excited-state internuclear distance is supported by the intensity pattern of the $||b$ vibrational progression. This would in turn tend to indicate that what would be the antibonding t_2 orbital in T_d symmetry is not so strongly antibonding in character in D_{2d} symmetry.[24] In the $||a$ polarization it is likely that the exciting mode is a combination of the $T_2(\nu_4)$ and a lattice vibration. Such a mode is observed at ~500 cm^{-1} in the infrared spectrum of Ca_2CrO_4Cl.[25]

The analysis of the ~28,000-cm^{-1} manifold is much more clear-cut and undoubtedly is associated with one of the components of the $T_2(\nu_3)$ fundamental which occur at 865, 810, and 760 cm^{-1} in the ground state.

Electronic Structure.—Various approximate molecular orbital calculations yield, at best, a reasonable ground-state, "one-electron" energy level diagram. Attempts to assign electronic spectral bands on the basis of these in any case other than d^0 ignores the excited-state electron–electron interactions and have led to a variety of speculations in the d^1 and d^2 cases.[3,6,7,13,18,26] This has, of course, been recognized[4] and some attempt is being made to include a correction for repulsion.[27] One of the more recent and successful efforts has been that of Dahl and Johansen.[10] Their calculations suggest that the correct value of $\Delta\nu$ for MnO_4^- is of the order of 10,000 cm^{-1} and not 26,000 cm^{-1} as has been previously supposed.[6] This value agrees closely with our results on CrO_4^{3-},[14] MnO_4^{3-},[21] and MnO_4^{2-} [28] and prompts us to disregard both our previous tentative assignment made for MnO_4^- and assignments made by others for the MO_4^{n-} system. Indeed, it is perhaps pertinent here to comment upon the crystal field splitting for various MO_4^{n-} ions.

As noted earlier most current interpretations of the absorption spectra of MO_4^{n-}, where n = 1–3, have indicated that Δ is a sharply increasing function of formal oxidation state.[6,11] This is clearly seen in the data presented in the center column of Table IV.

Our experimental work, however, belies the validity of the Δ values reported for the d^1 systems CrO_4^{3-} [14] and MnO_4^{2-},[28] while the Dahl and Johansen interpretation of the spectra of MnO_4^- must be considered to be the correct one.

The newer values of Δ which arise from these current efforts are shown in the last column in Table IV along with Δ values for a number of other manganese tetrahedral oxyanions.

It will be noted that the values in the right-hand side of Table IV do *not* reflect a large increase in Δ with formal oxidation state. Based upon the older values of Δ and making the reasonable assumption that changes in effective oxidation state should be reflected by similar variations in Δ, we should conclude that the effective oxidation state of Mn(VII) in MnO_4^- is much larger than that of Mn(VI) in MnO_4^{2-} which is in turn much larger than that of Mn(V), etc. This is clearly not true if one considers the newer values of $\Delta\nu$. Here, one finds that $\Delta\nu$ has reached a plateau by the time that the formal charge on the manganese ion has become +5. (This contention derives added support from the reported values of Δ for CrO_4^{3-} and CrO_4^{2-}.) From this we must conclude that the *effective charge upon the manganese ion does not increase beyond that found for Mn(V).*

TABLE IV

Complex	Metal formal charge	Δ,[a] cm^{-1}	Δ, cm^{-1}
CrO_4^{3-}	5	16,000	10,000[b]
CrO_4^{2-}	6		~9,000[c]
MnO_4^{6-}	2		4,500[d]
MnO_4^{5-}	3		7,000[e]
MnO_4^{4-}	4		10,000[f]
MnO_4^{3-}	5	11,000	11,000[g]
MnO_4^{2-}	6	19,000	~10,000[f]
MnO_4^-	7	26,000	~10,000[c]

[a] Reference 6. [b] Reference 14. [c] Reference 10. [d] Estimated from the values given for MnO_6^{10-} and MnF_6^{2-} by C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962, p 110. [e] Estimated from work of R. Dingle, *Acta Chem. Scand.*, **20**, 33 (1966). [f] Reference 27. [g] References 2, 18, 21.

