between 1158 and 1387 K. This fit lies more than a factor of 2 higher than the predictions of Johnston-Parr calculations,¹⁴ which give $k(T) = (4.3 \times 10^{-13})T^{0.68} \exp(-9410/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. A similar discrepancy is noted between our measurements and the 1285 K value for k extracted from flame measurements by Fenimore and Jones.⁸ The flame measurement by Dixon Lewis et al.⁹ falls about 30% below the extrapolation of our k data to their measurement temperature, 1070 K.

Somewhat more consistent agreement is found with values calculated from k'(T) and the equilibrium constant. At high temperature, we use the 1200-1800 K shock tube measurements of Gardiner et al.¹⁵ (as modified by Dixon-Lewis and Williams⁷ in view of more recent data for the $H + O_2$ reaction). Other high-temperature data on k' are reviewed in ref 7. Our data are seen to be larger than the values derived from the shock tube k'values by about 50%.

To compare the present data with direct k' measurements at lower temperatures, we have taken the FP/RF data of Tully and Ravishankara¹⁶ and of Ravishankara et al.³ which, together, span the temperature range 250–1050 K. Their individual k' data points were converted to values of k and were best fitted by nonlinear least squares to the expression $k(T) = (2.2 \times 10^{-20})T^{3.04}$.

 $\exp(-8620/T)$ cm³ molecule⁻¹ s⁻¹. This expression, extrapolated through ≈ 1550 K, is shown in Figure 4; it lies some 10–30% below our measurements. Finally, when the present data are combined with those of ref 3 and 16, the fit $k(T) = (1.09 \times 10^{-20})T^{3.15}$. $\exp(-8570/T)$ cm³ molecule⁻¹ s⁻¹ is obtained for the temperature range 250-1400 K.

The present measurements of k(T) are unique in that no knowledge is required of other rate constants (as in shock tube and flame studies), molecular parameters (as in Johnston-Parr calculations), or equilibrium data (as in FP/RF and shock tube studies) to calculate k from k'. Nevertheless, the general agreement between k(T) values obtained by these different techniques is fairly good, especially with respect to the temperature dependence over the temperature range of the present measurements. Thus, if a local activation energy is defined over 1160-1390 K, the values 20.4 (Johnston-Parr), 25.8 (shock tube, from k), and 25.0 (FP/RF, from k') kcal/mol fall within 15% of our determination, $22.1 \pm 2.2 \text{ kcal/mol}$.

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Influence of Specific Reactant–Solvent Interactions on Intrinsic Activation Entropies for Outer-Sphere Electron-Transfer Reactions

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The physical basis of the solvent contribution to the intrinsic activation entropy, ΔS^*_{int} , for outer-sphere electron-transfer reactions in homogeneous solution is examined in terms of the entropic parameters for the constituent electrochemical half-reactions. A relationship for calculating ΔS^*_{int} is derived which takes into account specific reactant-solvent interactions for the isolated redox centers by employing electrochemical reaction entropy data. This relation yields rather larger and more structure-sensitive values of ΔS^*_{int} than those deduced on the basis of the usual dielectric continuum treatment. These considerations indicate that the more negative values of ΔS^*_{int} typically extracted from experimental kinetic data arise largely from the modification to the specific reactant-solvent interactions within the precursor complex caused by the proximity of the other redox center.

Introduction

In recent years increasingly detailed and sophisticated theories of outer-sphere electron-transfer kinetics have been formulated.¹ These enable rates and activation parameters to be calculated from reaction thermodynamics together with reactant and solvent structural information. Although treatments of inner-shell (intramolecular reactant) reorganization have reached a high degree of sophistication,² the important contribution to the free energy barrier arising from outer-shell (noncoordinated solvent) reorganization is usually treated in terms of the classical dielectric continuum model as originally formulated by Marcus.³ While comparisons between theory and experiment for bimolecular outer-sphere processes show reasonable agreement in a number of cases, significant and often large discrepancies still remain.^{4,5} Among other things, such discrepancies call into question the quantitative validity of the dielectric continuum model, especially in view of the well-known failure of similar treatments to describe the thermodynamics of ion solvation.

