containing P–F linkages,[8] such as diisopropyl phosphorofluoridate. For such reactions, Gustafson and Martell proposed a mechanism in which the metal chelate forms bonds to an oxygen on the phosphorus and to the fluoride, using coordination sites which are otherwise occupied by water or a hydroxide ion. This facilitates the attack of water or hydroxide and thus catalyzes the hydrolysis. Because most of these studies were done at pH 6.9 or above the partly hydrolyzed chelates (such as Cu(OH)L) played an important role as catalysts. An analogous mechanism seems very attractive in the present case.

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[8] (a) T. Wagner-Jauregg, B. E. Hackley, Jr., T. A. Lies, O. O. Owens' and R. Proper, *J. Am. Chem. Soc.*, **77**, 922 (1955); (b) R. C. Courtney, R. L. Gustafson, S. J. Westerback, H. Hyytiainen, S. C. Chaberek, Jr., and A. E. Martell, *ibid.*, **79**, 3030 (1957); (c) F. M. Fowkes, G. S. Ronay, and L. B. Ryland, *J. Phys. Chem.*, **62**, 867 (1958); (d) R. L. Gustafson and A. E. Martell, *J. Am. Chem. Soc.*, **84**, 2309 (1962). The similarity is enhanced by the presence of basic complexes in the iron(III)–Ferron system: C. F. Richard, R. L. Gustafson, and A. E. Martell, *ibid.*, **81**, 1033 (1959).

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The Oxidation of Iron(II) by Chlorine

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The kinetics of the oxidation of iron(II) by aqueous chlorine has been investigated spectrophotometrically at an ionic strength of 1.00. In solutions with $[H^+] = 0.05\text{–}1.00\ F$, $[Cl^-] = 0.10\text{–}1.00\ F$, $[Fe^{2+}] = 10^{-5}\text{–}10^{-4}\ F$, $Cl_2 = 10^{-5}\text{–}10^{-4}\ F$, and $[Fe^{3+}]_0 = 0\text{–}10^{-4}\ F$, the rate law is $d[Fe^{3+}]/dt = 2k_1[Fe^{2+}][Cl_3^-] + 2k_3[Fe^{2+}][Cl_2]$; $k_1 = 910\ M^{-1}\ sec^{-1}$, $k_3 = 163\ M^{-1}\ sec^{-1}$, and $\bar{k} = (k_1K_{Cl_3}[Cl^-] + k_3)/(1 + K_{Cl_3}[Cl^-]) = 10^{10.5} \exp(-11{,}200/RT)$, all at 30.0°. There is no apparent ferric inhibition of the reaction. Small amounts of copper(II) catalyze the reaction; the data do not distinguish between a copper(I) or a copper(III) intermediate for the catalyzed reaction. In solutions with $[H^+] = [Cl^-] = 1.00\ F$, $[Fe^{3+}]_0 = 0.00\text{–}4.40 \times 10^{-5}\ F$, and $[Cu^{2+}]_0 = 10^{-6}\text{–}10^{-4}\ F$, the data are consistent with the rate law $d[Fe^{3+}]/dt = 2k_1[Fe^{2+}][Cl_3^-] + 2k_3[Fe^{2+}][Cl_2] + 2k_{11}[Fe^{2+}][Cu^{2+}]$; $k_{11} = 145\ M^{-1}\ sec^{-1}$ at 30.0°.

Introduction

The mechanism of the reaction

$$2Fe^{2+} + Cl_3^- \text{ (or } Cl_2) \longrightarrow 2Fe^{3+} + 3Cl^- \text{ (or } 2Cl^-) \qquad (1)$$

is of interest because it may proceed through an iron(IV) intermediate

$$Fe^{2+} + Cl_3^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 3Cl^- + Fe(IV) \qquad (2)$$

$$Fe^{2+} + Cl_2 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} 2Cl^- + Fe(IV) \qquad (3)$$

$$Fe^{2+} + Fe(IV) \xrightarrow{k_5} 2Fe^{3+} \qquad (4)$$

or as suggested by Taube[1,2] through a chlorine radical

$$Fe^{2+} + Cl_3^- \underset{k_7}{\overset{k_6}{\rightleftharpoons}} Fe^{3+} + Cl_2^- + Cl^- \qquad (5)$$