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Application of Diffusion Constant Measurement to the Determination of the Rate Constant of Electron-Exchange Reactions

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Recently a new method was suggested by I. R. for the determination of the rate constant of very fast electron-exchange reactions,[1] based on Dahms' prediction[2] of the existence of electronic conduction in aqueous solutions. Electronic conduction takes place, when there is a concentration gradient in the solution containing particles of both oxidation states of an oxidation–reduction couple and the gradient of one of them differs from that of the other in every point of the system. For the sake of simplicity, let the system consist of two parts at the time $t = 0$ which are divided by an imaginary plane at the linear coordinate perpendicular to this plane $x = 0$. Let the concentration of the species be $c_{red} = 0$ and $c_{ox} = c_0$, if $x < 0$, and $c_{ox} = 0$

[1] I. Ruff, *Electrochim. Acta*, in press.

[2] H. Dahms, *J. Phys. Chem.*, **72**, 362 (1968).

and $c_{\mathrm{red}} = c_0$, if $x > 0$. At $x = 0$, $c_{\mathrm{ox}} = c_{\mathrm{red}} = c_0/2$ and so $\mathrm{d}c_{\mathrm{ox}}/\mathrm{d}x = -\mathrm{d}c_{\mathrm{red}}/\mathrm{d}x = -\infty$. According to this, the species of the two oxidation states would diffuse in opposite directions, and simultaneously an electron-transfer reaction occurs between the two types of particles, which results in a "diffusion of electrons." So the final result is that, besides the diffusion due to ionic migration, a parallel electronic conduction produces an additional apparent diffusion. It can be shown[2] that the diffusion constant observed in such a system is $D' = D + kd^2c_0$, where D is the true diffusion coefficient (approximately equal for both species), k is the second-order rate constant of the corresponding electron-exchange reaction, and d is the distance in the activated complex. Since D is in the order of magnitude of 10^{-6} or 10^{-5} cm^2/sec, d^2 is about 10^{-14} cm^2. k must be equal to or larger than 10^7 or $10^8/c_0\ M^{-1}\ \mathrm{sec}^{-1}$ so that the second term of the above equation exceeds the errors in the determination of D.

Thus the applicability of this method has a rather high lower limit in k, and there are only a few electron-exchange reactions proceeding so fast. This is, however, an advantage, since these reactions could not be studied so far considering the upper limit of the isotopic exchange and nmr line broadening methods being about 10^5–$10^6\ M^{-1}\ \mathrm{sec}^{-1}$.

This diffusion of electrons produces, however, an electronic double layer, whose field would operate against this diffusion, if some ions with much higher diffusion constant could not compensate it. In other words, when, say, an excess of positive charges due to the diffusion of electrons appears at a certain distance x, some fast anions or cations should move immediately into or out of this plane, respectively. Probably the hydrogen ions can serve for this compensation concerning the kinetic data of the proton-exchange reaction between H_3O^+ and H_2O.[3] The upper limit in k can be estimated to be $(2 \times 10^9)/c_0\ M^{-1}\ \mathrm{sec}^{-1}$ at 0.1 M acid concentration.

With the aqueous ferrocene–ferricinium perchlorate system a k value of $2 \times 10^{11}\ M^{-1}\ \mathrm{sec}^{-1}$ has been calculated from the dependence of D' on c_0 determined polarographically. This value seemed to be independent of temperature and therefore likely the upper limit mentioned above, since the energy of activation of the proton migration is only 2.4 kcal/mol.[3] In the present work, D' and D have been determined for the same oxidation–reduction couple by direct diffusion constant measurements in methanol. The use of this solvent was necessary because of the low solubility of ferrocene in water.

Solutions were prepared in the same way as described earlier.[1] The water content of the methanol was about 0.3% arising from the concentrated perchloric acid, diluted with methanol to obtain a final concentration of 0.1 M for every solution used.