In principle, a useful way of monitoring the influence of outer-shell solvation upon electron-transfer energetics is to evaluate entropic parameters since these are expected to arise chiefly from the changes in the degree of solvent polarization associated with electron transfer. The activation entropy, ΔS^* , as for other reorganization parameters, can usefully be divided into "intrinsic"

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and "thermodynamic" factors: 6,7

$$\Delta S^* = \Delta S^*_{\text{int}} + \beta \Delta S^{\circ} \tag{1}$$

where the coefficient β is predicted to usually be close to 0.5.⁸ The intrinsic activation entropy, ΔS^*_{int} , is that component of ΔS^* that remains in the absence of the entropic driving force ΔS° . When values of ΔS^* are estimated from eq 1, it is usual to employ experimental values of ΔS° and yet use values of ΔS^{*}_{int} calculated from dielectric continuum theory. Although these calculated values of ΔS^*_{int} are often small, given that the values of ΔS° are often much larger and more variable than those calculated from the dielectric continuum model, it is reasonable to inquire if a more trustworthy method for estimating ΔS^*_{int} could be formulated.

A useful and often enlightening approach for understanding electron-transfer processes on both a conceptual and an experimental basis is to examine the thermodynamics and kinetics of electrochemical reactions: 9-13

$$Ox. + e^{-}(\phi_m) \rightleftharpoons Red.$$
 (2)

where $\phi_{\rm m}$ is the (Galvani) electrode-solution potential difference. Although absolute values of ϕ_m cannot be evaluated with useful accuracy, the temperature dependence of ϕ_m can be obtained by using a nonisothermal cell arrangement.^{10,12} This enables the entropic change induced by reduction of a single redox center, the so-called "reaction entropy" ΔS°_{rc} , to be determined from the temperature dependence of the standard (or formal) potential $\phi_{\rm m}^{\circ}$ under these conditions.¹² Activation parameters for such electrochemical "half-reactions" can be obtained by using an analogous procedure.^{9,10} These quantities provide insights into the structural changes accompanying electron transfer at each redox center that remain hidden for homogeneous bimolecular reactions.

The aim of this communication is first to provide a simple physical picture, based on electrochemical half-reactions, of the origin of the intrinsic activation entropy in homogeneous and electrochemical redox reactions. With this background a new approach for estimating ΔS^*_{int} will be outlined based on reaction entropy data whereby the effects of specific reactant-solvent interactions can be taken into account. Despite their potential importance, such interactions have yet to be considered even in the more sophisticated theories of electron transfer.

Origin of the Intrinsic Activation Entropy

The actual entropic barriers, ΔS^*_{f} and ΔS^*_{r} , to electron transfer for the forward (reduction) and reverse (oxidation) electrochemical reactions at a given electrode potential have been termed "ideal" activation entropies.⁹⁻¹¹ These can be formulated as

$$\Delta S^*{}_{\rm f} = \alpha \Delta S^{\circ}{}_{\rm rc} + \Delta S^*{}_{\rm int,c} \tag{3a}$$

$$\Delta S^*_{r} = (\alpha - 1)\Delta S^{\circ}_{rc} + \Delta S^*_{int,e}$$
(3b)

where α is the electrochemical transfer coefficient and $\Delta S^*_{int,e}$ is the so-called "real" (or intrinsic) electrochemical activation entropy, i.e., that which remains after accounting for the entropic driving force.9 For convenience, we shall assume that the interactions between the reactant and electrode, and between the reactant pair in homogeneous solution, are weak and nonspecific (i.e., the "weak-interaction" limit.¹³ Under these circumstances $\Delta S^*_{\mathrm{int,e}}$ is related to the intrinsic activation entropy for the corresponding self-exchange reaction by

- (12) Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J.

 $\Delta S^*_{int} = 2\Delta S^*_{int,e}$ (4)

Relationships such as eq 4 reflect the fact that homogeneous outer-sphere reactions can be regarded as coupled pairs of reductive and oxidative electrochemical reactions.

