (covalent) interaction in addition to the coulombic, or especially feeble solvation, is to be inferred. Prue, in an obscure note,[24] examined the application of Eq.(1) to gas phase Li^+X^- pairs (Table III). The "experimental" K values are from statistical mechanics, employing good approximate partition functions together with experimental dissociation energies, and the "precise" a values are Rittner's estimates[25]; the choice of a rather large d was determined by consideration of these equilibria in *solutions.* Even so, the reasonable accord between the two sets of a values shows Eq.(1) to be a useful approximation to more exact quantum-statistical formulations. In the simplified form (2), classical translation in a "square well" of depth $w(a)$ and width δa, formed at the spherical shell at a, replaces vibration (and accompanying rotation) in the more exact continuous potential having a soft repulsive branch and a coulombic attractive branch, to give a minimum somewhere near (not at) a. Only for isolated (gas phase) systems are such unambiguous, direct comparisons possible.

TABLE III

Experimental K values for $Li^+ + X^- \rightleftarrows LiX$ *in vacuo*, and inferred a values

Ion Pair	LiCl	LiBr	LiI
log $K/\mathrm{dm^3\ mol^{-1}}$	107.35	103.10	98.87
Assigned d/Å	5.00	5.00	5.00
a/Å calculated from K via (1)	2.30	2.40	2.50
precise a/Å values	1.97	2.13	2.37

EFFECT OF IONIC STRENGTH

So far we have only considered interactions between the paired species. In ion association because of *free*-ion interactions it is necessary to define $K = ([AB]/[A][B])\,(\gamma_{AB}/\gamma_A\gamma_B)$ where γ_A and γ_B are commonly given by the Debye–Hückel (DH) expression

$$ln\gamma_A = -z_A^2 \mathcal{A}\sqrt{I}/(1 + a_\gamma\beta\sqrt{I}) \tag{4}$$

for ionic strength I. In this expression a_γ represents the closest approach for free ions of opposite charge, and in single symmetrical electrolytes, defines an A–B distance; in Eq.(1) d therefore must be set equal to a_γ. This value of $d = a_\gamma$, and of a_γ defined only by Eq.(4), is almost invariably taken to be concentration independent, but this restriction, as will be seen, is not obligatory. $\gamma_{AB} = 1$ is assumed for uncharged AB pairs but must be assigned a value requiring a choice of $a_{\gamma(AB)}$ in Eq.(4) if AB is charged as in the case of unsymmetric electrolytes. Already a problem arises in the latter case since the system now has the nature of a mixed electrolyte, and here thermodynamic inconsistencies[26] arise if $a_{\gamma(AB)}$ is assumed to differ from $a_{\gamma(A)} = a_{\gamma(B)}$. (The problem becomes even more acute when the juxtaposition of similarly charged reactants occurs, as in kinetics.) Developments from the classical Debye–Hückel and Bjerrum views of electrolytes have been reviewed[27,28]; although the prospects for concise algebraic representations of γ in concentrated electrolytes, depending on readily comprehensible parameters such as a_γ, may seem elusive, fortunately the physical picture implied by non-DH formulations is often clearly expressed.[9]

At modest ($I \leq 0.1$ M) concentrations DH formulations are useful, and it has been pointed out that for single-electrolyte solutions $K(I)$ values (i.e., the values of $[AB]/[A][B]$ at ionic strength I, without γ's) should also be expressible by an equation of form (1).[29] Since $K(I) < K(I = 0)$ for anion–cation pairs this can be effected by one of two methods.

(i) With a_γ constant, DH screening can be introduced into $w(r)$, which implies that pairs interact with the "ionic atmosphere" (the field effects of the free ions). In some views[20] this vitiates the pair definition and complicates the pair contribution to the ionic atmosphere (taken as zero, in "clean" definitions of paired ions deemed to interact only coulombically and only with each other[20]). Such DH screening in $w(r)$ for juxtaposition of *oppositely* charged ions appears not to have been examined, though it has been included in treatments of $M^{2+} - M^{3+}$ reactant juxtaposition in electron-transfer and ionic nuclear-spin interaction studies.[9,30] It is moot whether in the former case of anion–cation pairs simple screening alone will suffice, but there is sufficient scope in dealing with the problems of definition to effect internal consistency of the whole treatment.