A conventional Oeholm diffusion column was used in which nonlimited diffusion of $2 \times 10^{-2}\ M$ ferricinium perchlorate was permitted either into the pure solvent, containing only perchloric acid in the same concentration as the ferricinium solution (determination of D), or into the solution of ferrocene of the same concentration and acidity (determination of D'). The thickness of the two diffusing layers upon each other was about 2 cm each. The diffusion time was $\tau = 3.5$ hr in each run. The concentration of ferricinium ions was determined spectrophotometrically in every 1-mm thick layer of the column by collecting each fraction of the solution slowly drained through a capillary tube on the bottom of the column. The height of these layers was determined by the number of drops leaving this capillary outlet. After plotting the concentration of ferricinium ions $vs.$ x, the diffusion constant was evaluated according to

$$\frac{1}{c_0}\left(\frac{\mathrm{d}c_{\mathrm{ox}}}{\mathrm{d}x}\right)_{x=0} = -\frac{1}{\sqrt{4\pi D\tau}}$$

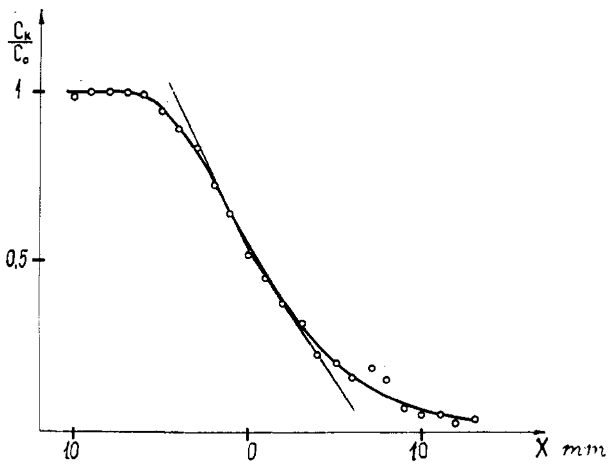

Figure 1.—A typical c_{ox} $vs.$ x plot (15°).

Though the separation of the layers in different heights was sufficiently slow, the c_{ox} $vs.$ x functions still showed a slight asymmetry due to the retardation of a solution sheet adhered to the wall. The greatest part of the error both in D' and in D (see Figure 1) could be attributed to this phenomenon. Therefore, two slopes, defined by the former equation, have been drawn with respect to the points below and above $x = 0$, and their average has been used with the deviation due to both the two extreme values of the slopes and the reproducibility of independent measurements.

As seen in Table I, the difference $D' - D$ that gives the value of kd^2c_0 exceeds the errors undoubtedly. Thus the first important conclusion is that the *predicted short-range electronic conductivity really exists* in a system of such a fast electron-transfer reaction as the ferrocene–ferricinium appears to be. Some experiments have been done with aqueous iron(II) and iron(III) ions determining the iron(II) concentration by the absorbance of its 2,2′-dipyridyl complex. No effect could be observed in agreement with the slowness of this reaction.

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The values of k, calculated with respect to a value of $d = 7.08$ Å, as the function of the temperature (Table I and Figure 2), and determined in the present work at 11.5, 15.0, 20.0 and 25.0°, fit satisfactoily the Arrhenius plot of Stranks' data[4] obtained by isotopic-exchange measurements. The enthalpy and entropy of activation are 13.4 ± 0.6 kcal/mol and 35 ± 2 eu, respectively. These data are much more accurate than those of Stranks because of the broad temperature range involved.

TABLE I

Range of evaluation	Temp, °C	cm²/sec $10^6D'$	10^6D	$10^6(D'-D)$	$10^{-10}k$, M^{-1} sec^{-1}
$x < 0$	11.5	1.0	0.8	0.2	0.5
	15.0	4.7	3.6	1.1	1.0
	20.0	9.9	7.9	2.0	2.9
	25.0	16.0	8.9	7.1	6.6
$x > 0$	11.5	3.4	2.2	1.2	1.9
	15.0	9.1	5.6	3.5	5.4
	20.0	25.9	13.9	12.0	17.9
	25.0	32.1	9.9	22.2	22.6