Equations 3a and 3b point to a key difference between homogeneous self-exchange and electrochemical exchange reactions: the latter are characterized by a net entropy driving force ΔS°_{rc} even when the free energy driving force is zero. This results from the inherent chemical asymmetry of the electrochemical halfreactions. This entropy driving force contributes to the forward or reverse entropic barrier for each redox center to an extent determined by the difference in (hypothetical) charge between the oxidized or reduced reactant and the transition state, namely, α or $\alpha - 1$. The transition state of course never acquires a fractional charge since electron transfer occurs approximately independently of nuclear motion, but nonetheless is characterized by a polarized solvent environment appropriate to a molecule possessing such a charge.^{1,3}

According to the theoretical approach of Marcus,³ solvent reorganization to form the transition state can be viewed as occurring by a hypothetical two-step process.^{1a,14} First the charge of the reactant is slowly adjusted to a fractional value approximately midway between the reactant and product charges, with attendant reorientation of the surrounding solvent. Then in a rapid step (much faster than solvent motion) the transition-state charge is reset to that of the reactant. Taken together, the energies of the two steps are equivalent to the nonequilibrium solvent polarization energy. On the basis of the conventional dielectric continuum approach, the energetics of the first step are determined by the static solvent dielectric constant ϵ_s , while the optical (i.e., infinite frequency) dielectric constant ϵ_{op} determines the energy of the fast second step. We shall term these two steps the "static" and "optical" components, respectively. Generally the optical component is anticipated to provide the dominant contribution to the free energy of solvent reorganization due to the relative magnitudes of ϵ_{op} and ϵ_{s} . However, the temperature coefficients of the two dielectric constants are such that in many solvents the optical and static components are calculated to contribute roughly equally to the entropic component of the solvent barrier.

The conventional calculation of the solvent reorganization energetics involves an application of the Born ion solvation model to transition-state theory.^{1a,14} The Born model predicts that entropies of ions will vary with the square of the charge number.¹⁵ It is reasonable to suppose that the static component of the electrochemical transition-state entropy will also depend on the square of the effective charge. The difference in static entropy between the transition and ground states should be appropriately weighted fractions of the total entropy difference ΔS^{o}_{rc} between the two ground redox states. We can therefore express the static components of the forward and reverse electrochemical activation entropies as

$$\Delta S^*_{\rm f}({\rm static}) = \frac{\left[(n+1)^2 - (n+1-\alpha)^2\right]}{\left[(n+1)^2 - n^2\right]} \Delta S^{\rm o}_{\rm rc} \quad (5a)$$

$$\Delta S^*_{\rm r}({\rm static}) = \frac{[n^2 - (n+1-\alpha)^2]}{[(n+1)^2 - n^2]} \Delta S^{\circ}_{\rm rc}$$
(5b)

where n and n + 1 are the charge numbers of the two forms of the redox couple, and $n + 1 - \alpha$ is the effective transition-state charge.

It can be seen from eq 5a and 5b that, even for a transition state that is symmetrical with respect to charge, i.e., $\alpha = 0.5$, $\Delta S^*_{f}(\text{static})$ will differ from $-\Delta S^*_{r}(\text{static})$. In other words, the transition state will not lie midway in terms of entropy between the reduced and oxidized states even though it may be equally accessible in terms of free energy from either oxidation state. This mismatch of the energetics of the forward and reverse half-re-

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⁽⁸⁾ The value of β is related to both the magnitude of the entropic and free energy driving forces, ΔS° and ΔG° ; ⁷ however, for reactions having small or moderate values of ΔG° , $\beta \approx 0.5 \pm 0.05$.

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Figure 1. Schematic representation of the ionic entropy of an individual redox center as a function of its effective ionic charge during the electron-transfer step. See text for details.

actions follows from the linear variation of driving-force contributions with charge (eq 3), coupled with the quadratic dependence of static entropy on charge.