(ii) Alternatively, for anion–cation pairs $d = a_\gamma$ can be made to vary with concentration[29] so effecting internal consistency, and retaining the clean definition of paired ions. While such a treatment has not yet been experimentally employed, its use will at least marginally affect the numerical values of K fitted to observation. For a hypothetical bibivalent electrolyte having $r_{\min} = a = 3.75$ Å, a typical value for say sulphates, a value of $d(0)$ at $I = 0$ of 14.3 Å becomes $d(0.1\text{ M}) = 3.86$ Å at $I = 0.1$ M, while a choice of $d(0) = 5.0$ Å becomes $d(0.1\text{ M}) = 3.78$ Å at $I = 0.1$ M. The benefits of thus proceeding are manifest, virtually excluding triplets and reinforcing the clean definition since the width $(d - a)$, which defines pairs, becomes very small, 0.11 Å and 0.03 Å only, in the given examples. For juxtaposed pairs of similarly charged ions, however, this procedure is disastrous, since $d(I)$ will now expand rather than contract with ionic strength I, with obvious exacerbation of already substantial complications. Clearly, here the internal screening procedure of (i) above is physically better from almost every standpoint.

The question of like-charged ions forming appreciable numbers of pairs has been raised by Hemmes,[33] employing K^F. The volume preexponential for large ions can outweigh the repulsive exponential. However, in the shell model, if $\delta a \sim 1$ Å is assumed, $a \sim 20$ Å is required which involves very large ions indeed. On the other hand, the Debye–Hückel screening outlined in Eq. (6) below should allow sufficient diminution of the repulsion to induce pair formation for single like charges at experimental concentrations.

It must be emphasized that ion association in dilute electrolytes is a theoretical device invoked to deal with imperfections in the DH (or equivalent) theories; a perfect statistical-mechanical account of electrolytes would include the formation of pairs as a natural outcome of the description.[31] In no way does this statement mean that juxtaposition, i.e., pairing, i.e., association, does not occur: Invocation of a pairing *equilibrium* is just one (very successful) way of treating it theoretically.

TYPES OF PAIRED SPECIES ENCOMPASSED BY LARGE *d* VALUES

In favorable cases contact and solvent-separated pairs can be distinguished,[32] especially where the contact bonding is covalent rather than coulombic; such molecularity of solvent and specificity of ion–ligand interaction will remain special cases. However, where the *integral* of contact and solvent-separated pairs (regardless of their specific ratio) conforms with a general (e.g., coulombic) formulation, such as involves a juxtaposition equilibrium, then this will represent but a local perturbation of the smooth distribution implied where solvent is treated as a featureless continuum. For example, strong cation solvation would disfavor contact anion association, but marked polarization of the solvating molecule (arising from the very strength of its solvation interaction) could enhance attraction to an outer-sphere anion, such supposed compensation allowing of an integrated K, over both paired species, differing little from that for an ordinarily solvated cation of otherwise similar type. Only in this way can we rationalize the near constancy of experimental K values for the association of M^{2+} with SO_4^{2-} when the M^{2+} ions have as different solvation energies as do Mg^{2+} and Co^{2+} (Table II).

Subclasses of ion pairs might be expected to have specific reactivities, but this has not been observed for aquo-ion systems of the kind we have been examining. However, for reaction[34] of the anionic complexes Co^{II}edta and $Fe^{III}(CN)_5L$ (to which Hemmes' view[33] would apply) consideration of rates and spectra suggests that the identifiable linked species edta $Co^{III}NCFe^{II}(CN)_4L$ is a dead end, while electron transfer proceeds by the less intimately juxtaposed outer-sphere configuration, demonstrating a clear parallel to our expectations. The sequence may be summarized as

$$\begin{tikzcd}
A + B \arrow[r, shift left] & A/B \arrow[l, shift left] \arrow[r, shift left] \arrow[d] & AB \arrow[l, shift left] \\
& \text{Products} &
\end{tikzcd}$$

The mechanistic arguments are admittedly indirect. Further consideration of kinetic aspects follows.