$$Fe^{2+} + Cl_2 \underset{k_9}{\overset{k_8}{\rightleftharpoons}} Fe^{3+} + Cl_2^- \qquad (6)$$

$$Fe^{2+} + Cl_2^- \xrightarrow{k_{10}} Fe^{3+} + 2Cl^- \qquad (7)$$

Carter and Davidson[3] have reported that the reaction path $Fe^{2+} + Br_3^- \rightarrow Fe^{3+} + Br^- + Br_2^-$ is preferred to the reaction path $Fe^{2+} + Br_3^- \rightarrow Fe(IV) + 3Br^-$. Connick and Awtrey[4] have made preliminary studies of the iron(II)–chlorine reaction and reported a second-order rate constant approximately the same as for the iron(II)–bromine reaction, although no attempt was made to identify the active chlorine species or to establish the existence of an iron(IV) intermediate. Connochioli, Hamilton, and Sutin[5] have begun a study of the oxidation of iron(II) by 2-equivalent oxidants, including chlorine. Their experiments using chlorine in 3.0 *F* perchloric acid with no added chloride are incomplete, but iron(IV) is suggested as an intermediate in the reactions of Fe(II) with HOCl and O_3. We have measured the rate of reaction 1 in chloride media by observing the increase with time of the concentration of the iron(III) ion spectrophotometrically when the reagents are present at concentrations in the range $10^{-5}\text{–}10^{-4}\ F$. The kinetic results have been interpreted as demonstrating the existence of two active chlorine species, Cl_2 and Cl_3^-, but we are not able to identify the intermediate iron species involved in the reaction.

Experimental Section

Materials.—Ferrous ammonium sulfate (0.2 g) was dissolved in 500 ml of 1.00 *F* HCl; the solution was degassed with dry nitrogen and stored under nitrogen in a storage buret. This

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[1] H. Taube, *J. Am. Chem. Soc.*, **65**, 1876 (1943); *ibid.*, **68**, 611 (1946).

[2] I. L. Hochhauser and H. Taube, *ibid.*, **69**, 1582 (1947).

[3] P. R. Carter and N. Davidson, *J. Phys. Chem.*, **56**, 877 (1952).

[4] Results quoted by P. R. Carter and N. Davidson in ref 3.

[5] T. J. Connochioli, E. J. Hamilton, Jr., and N. Sutin, *J. Am. Chem. Soc.*, **87**, 926 (1965).

stock solution contained less than 1% ferric ion. The ferrous ion concentration was determined by coulometric titration with bromine; there was no measurable oxidation of this solution in a 2-month period. An aqueous chlorine solution was prepared by bubbling dry chlorine gas through a 1.00 *F* HCl solution. The *ca.* 10^{-3} *F* solution was stored under nitrogen in a storage buret. This stock solution was used for all the experiments. Ferric ammonium sulfate (0.10 g) was dissolved in 250 ml of 1.00 *F* HCl. The actual $[Fe^{3+}]_0$ of each reaction mixture was determined spectrophotometrically prior to the reaction. The initial chlorine concentration was determined by measuring $[Fe^{3+}]_\infty$ spectrophotometrically and calculating from that the total amount of chlorine originally added. The ferrous concentration of several reaction mixtures was checked by adding an excess of chlorine solution and observing the new $[Fe^{3+}]_\infty$; the ferrous content determined this way agreed within 3% with the amount added.

Procedure.—A measured amount of the ferrous solution was placed in a 10-cm quartz cell with appropriate volumes of the reagents: 1.00 *F* HCl, 1.00 *F* $HClO_4$, 1.00 *F* NaCl, and 0.0010 *F* Fe^{3+}. The solution was brought to 30.0° and diluted to 30 ml by rapid addition of the stock chlorine solution; the cell was stoppered and shaken for 10 sec. The zero time point was taken when all of the chlorine had been added. The cell was then placed in the thermostated cell compartment of a Cary Model 14 spectrophotometer, using as a blank another cell containing all of the components except the chlorine; absorption due to the trichloride ion and aqueous chlorine was less than 5% of the ferric ion absorption at 335 mμ. The first optical density reading was usually obtained about 20 sec after mixing, and the half-time of a typical experiment was about 1 min. The response time of the spectrophotometer to small changes in the optical density was less than 1 sec.