Equations 3a and 3b can be combined to yield

$$\Delta S^*_{\text{int,e}} = (1 - \alpha) \Delta S^*_{\text{f}} + \alpha \Delta S^*_{\text{r}}$$
(6)

The intrinsic activation entropy therefore is a measure of the extent of the mismatch between forward and reverse half-reaction entropic barriers after normalizing for driving-force contributions. This is seen most clearly when $\alpha = 0.5$ and the driving-force components of ΔS^*_{f} and ΔS^*_{f} exactly cancel. The connections between the various entropic quantities are illustrated schematically in Figure 1. The magnitude of ΔS^*_{int} is given by the vertical displacement of the curve AB, describing the dependence of the entropy upon the effective ionic charge, from the chord to this curve shown as a dashed line.

Equations 5a and 5b can be combined with eq 6 to yield an expression for the static component of $\Delta S^*_{int,e}$:

$$\Delta S^*_{\text{int,e}}(\text{static}) = \frac{\alpha(1-\alpha)}{2n+1} \Delta S^\circ_{\text{rc}}$$
(7)

Taking $\alpha = 0.5$ and inserting the Born expression for the reaction entropy16

$$\Delta S^{\circ}_{\rm rc} = -\frac{Ne^2}{2r\epsilon_{\rm s}^2} \left(\frac{\mathrm{d}\epsilon_{\rm s}}{\mathrm{d}T}\right) [(n+1)^2 - n^2] \tag{8}$$

into eq 7 yields

$$\Delta S^*_{\text{int,e}}(\text{static}) = -(Ne^2/8r\epsilon_s^2)(d\epsilon_s/dT)$$
(9)

where N is the Avogadro number, e is the electronic charge, and r is the reactant radius. Note that the apparent dependence of $\Delta S^*_{int,e}(static)$ on reactant charge (eq 7) has now been eliminated.

Equation 8 can be compared with the relation obtained from the temperature derivative of the usual dielectric continuum expression for the reorganization free energy: 3,10

$$\Delta S^*_{\text{int,e}} = [(Ne^2/8)(1/r - 1/R)][(1/\epsilon_{\text{op}}^2)(\mathrm{d}\epsilon_{\text{op}}/\mathrm{d}T) - (1/\epsilon_s^2)(\mathrm{d}\epsilon_s/\mathrm{d}T)]$$
(10)

Equations 9 and 10 differ in that the latter takes account of image stabilization of the ion in the vicinity of the electrode by including the ion-image separation distance R; furthermore, the optical portion of the activation entropy is included. This term is similar

in form to the static term since it is assumed, on the basis of a linear response of solvent polarization to the field of the ion, that the optical portion of $\Delta S^*_{int,e}$ also varies with the square of the effective charge of the transition state.1b

Similarly, from eq 4 and 7 the static portion of the intrinsic entropy for homogeneous self-exchange reactions can be expressed as

$$\Delta S^*_{\text{int}}(\text{static}) = \frac{2\alpha(1-\alpha)}{2n+1} \Delta S^\circ_{\text{rc}}$$
(11)

Again, for $\alpha = 0.5$ and on the basis of the Born model (eq 8), this leads to

$$\Delta S^*_{int}(\text{static}) = \left[(Ne^2/4r\epsilon_s^2)(\mathrm{d}\epsilon_s/\mathrm{d}T) \right]$$
(12)

This is identical in form with the dielectric continuum expression for ΔS^*_{int} (cf. eq 10)

$$\Delta S^*_{\text{int}} = (Ne^2/4)(1/r - 1/R_{\text{h}})[(1/\epsilon_{\text{op}}^2)(d\epsilon_{\text{op}}/dT) - (1/\epsilon_{\text{s}}^2)(d\epsilon_{\text{s}}/dT)]$$
(13)

allowing again for the addition of the optical term and the presence of the nearby coreactant through the internuclear distance term $R_{\rm h}$.

Real Chemical Environments. Incorporating Specific **Reactant-Solvent Interactions in Activation Entropy** Calculations

In general, the experimental values of ΔS°_{rc} differ widely from the continuum predictions of eq 8. In water, for example, ΔS°_{rc} for the $Cr(H_2O)_6^{3+/2+}$ couple is 7 times greater than predicted, while the experimental value of ΔS°_{rc} for Fe(bpy)₃^{3+/2+} is less than a third of the theoretical value.¹² Furthermore, the expected variation of reaction entropies with solvent dielectric properties is not observed.¹⁶⁻¹⁸ The discrepancies between theory and experiment have variously been attributed to dielectric saturation, hydrogen bonding between reactants and solvent,¹² long-range solvent structuring,¹⁶⁻¹⁹ and hydrophobic interactions.²⁰ Consequently, in view of eq 11 dielectric continuum theories of solvent reorganization are not expected to provide accurate estimates of intrinsic activation entropies.