JUXTAPOSITION AS A PREEQUILIBRIUM IN KINETICS

Traditional transition state theory[35] appears to arrive at rate constants as

$$k = \frac{k_B T}{h} \exp(-\Delta G^{\neq}/RT)$$

irrespective of molecularity, thus appearing to confer dimensions of unimolecularity (s^{-1}) on all reactions. However, the entropy terms in the exponential contain the volumes available to the species and thus a prejuxtaposition can be inferred, as by North.[6] We paraphrase his exposition as

$$A + B \overset{K_{\text{jux}}}{\rightleftharpoons} \{AB\} \overset{K^{\neq}}{\rightleftharpoons} \{AB^{\neq}\} \longrightarrow \text{Products},$$

giving

$$k = (k_B T/h)\, K_{\text{jux}} \exp(-\Delta G^{\neq}/RT),$$

where in simple cases K_{jux} is given by Eq.(2). By taking partition functions per unit volume in the conventional manner, collisional and transition state formulations may be related.[36] Thus, with reasonable assumptions, the partition function ratio yields

$$K_{\text{jux}} = Zh/k_B T,$$

where Z is the usual gas kinetic collision frequency. It is not self-evident that this relationship and that of North just cited [employing Eq. (2)] are in accord; the events viewed as collisions resemble the "excluded volume" property imputed by Eigen[19] to K^F [Eq. (3)] which is in this sense incompatible with the spherical shell model. The latter was subsequently adopted by Sutin[37] for formulating the rate constants for electron exchange reaction such as $Fe^{2+} + Fe^{3+}$ in solution, in the form

$$k = K_{\text{jux}}\nu_e , \tag{5}$$

in which

$$\nu_e = \nu_n \kappa_{\text{el}} \kappa_n ,$$

where ν_n is the frequency of the transfer-effecting process (it is either a nuclear vibrational frequency or, if combined with κ_{el} in cases where $\kappa_{\text{el}} < 1$, an electronic resonance frequency depending on theoretically derived criteria involving molecular properties of the reaction under study), κ_{el} is essentially the Landau–Zener transfer probability depending on the (electronic) resonance energy H_{AB} and κ_n incorporates the nuclear tunnelling factor and is usually put at unity.

In the simplest case, as outlined earlier, K_{jux} would be given by Eqs.(1) or (2), but in the presence of electrolyte the factor $(\gamma_{AB}/\gamma_A\gamma_B)$ is required if the reactants are ionic. The use of the Debye–Hückel expression in the Bjerrum–Brönsted treatment of the ionic strength effect on the logarithm of the rate constant gives rise to the term $+2z_A z_B \mathcal{A}\sqrt{I}/(1 + \sqrt{I})$ which holds in several cases up to $I = 1$ M. This form of equation implies that $a_\gamma = 1/\beta = 3.03$ Å at 298 K but the unit coefficient for $\sqrt{I}$ in the denominator is retained arbitrarily at other temperatures.

More realistically, if a_γ in the DH expression can be set approximately equal to the a employed in the coulombic juxtaposition energy, Sutin and Brunschwig[38] have shown that an elegant conflation of DH and Coulomb terms occurs, giving

$$w(a) = \frac{z_A z_B e^2}{Da(1 + a\beta\sqrt{I})} . \tag{6}$$

Tembe *et al.*[9] have constructed, instead of expressions (5) and (6), a general r-dependent function for electron transfer integrated over r:

$$k = \int_0^\infty g_{AB}(r) 4\pi r^2 \nu_n(r) \kappa_{el}(r) \kappa_n(r) dr \qquad (7)$$