Extinction Coefficients.—The formal extinction coefficients, $\epsilon = A/[Fe^{3+}] \times l$, of various ferric solutions were measured and are listed in Table I. The data of Sherrill and Izard[6] and of Zimmerman and Strong[7] at $\mu = 1.00$, $T = 25.0°$, give $K_{Cl_3} = [Cl_3^-]/[Cl_2][Cl^-] = 0.176\ M^{-1}$. This value was used in our calculations although, because of the temperature difference, a small error is introduced.

TABLE I

FORMAL EXTINCTION COEFFICIENTS, ε, OF FERRIC IRON AT λ 335 mμ IN VARIOUS SOLUTIONS

$[H^+]$, *F*	$[Cl^-]$, *F*	*T*, °C	ε
1.00	1.00	30.0	2090
0.10	1.00	30.0	1900
0.05	1.00	30.0	1895
1.00	0.50	30.0	1511
1.00	0.10	30.0	695
1.00	1.00	15.0	1783

Results and Discussion

All reaction rates were measured at a constant ionic strength of 1.00, maintained with sodium and perchlorate ions. The ferrous, ammonium, and sulfate ions made a negligible contribution to the ionic strength. Check experiments showed that there was no photochemical reaction due to the light of the spectrophotometer. The rate constants were independent of the hydrogen ion concentration over the limited range studied.

The data at a given chloride ion concentration are consistent with the second-order rate equation

$$\frac{d[Fe^{3+}]}{dt} = 2\bar{k}[Fe^{2+}][\Sigma Cl_2] \tag{8a}$$

where

$$[\Sigma Cl_2] = [Cl_2] + [Cl_3^-] = [Cl_2](1 + K_{Cl_3}[Cl^-])$$

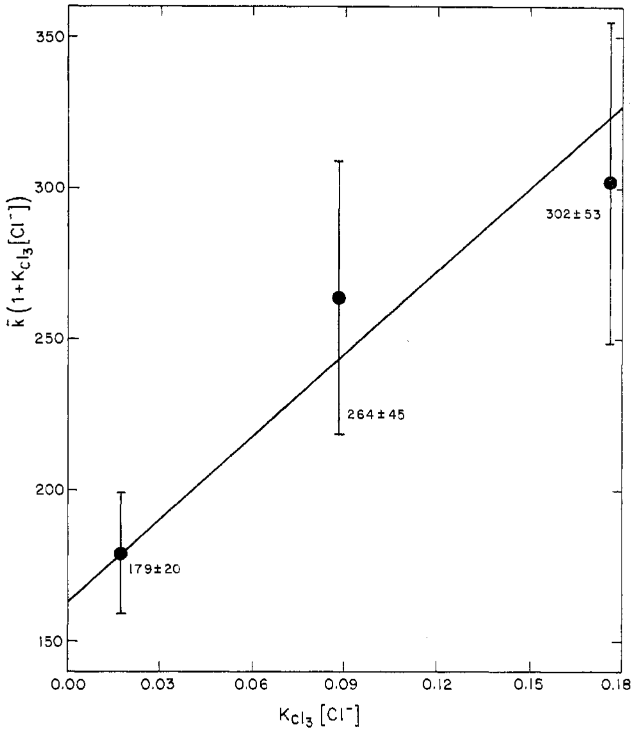

Figure 1.—Determination of k_1 and k_3.