Nevertheless eq 11 suggests a means of incorporating the numerous factors neglected in the dielectric continuum treatments. Rather than employing estimates of ΔS°_{rc} based on eq 8, one can use experimental values of ΔS°_{rc} to determine the static component of ΔS^*_{int} . Therefore, instead of eq 13 the intrinsic activation entropy can be expressed as

$$\Delta S^*_{int} = (Ne^2/4)(1/r - 1/R_h)[(1/\epsilon_{op}^2)(d\epsilon_{op}/dT)] + \Delta S^{\circ}_{rc}/(4n+2)$$
(14)

The optical component of ΔS^*_{int} , the first term on the right-hand side of eq 14, is unchanged from eq 13; however, the static component embodied in the second term is taken instead from eq 11 with $\alpha = 0.5$ (as expected, α is commonly observed to be close to 0.5 for outer-sphere electrochemical reactions¹¹). Equation 14 is therefore anticipated to yield more reliable values of ΔS^*_{int} , at least in the weak-interaction limit, since it circumvents the known severe limitations of the Born model for calculating static entropies.

The latter model is retained for estimating the optical component in lieu of any direct experimental information to the contrary. The justification for this approach is that the Born model is likely to be much more reliable for estimating the optical rather than the static component in view of the relative insensitivity of ϵ_{op} to solvent structure. Thus, the extensive local perturbations

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TABLE I: Intrinsic Activation Entropies for Selected Homogeneous Self-Exchange Reactions, ΔS^*_{int} (J deg⁻¹ mol⁻¹), Calculated without (Eq 13) and with (Eq 14 and 17) Consideration of Specific Reactant-Solvent Interactions, and Comparison with Experiment

	solvent		$\Delta S^*_{ ext{int}}$			
redox couple		r, ^a Å	eq 13 ^b	eq 14 ^c	eq 17 ^d	expt ^e
$Fe(OH_2)_6^{3+/2+}$	H,O	3.3	-1.5	13	17	-62
V(OH,), 3+/2+	H,O	3.3	-1.5	12.5	16.5	-61
$Ru(NH_3)^{3+/2+}$	H,O	3.3	-1.5	2.5	6.5	-24^{f}
$Co(en)_{3}^{3+/2+g}$	н,о	4.2	-1.5	9.5	13.5	-45
$Ru(bpy)_{3^{3+/2+h}}$	H, O	6.7	-1.0	-4.5	0	
ferrocinium- ferrocene	H ₂ O	3.8	-1.5	-15	5	
ferrocinium- ferrocene	methanol	3.8	-6.5	-9.5		-44
ferrocinium- ferrocene	nitro- methane	3.8	-6.0	16		-29