where essentially the value of $H_{AB}(r)$ for the interaction at separation r governs most of the factors except $g_{AB}(r)$ which is the pair distribution function for A and B; $g(r)$ is subject to the influence of inert electrolyte. For the $M^{2+} + M^{3+}$ systems studied, the general function which is the integrand of Eq.(7) above peaks in the vicinity of ~5.5 Å, having a peak width of about 0.8 Å. Guided by these results, Sutin has taken $a \sim 6.5$ Å, in Eqs. (2), (5) and (6). This a value is less than the contact distance for the envelopes about hydrated ions in contact. There is a growing view that the solvation molecules of the one reactant ion can indeed interpenetrate the corresponding (inner) solvation shell of the other; the choice of 6.5 Å represents a modest allowance for this possibility. Use of Eqs. (2), (5) and (6) with appropriate a values, together with new measurements of changes in reactant bondlengths (a dominant feature in ν_e especially for the slower reactions) has allowed the theoretical estimation of a number of electron transfer rates to within a factor of 30, for a range of 10^{15} in observed k values.[37] δa is taken[37] as 0.8 Å.

Part of the (systematic) deviation of theory from experiment may arise from the ionic strength effects. There is evidence of ClO_4^- association with cationic activated complexes, and if as is likely $\Delta S^{\neq}$ and especially its I dependence is due predominantly to electrolyte interactions, these have not been satisfactorily accounted for. Thus, prediction of the change in $\Delta S^{\neq}$ from $I = 0$ to $I = 1$ M for $M^{2+} + M^{3+}$ is unsuccessful if the DH theory above is employed, and in the writing of this Comment, some alternatives have been examined. These are

(A) from the temperature dependence[37] of Eq. (6);

(B) from the temperature dependence of the usual DH expression using throughout for a_γ the value taken for a_{AB}: The result of (B) is equal to that of (A) as it should be;

(C) use of the Bjerrum–Brönsted expression employing $(1 + \sqrt{I})^{-1}$;

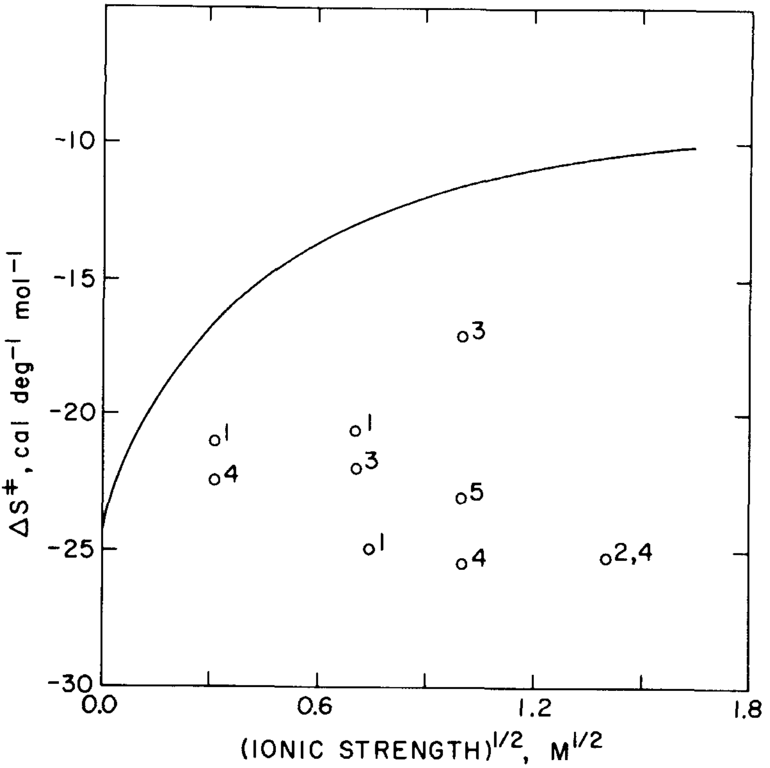

FIGURE 2 Observed and DH prediction of $\Delta S^{\neq}$ dependence on ionic strength. From Ref. 37.