The integrated form of eq 8a is

$$2\bar{k}t = \frac{1}{2[\Sigma Cl_2]_0 - [Fe^{2+}]_0} \times \ln\left(\frac{2[\Sigma Cl_2]_0 + [Fe^{3+}]_0 - [Fe^{3+}]}{[Fe^{2+}]_0 + [Fe^{3+}]_0 - [Fe^{3+}]}\right) \tag{8b}$$

The rate constants $\bar{k}$ obtained using this integrated equation are listed in Table II. As can be deduced from Table II, the quantity $\bar{k}$ increases with increasing chloride ion concentration. This suggests that both Cl_2 and Cl_3^- are effective as oxidants and that the rate equation is

$$d[Fe^{3+}]/dt = 2k_1[Fe^{2+}][Cl_3^-] + 2k_3[Fe^{2+}][Cl_2] \tag{9}$$

If the ratio of trichloride ion to aqueous chlorine is constant for a given run, it can be shown that

$$\bar{k} = \frac{k_1K_{Cl_3}[Cl^-] + k_3}{1 + K_{Cl_3}[Cl^-]} \tag{10}$$

In Figure 1 the quantity $\bar{k}(1 + K_{Cl_3}[Cl^-])$ is plotted *vs.* $K_{Cl_3}[Cl^-]$, as suggested by eq 10. A straight-line fit to the data was calculated by least squares and is shown as a solid line; the slope and intercept with our estimates of their errors are $k_1 = 910 \pm 100\ M^{-1}\ sec^{-1}$ and $k_3 = 163 \pm 20\ M^{-1}\ sec^{-1}$. These values may be compared with those obtained by other workers: our value of k_1 is in excellent agreement with the value of 878 M^{-1} sec^{-1} at 25°, $\mu = 3.0$ obtained by Sutin using a flow technique,[8] and our value of k_3 is in fair agreement with the value of 85 M^{-1} sec^{-1} at

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[6] M. S. Sherrill and E. F. Izard, *J. Am. Chem. Soc.*, 1667 (1931).

[7] G. Zimmerman and F. C. Strong, *ibid.*, **79**, 2063 (1957).

[8] N. Sutin, personal communication.

TABLE II

CALCULATED RATE CONSTANTS[a]

$[H^+]$	$[Cl^-]$	$10^5[Fe^{2+}]_0$	$10^5[\Sigma Cl_2]_0$	$10^5[Fe^{3+}]_0$	$\bar{k}$ at 30°, M^{-1} sec^{-1} × 10^{-2}
1.00	1.00	4.37	0.66	0	2.99
		8.75	0.32	0	2.82
		8.75	0.81	0	2.49
		8.75	1.26	0	3.15
		8.75	1.92	0	2.28
		4.37	1.48	0	5.64[b]
		8.75	3.53	0	3.54
		13.12	4.94	0	2.19
		8.75	0.96	2.48	2.05
		8.75	1.88	2.25	2.31
		8.75	2.58	2.28	2.29
		8.75	3.56	2.26	2.22
		4.37	1.03	2.11	2.37
		4.37	1.72	2.11	2.39
		8.75	1.09	4.22	1.99
		8.75	1.78	4.14	2.31
		8.75	2.46	4.26	2.34
		8.75	1.43	8.48	1.39
		8.75	2.96	8.66	2.01
		8.75	1.59	0	2.66
		8.75	2.38	0	2.23
		8.75	3.14	0	2.11
0.05	1.00	4.37	0.75	0	2.87
		4.37	1.64	0	3.66
		4.37	2.46	0	3.78
		4.37	4.10	0	4.55[b]
0.10	1.00	8.75	1.36	0	2.71
		8.75	2.15	0	2.93
		8.75	2.87	0	2.95
		8.75	3.68	0	2.94
		4.37	1.29	0	2.79
		4.37	2.30	0	2.48
				Av	2.57 ± 0.53
1.00	0.50	8.75	1.28	0	2.61
		8.75	2.02	0	2.08
		8.75	2.71	0	2.31
		8.75	3.48	0	1.92
		4.37	1.04	0	3.21
		4.37	3.48	0	2.45
				Av	2.43 ± 0.45
1.00	0.10	8.75	1.24	0	1.74
		8.75	1.97	0	1.83
		8.75	2.54	0	1.55
		8.75	3.36	0	1.74
		4.37	1.32	0	1.58
		4.37	3.36	0	2.09
				Av	1.76 ± 0.20
					$\bar{k}$ at 15°
1.00	1.00	8.75	0.85	0	0.867
		8.75	1.45	0	0.975
		8.75	2.28	0	0.957
		8.75	3.28	0	0.915
		4.37	1.75	0	1.34
		4.37	3.28	0	1.09
				Av	1.02 ± 0.17

[a] All concentrations: *F*. [b] These values not included in the average.