^a Reactant radius, used to calculate ΔS^*_{int} (eq 13). Values taken from ref 4 and 18. ^b Intrinsic activation entropy, calculated from eq 13 by using the listed values of r and assuming that⁴ Refer to the equation of the equation of the second values of the dependence of the equation $d\epsilon_{op}/dT = -0.0011$ (Riddick, J. A.; Bunger, W. B. "Organic Solvents"; Wiley-Interscience: New York, 1970; p 145); nitro-methane, $\epsilon_s = 35.5$, $d\epsilon_s/dT = -0.16$ (Smyth, C. P.; Walls, W. S. J. *Chem. Phys.* **1935**, *3*, **5**57), $\epsilon_{op} = 1.90$, $d\epsilon_{op}/dT = -0.0010$ (Riddick, J. A.; Bunger, W. B. *Op. Cit.*, p 391). ^c Intrinsic activation entropy, calculated from eq 14 similarly to footnote b, using the experimental values of ΔS°_{rc} taken from ref 12 and 18. ^d Intrinsic activation entropy, calculated as in footnote c, but using eq 17 instead of eq 14, with $K_1 = -40 \text{ J deg}^{-1} \text{ mol}^{-1}$ (see text). e Values extracted from published rate data by using eq 15 and correcting for nuclear tunneling effects. Values of $K_p \nu_n$ are ca. $3 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$ (see ref 4 and 5). Literature sources for rate data: Fe(H₂O)₆^{3+/2+}-Silverman, J.; Dodson, R. W. J. Phys. Chem. **1952**, 56, 846; V(H₂O)₆^{3+/2+}-Krishnamurty, K. V.; Wahl, A. C. J. Am. Chem. Soc. **1958**, 80, 5921; Ru(NH₃)₆^{3+/2+}-Meyer, T. J.; Taube, H. Inorg. Chem. 1968, 7, 2369; Co(en), 3+/2+-Dwyer, F. P.; Sargeson, A. M. J. Phys. Chem. 1961, 65, 1892; ferrocinium/ ferrocene-Yang, E. S.; Chan, M. S.; Wahl, A. C. J. Phys. Chem. 1980, 84, 3094. ⁴ Brown and Sutin (J. Am. Chem. Soc. 1979, 101, 883) have questioned the accuracy of this result, based on the more negative ΔS^* value for the Ru(en)₃³⁺-Ru(NH₃)₆²⁺ cross-reaction. ^g en = ethylenediamine. ^h bpy = 2,2'-bipyridine.

in solvent structure induced around an ionic solute that are responsible for the failure of the dielectric continuum model for predicting ionic solvation thermodynamics should have a much smaller influence on the intramolecular electronic perturbations which constitute the optical component of the reorganization barrier.

A comparison between values of ΔS^*_{int} calculated from eq 13 and 14 for some representative redox couples in aqueous media is presented in Table I. Whereas the dielectric continuum model (eq 13) predicts that ΔS^*_{int} will be small and largely independent of the chemical nature of the redox couple, somewhat larger and more varying values of ΔS^*_{int} are predicted by eq 14 since this takes into account specific reactant-solvent interactions via inclusion of the experimental values of ΔS°_{rc} .

Although the differences between eq 13 and 14 have been emphasized here, it should be noted that the ΔS^*_{int} values obtained by the latter are still relatively small. An interesting result is that especially for multicharged reactants very large thermodynamic solvation effects translate to much smaller intrinsic entropic barriers. For example, the $Fe(H_2O)_6^{3+/2+}$ self-exchange reaction involves thermodynamic entropy changes amounting to 360 J deg⁻¹ mol⁻¹ (180 J deg⁻¹ mol⁻¹ for each half-reaction) which yields an entropic contribution of just 17 J deg⁻¹ mol⁻¹ to the Franck-Condon barrier (Table I). Still, the effects are large enough to warrant consideration. For example, for the $Fe(H_2O)_6^{3+/2+}$ reaction ΔS^*_{int} should contribute a factor of 7 to the self-exchange rate constant provided that compensating enthalpic effects are absent. This effect is therefore comparable in magnitude to the nuclear tunneling corrections and nonadiabatic electron tunneling factors which have been emphasized in the recent literature.^{2,21}

Comparisons with Experiment

In addition to the calculated values of ΔS^*_{int} , some "experimental" values for these homogeneous self-exchange reactions, $\Delta S^*_{int}(exptl)$, are given in Table I. The latter were extracted from the measured activation enthalpies, ΔH^* , and the rate constants, k, by using

$$k = K_{\rm p} \Gamma_{\rm n} \nu_{\rm n} \exp(\Delta S^*_{\rm int}/R) \exp(-\Delta H^*/RT) \qquad (15)$$

where K_p is the equilibrium constant for forming the precursor complex immediately prior to the electron-transfer step, Γ_n is the nuclear tunneling factor, and ν_n is the nuclear frequency factor.^{2,21} [Note that the activation entropy in eq 15 can be directly identified with ΔS^*_{int} since $\Delta S^\circ = 0$ for self-exchange reactions (eq 1)]. The values of K_p and ν_n were calculated as described in ref 4. The values of $\Delta S^*_{int}(exptl)$ were corrected for the variation of Γ_n with temperature by calculating this quantity with the relationships given in ref 2.²²