(D) as (C) but with a put equal to β^{-1} at 298 K and that value employed as coefficient of β throughout;

(E) the Pitzer function[28] in κa $(= a\beta\sqrt{I})$ taking electrostatic terms only (κ^{-1} is here the DH length);

(F) as read off from Figure 10 of Ref. 9;

(G) with a novel extension[26] of the DH form prompted by (A)–(F) here:

$$\log \frac{\gamma_{AB}{}^{\neq}}{\gamma_A \gamma_B} = \frac{-2z_A z_B \mathcal{A}\sqrt{I}}{1 + a\beta\sqrt{I}} - K'_{\text{jux}}\, I. \tag{7}$$

The $\Delta S^{\neq}$ contribution (as in the preceding) is obtained from temperature differentiation of the log term multiplied by RT. The need for a term linear in I and the choice of its coefficient arise as follows. It has been shown[30,35] that the I dependence of observed log k values for $V^{2+} + Fe^{3+}$ requires the insertion of an I term in addition to the first (DH "electrostatic") term; it is well known[26] that for log γ of a single electrolyte the coefficient of I includes contributions from: (i) any correction for a poor choice (or poor fit) of a in the demoninator of the DH term, (ii) the effect of solvation in the simplest sense of removing free solvent and more indirectly of ionic modification of solvent permittivity, (iii) association (ion-pairing) of the ions of opposite charge z_A' in the present case z_A' is $+5$ (for the M_2^{5+} activated complex) and z_B' is -1 (for the perchlorate medium ion). In order to give some physical meaning to the I coefficient we have summarily assigned all of it to the association considered in (iii):

$$M_2^{5+} + ClO_4^- \overset{K'_{\text{jux}}}{\rightleftharpoons} M_2^{5+}ClO_4^- \,,$$

with the additional reasonable constraints that a for the cation–anion distance in this association is exactly equal to that between M^{2+} and M^{3+}, and that δa is also 0.8 Å as for the latter. It is furthermore implied that the only cation that associates with ClO_4^- is the M_2^{5+} ion (the reactant components of the activated complex), not M^{3+} or M^{2+}. Then this raft of assumption, none of which is entirely arbitrary, gives for the I coefficient

$$K'_{\text{jux}} = 4\pi L a^2 \delta a \exp\{-z_A' z_B' e^2 / k_B T D a (1 + \beta a \sqrt{I})\} \,.$$

It may be noted that this procedure provides a method of encompassing triple ion interactions of the type referred to earlier within the usual DH formalism. The results of the calculations (A)–(G) are given in Table IV. While none of the calculations approach the experimental value very well, the last two do show some promise of approximating the facts, and at low I, method (G) gives a variation with I not achieved by the other methods. It is clear that advances in the theoretical prediction of k values require a better understanding of electrolyte interactions, and studies of the activity coefficients of inert 5+ ions (such as $[Ru^{II}\text{-(pyz)-}Ru^{III}]^{5+}$ in mixtures with per-

TABLE IV
Calculation of the effect on $\Delta S^{\neq}$ on changing I from 0 to 1 M, for the $M^{2+} + M^{3+}$ exchange at 25°C

Procedure	Change in $\Delta S^{\neq}$/cal K^{-1} mol^{-1}	Procedure	Change in $\Delta S^{\neq}$/cal K^{-1} mol^{-1}
A	12.7	E	12.1
B	12.7	F	9
C	20.4	G	7.6
D	21.7	Exp.	~0

chlorate, as a guide to the behavior of say juxtaposed ferrous and ferric ion, would significantly aid these endeavors.