25°, $\mu = 3.0$ found by Sutin and his co-workers.[5] On the other hand, our value for the over-all rate constant is roughly an order of magnitude larger than the value quoted by Davidson.[3] We feel that the higher value we find is more nearly correct, especially in view of the agreement of our individual rate constants with those found by Sutin.

Our data are not sufficiently detailed to permit determination of the temperature coefficient of the rate constants k_1 and k_3. For the over-all rate constant at $[Cl^-] = 1.00$ between 15 and 30°

$$\bar{k} = 10^{10.5} \exp[-(11{,}200 \pm 100)/RT] \tag{11}$$

Inhibition

There was no demonstrable inhibition by added ferric ion over the limited range studied; it was impractical to attempt high initial ferric ion concentration because of the high absorptivities of the ferric ion and its chloride complexes. Thus, there is no positive evidence for the chlorine radical reaction path of eq 5–7. On the other hand, Figure 1 shows a small negative curvature. This would be expected if the reaction proceeded through an iron(IV) intermediate *via* reactions 2–4, since chloride ion can act as an inhibitor by back-reaction with Fe(IV) [reverse of reactions 2 and 3]. Since the negative curvature lies well within the experimental error of the measurement, the above chain of reasoning is clearly not conclusive, and it is not possible to determine with certainty whether Cl_2^- or Fe(IV) is the important intermediate. Experiments at very high chloride ion concentrations might distinguish between the two mechanisms.

Copper Catalysis

While developing a procedure for the coulometric titration of ferrous iron with electrolytically generated chlorine using an amperometric end point, Farrington, Schaefer, and Dunham[9] observed that the rate of reaction between iron(II) and chlorine was catalyzed by small amounts of cupric ion. We have studied this effect briefly at one initial concentration of chloride ion, ferrous ion, and chlorine, and at two different ferric ion concentrations. It was not possible from our data to distinguish a mechanism involving a copper(III) intermediate from one involving a copper(I) intermediate such as that observed by Cher and Davidson[10] for the iron(II)–oxygen reaction; our spectrophotometric technique was not well adapted to these fast reactions. Nevertheless, the data we obtained are consistent with the rate law

$$\frac{d[Fe^{3+}]}{dt} = 2\bar{k}[Fe^{2+}][\Sigma Cl_2] + 2k_{11}[Fe^{2+}][Cu^{2+}] \tag{12}$$

This may be integrated to give

$$2\{\bar{k}(2[\Sigma Cl_2]_0 - [Fe^{2+}]_0) + k_{11}[Cu^{2+}]\}t = \ln \frac{([Fe^{2+}]_0 + [Fe^{3+}]_0)\{\bar{k}(2[\Sigma Cl_2]_0 + [Fe^{3+}]_0 - [Fe^{3+}]) + k_{11}[Cu^{2+}]\}}{([Fe^{2+}]_0 + [Fe^{3+}]_0 - [Fe^{3+}])\{\bar{k}(2[\Sigma Cl_2]_0 + [Fe^{3+}]_0) + k_{11}[Cu^{2+}]\}} \tag{13}$$

The values of k_{11} derived from eq 13 are listed in Table III. These were calculated using an iterative tech-

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(9) P. S. Farrington, W. P. Schaefer, and J. M. Dunham, *Anal. Chem.*, **33**, 1318 (1961).

(10) M. Cher and N. Davidson, *J. Am. Chem. Soc.*, **77**, 793 (1955).