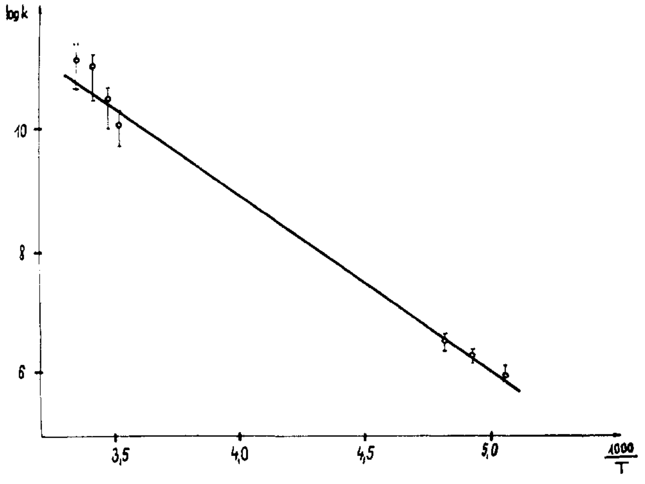

Figure 2.—The Arrhenius plot of the rate constants calculated with $d = 7.08$ Å. The three points on the right-hand side have been determined by isotopic exchange.[3]

It should be mentioned, however, that there is a large uncertainty in calculating with the former value of d. Though this involves the reasonable assumption that the reactants are as close as possible, there are some theoretical models supposing significantly higher distances.[5,6] This possibility is not excluded, and, if true, k would be considerably lower and the activation parameters altered.

A modification of the diffusion constant measurement which does not necessitate the fractioning of the liquid column will probably yield a higher accuracy. This work is in progress in our laboratory.

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Single Crystal Polarized Electronic Spectrum of *trans*-Difluorobis(ethylenediamine)chromium(III) Perchlorate

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The single crystal polarized spectra of a number of tetragonal Co(III) complexes have been measured[1,2] but except for *trans*-$[Cr(en)_2Cl_2]Cl\cdot HCl$[3] no corresponding measurements on tetragonal Cr(III) complexes have been reported. The compound *trans*-$[Cr(en)_2F_2]ClO_4$ is of particular interest because the large splitting of the $^4T_{1g}(a)$ band requires κ ($=Ds/Dt$) to be large. In an attempt to rationalize the sign and magnitude of κ by applying the empirical molecular orbital theory of Yamatera[4] and McClure[5] it has been predicted that κ is negative and that $\sigma_{F^-} > \sigma_{en}$ for this complex.[6] σ_X is the σ component of the antibonding energy experienced by a d orbital in the field of a ligand X.

We have measured the spectra of single crystals of *trans*-$[Cr(en)_2F_2]ClO_4$ using polarized light over a temperature range down to 4°K. It is now established that a vibronic mechanism[7] provides most of the intensity of the "d–d" transitions in a complex of this type, and it has been shown that the electronic spectra of the related *trans*-bis(ethylenediamine)cobalt complexes can be adequately explained using the effective point group D_{4h}.[2] Assuming a vibronic mechanism, the only spin-allowed "d–d" transitions in Cr(III) forbidden in D_{4h} symmetry are $^4B_{1g} \rightarrow {}^4B_{2g}$ and $^4B_{1g} \rightarrow {}^4A_{2g}$, both in z polarization (*cf.* Table I). Thus, if the orientation of the molecules is favorable, considerable information can be derived from the crystal spectrum of *trans*-$[Cr(en)_2F_2]ClO_4$ even though the crystal structure is not known.

TABLE I

VIBRONIC SELECTION RULES FOR Cr(III) COMPLEXES IN D_{4h} SYMMETRY

Transition	Polarization xy	z
$^4B_{1g} \rightarrow {}^4E_g$	α_{2u}, β_{2u}	ϵ_u
$^4B_{2g}$	ϵ_u	. . .
$^4A_{2g}$	ϵ_u	. . .

The complex *trans*-$[Cr(en_2)F_2]ClO_4$ crystallizes as large needles with each crystal face having extinction directions at 42 and 132° to the needle axis. The spectra of several crystals were measured at room temperature with the vector of polarized light along each extinction direction, and the spectrum of one crystal

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