Data are available to test the prediction of perchlorate association with M_2^{5+}, since Brown and Sutin[16] have shown that the rate for the $Ru(NH_3)_4bpy^{3+/2+}$ reaction follows the DH formulation in CF_3SO_3H but not in $HClO_4$. This suggested a path containing ClO_4^-. This system lends itself to further examination in the light of the potential usefulness of the K'_{jux} term in Eq.(7). It is not clear why the DH form fits the CH_3SO_3H data at low I but not $\Delta S^{\neq}$, and the origin of the cancellation of errors implied will bear examination.

The question of what separation to take between reactants is not clearly resolved and varies from[9] 4.5 Å to[34] 10 Å (or guided[16] by fits to the extended DH γ expression, 13.5 Å); variations predicted from other wave mechanical forms have been considered (footnote 5, Ref. 9). Distant transfer has been invoked in biological systems, e.g., metalloproteins.[39] Clearly, there remains some doubt regarding a final choice in reactions such as $Fe^{2+} + Fe^{3+}$.

SUBSTITUTION REACTIONS

A major preoccupation in the study of substitution[1,15] is whether the mechanism is associative (A) or dissociative (D), to which there are the interchange gradations (I_A and I_D). The associative involves outer-sphere association before bonding of the incoming ligand together with expulsion of solvation molecule or leaving ligand; the dissociative implies a rate determining unimolecular ligand-leaving step. Since clear examples of the extreme cases are rare, there is scope for extensive debate regarding detailed assignments of mechanism. In essence these involve the relative participations of pair subspecies in the rate determining step (5), and some guidance is provided by $\Delta V^{\neq}$ studies.[40,41] While the complications are evident, relative to electron transfer cases it appears that exploration of the field by *ab initio* calculations similar to those employed for electron transfer might be essayed; quite good results are available from wave mechanical treatments of equilibrium hydration, and possibly similar or equivalent procedures could be followed in the case of substitution mechanisms.

THE KINETICS OF GAS REACTIONS

In a separate exercise, the distributions of Arrhenius A values for some three thousand gas reactions of unimolecular,[2] bimolecular[3] and termolecular[3] mechanism have been surveyed[42] The aim was to test Pratt's assertion,[43] in effect that $A_{\mathrm{Arr}}/(c^{\ominus})^{-(n-1)}$ values for all three groups (where n = molecularity) were most frequently found to be $\sim 10^{14}$ s^{-1} if $c^{\ominus}$ were taken as the (now outdated) standard state of 1 mol cm^{-3}. The survey shows that Robinson and Holbrook's generalization for unimolecular reactions, $A_{\mathrm{Arr}} \sim 10^{13.5}$ s^{-1}, is borne out, but for bi- and termolecular the means are closer to 10^{12} and 10^{11}. If the reaction rate for bimolecular reactions is written in the activationless case as

$$k_{\mathrm{bi}} = K_{\mathrm{jux}} \nu \,,$$

where ν is a typical bond-breaking, therefore vibrational frequency, which might be rounded to 10^{14} s^{-1}, then Pratt's assertion is in effect that $K_{\mathrm{jux}} = 1$ cm^3 mol^{-1}. However, the deviations from his assertion can be rationalized by retaining 10^{14} s^{-1} as the typical frequency, but substituting $K_{\mathrm{jux}} \approx 10$–$50$ cm^3 mol^{-1}. The mid value would apply to a reaction having a ≈ 4 Å and δa ≈ 0.2 Å, both reasonable values and in conformity with the formulations proposed for solution reactions. For termolecular reactions

$$k_{\mathrm{ter}} \approx K_{\mathrm{jux}(1)} K_{\mathrm{jux}(2)} \nu \,,$$

if (1) and (2) here refer to two equilibria $\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{AB}$ and $\mathrm{AB} + \mathrm{C} \rightleftharpoons \mathrm{ABC}$. If we treat AB as spherical (a clearly Procrustean view) and equate $K_{\text{jux}(1)}$ and $K_{\text{jux}(2)}$ both having averaged values of a and δa, then the same values apply in termolecular as in bimolecular reactions to a rough approximation. Again, reconciliation of the shell-of-juxtaposition model with collisional and transition-state formulations will be required.

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