It is seen in Table I that the values of $\Delta S^*_{int}(exptl)$ are uniformly smaller, i.e., more negative, than the estimates of $\Delta S^*_{\mathrm{int}}$ from both eq 13 and 14. Such negative values of $\Delta S^*_{int}(exptl)$ are commonly observed for homogeneous outer-sphere reactions.23 They have been variously attributed to an unfavorable contribution to the precursor work term arising from reactant-solvent interactions, to the occurrence of nonadiabatic pathways, and to steric factors.^{23,24} In any case, in view of the present discussion it appears likely that these negative values of ΔS^*_{int} reflect properties of the bimolecular precursor complex rather than those of the individual redox couples, i.e., reflect the modification of the solvation environment around each redox center brought about by its proximity to the coreactant necessary for electron transfer. In fact, the inclusion of specific reactant-solvent interactions in the calculation of ΔS^*_{int} for the weak interaction limit by employing eq 14 rather than eq 13 leads in most cases to more positive values of ΔS^*_{int} (Table I).

Before this conclusion is accepted, however, it is worth examining further the various assumptions embedded in eq 14. Given the breakdowns observed thus far in the Born solvation model, it is possible that the assumed quadratic variation of entropy with charge is also incorrect. The magnitude of the intrinsic activation entropy obtained from eq 14 is closely connected to the functional dependence of entropy on charge. For example a linear dependence leads to a value of zero for ΔS^*_{int} . Other functions might lead to large imbalances of forward and reverse entropic barriers and therefore substantial intrinsic activation entropies. Since most couples exhibit positive values of ΔS^{o}_{rc} , a fractional dependence of entropy on charge would normally be required to deduce negative values of ΔS^*_{int} . The entropy-charge relation was the subject of a number of detailed examinations and some controversy in previous years and apparently was never unambiguously resolved. $^{25-27}$ One reason for this was the difficulty of varying the ionic charge while holding constant the other relevant parameters such as ionic size, ligand composition, coordination number, etc.

In order to determine the relation between entropy and charge for a prototype system we examined the reaction entropies of ruthenium tris(bipyridine), for which oxidation states 0, I, II, and III are accessible in acetonitrile. The experimental details are given in ref 16. The reaction entropies thus obtained for the

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⁽²¹⁾ Sutin, N. Prog. Inorg. Chem. 1983, 30, 441.

⁽²²⁾ In ref 2 the temperature dependence of Γ_n is formally considered to be a constituent of ΔS^*_{int} . Since Γ_n decreases with temperature, this yields a significant negative contribution to ΔS^*_{int} . For the present purposes, we prefer to correct for the nuclear tunneling factor separately since this forms part of the inner-shell, rather than the solvent, contribution to ΔS^*_{int} . (23) Weaver, M. J.; Yee, E. L. *Inorg. Chem.* **1980**, *19*, 1936. (24) Tembe, B. L.; Friedman, H. L.; Newton, M. D. J. Chem. Phys. **1982**,



Figure 2. Reaction entropies for $\operatorname{Ru}(\operatorname{bpy})_3^{n+1/n^+}$, with n = 2, 1, 0, in acetonitrile vs. the difference in the square of the charge numbers for the oxidized and reduced states $(Z_{ox}^2 - Z_{red}^2)$. The dashed line is the plot predicted from the Born model (eq 8).

Ru(bpy)₃^{3+/2+}, Ru(bpy)₃^{2+/+}, and Ru(bpy)₃^{+/0} couples, respectively, in acetonitrile (containing 0.1 M KPF₆ supporting electrolyte) are plotted against $Z_{ox}^2 - Z_{red}^2$, where Z_{ox} and Z_{red} are the charge numbers of the oxidized and reduced forms, respectively (Figure 2). A good straight line passing through the origin is obtained, indicating that the entropy is indeed quadratically dependent on the ionic charge for this system.