TABLE III

CALCULATION OF k_{11}[a]

$T = 30.0°$, $[H^+] = [Cl^-] = 1.00$, $[Fe^{2+}]_0 = 6.57 \times 10^{-5}$, $[\Sigma Cl_2]_0 = 3.19 \times 10^{-5}$, $\bar{k} = 257\ M^{-1}\ sec^{-1}$

$10^5[Fe^{3+}]_{20\ sec}$	$10^5[Cu^{2+}]$	k_{11} from (13), $M^{-1}\ sec^{-1}$
2.43	0.33	148
2.43	0.67	73
2.73	1.00	115
3.81	5.00	225
4.60	10.00	211
	Av	154 ± 60

[a] All concentrations: *F*.

nique. The rather high degree of uncertainty in k_{11} may be attributed to experimental difficulties in the spectrophotometric method and to reaction half-lives of less than 20 sec in some cases. However, we were able to measure the slope of one plot of ln $[Fe^{2+}]$ *vs.* time at 20 sec and from this to calculate a single value of 162 ± 15 M^{-1} sec^{-1} for k_{11}, in good agreement with the average.

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CONTRIBUTION FROM GENERAL CHEMICAL RESEARCH LABORATORY,
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The Electron Paramagnetic Resonance Spectrum of Chlorine Dioxide in Solution. Effect of Temperature and Viscosity on the Line Width

BY N. VANDERKOOI, JR., AND T. R. POOLE

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An epr study was made of chlorine dioxide in solution for the temperature range 25 to −180°, using as solvents CCl_4, CCl_3F, CCl_2F_2, $CClF_3$, and CF_4. The *g* value obtained was 2.0103, and the isotropic hyperfine splittings were found to be 17.0 and 13.7 gauss for the Cl^{35} and Cl^{37} isotopes, respectively. The effect of temperature and solvent viscosity on the line width of the hyperfine components of ClO_2 was found to agree with the theory of spin-rotational interaction as developed by Kivelson. From this the viscosity of the solvent could be estimated.

Several previous studies have been made on ClO_2 in both the liquid and solid phases. Using ethanol, water, acetone, and benzene as solvents for ClO_2, a single epr line was observed at 273°K and a partially resolved quartet at 193°K. This gave a hyperfine splitting of 17 gauss, a line width of 8 gauss, and a *g* value of 2.010.[1]

With ClO_2 dissolved in H_2O, H_2SO_4, H_3PO_4, CCl_4, and glycerol at room temperature, a four-line spectrum was observed.[2] In the case of CCl_4, a single broad line was observed at 25° and this was partially resolved into a quartet at −35°, but no line-width measurements were reported. However, it was observed that the line width was less in the hydrogen-containing solvents than in the CCl_4. It was suggested that this was due to hydrogen bonding. For ClO_2 dissolved in H_2SO_4 at room temperature, a hyperfine splitting of 16.5 gauss and a *g* value of 2.0093 were observed.[3]

The ClO_2 free radical was formed in a single crystal of $KClO_4$ by X-ray irradiation.[4] The isotropic hyperfine splitting of 15.4 gauss and an average *g* value of 2.0102 were calculated from the observed anisotropic hyperfine splitting.

We have studied the epr spectrum of ClO_2 in various solvents down to very low temperatures. The solvents were chosen so that the isotropic spectrum of ClO_2 could be observed over a wide temperature range along with large variations in the solvent viscosity. With these temperatures and solvents, the hyperfine splittings of the two chlorine isotopes were resolved and their splittings were measured accurately. The line width of the hyperfine components was studied as a function of the temperature and solvent. These line-width data could be related to the viscosity of the solvent and were found to agree with the theory of spin-rotational interaction developed by Kivelson.[5] The line-width data also lead to estimates of the viscosity of the solvent for temperature ranges in which the viscosity has not been measured by other methods.

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(1) J. E. Bennett, D. J. E. Ingram, and D. Schonland, *Proc. Phys. Soc.* (London), **A69**, 556 (1956); J. E. Bennett and D. J. E. Ingram, *Phil. Mag.*, **1**, 109 (1956).

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(3) P. W. Atkins, J. A. Brivati, N. Keen, M. C. R. Symons, and P. A. Trevalion, *ibid.*, 4785 (1962).

(4) T. Cole, *Proc. Natl. Acad. Sci. U. S.*, **46**, 506 (1960).

(5) R. Wilson and D. Kivelson, *J. Chem. Phys.*, **44**, 154 (1966); P. W. Atkins and D. Kivelson, *ibid.*, **44**, 169 (1966).