Unfortunately, there are relatively few systems for which the thermodynamics of such successive oxidation states can be examined. Nevertheless, we have noted²⁸ that the reaction entropies for a number of redox couples containing ammine, polypyridine, inorganic anion, and related ligands can be fitted to the simple semiempiricial relation

$$\Delta S^{\circ}_{\rm rc} = K_1 + K_2 (Z_{\rm ox}^2 - Z_{\rm red}^2) / r \tag{16}$$

where K_1 and K_2 are constants in a particular solvent. Even though eq 16 has a form similar to the Born expression (eq 8), as expected K_2 differs widely from the predictions of eq 8. The magnitude of K_1 can be related to the solvent acceptor number and has been interpreted in terms of disruption of the internal solvent structure by the charged solute.²⁸ Although $K_1 \approx 0$ in some solvents such as acetonitrile (Figure 2), K_1 is noticeably negative in solvents having high acceptor numbers, especially water for which $K_1 \approx$ -40 J K⁻¹ mol⁻¹. The form of eq 16 suggests the following modified version of eq 14:

$$\Delta S^*_{int} = (Ne^2/4)(1/r - 1/R_h)[1/\epsilon_{op}^2(d\epsilon_{op}/dT)] + (\Delta S^o_{rc} - K_l)(4n+2) \quad (17)$$

where ΔS^{o}_{rc} is now corrected for the charge-independent component K_1 .

(28) Hupp, J. T.; Weaver, M. J. Inorg. Chem., in press.

Values of ΔS^*_{int} for representative redox couples in aqueous solution calculated according to eq 17 are also included in Table I. It is seen that this correction has only a small influence upon the estimates of ΔS^*_{int} for 3+/2+ redox couples, although it has a larger effect for couples of smaller charge type, such as ferro-cinium-ferrocene (Table I).

Another way of exploring the possibility that the negative experimental values of ΔS^*_{int} might arise in part from mismatches in the thermodynamic entropic changes occurring in each halfreaction is to examine if the magnitude of ΔS^*_{int} depends on the sum of the constituent ΔS°_{rc} values. The larger these entropy changes, the larger should be the mismatch in ΔS^*_{f} and ΔS^*_{r} for each half-reaction, yielding larger (or more negative) values of ΔS^*_{int} . However, such an examination for about 30 self-exchange and cross-reactions shows no signs of such a systematic trend. (Details will be given elsewhere.⁵) In addition, the experimental values of ΔS^*_{int} also show no discernible dependence on the magnitude of the reorganization barrier, comparable negative values of ΔS^*_{int} being obtained even for extremely rapid reactions.^{5,23} This provides evidence that these negative values are associated with an entropically unfavorable work term and/or nonadiabaticity, rather than residing in the elementary reorganization barrier to electron transfer of which the estimates of ΔS^*_{int} obtained from eq 14 or 17 form a part.

Nevertheless, the method of calculating ΔS^*_{int} embodied in eq 14 or 17 is considered to be useful since it provides a reliable estimate of ΔS^*_{int} for the limiting weak-interaction case where the solvating environments of the two reactants do not modify each other, while accounting properly for the influence of the actual reactant-solvent interactions upon the entropic reorganization barrier for these isolated redox environments. It therefore provides a more trustworthy means of gauging the extent of reactantreactant interactions upon the activation entropy than is obtained by employing the conventional relationship (eq 13), as well as supplying useful insight into the physical and chemical factors that determine this quantity.

A related approach to that described here can also be employed to estimate the effects of isolated reactant-solvent hydrogen bonding on the intrinsic enthalpic component of the Franck-Condon barrier. This involves examining the solvent dependence of the half-cell redox thermodynamics.²⁹ Preliminary results indicate that such enthalpic effects can be markedly larger than the corresponding entropic factors examined here, contributing several kJ mol⁻¹ to the intrinsic free energy barriers for some reactions.²⁹ These findings suggest that such specific reactantsolvent interactions may indeed account in part for the common observation that the experimental rate constants for homogeneous outer-sphere reactions are significantly smaller than the theoretical predictions where the outer-shell reorganization energy is calculated by using the conventional dielectric continuum model.^{4,5}

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(29) Hupp, J. T.; Weaver, M. J., submitted for publication.