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BETWEEN Mn^{2+} AND F^- , Cl^- , I^- OR SO_4^{2-} .

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Electron Paramagnetic Resonance Studies of Complex Ion Formation
Between Mn^{2+} and F^- , Cl^- , Br^- , I^- or SO_4^{2-} . *

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Abstract

While Mn^{2+} in aqueous solution forms only rather weak complexes with simple anions, its epr line width is affected by the presence of such anions. The line width is a measure of the electron spin relaxation time and this time is influenced by the rates of reaction and the equilibrium of complex ions. Hayes and Myers proposed a theory which assumes a two step process for complex ion formation and they related the

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epr line width to the rate constants for each step. We have measured the line width for Mn^{2+} in aqueous solutions containing either F^- , Cl^- , Br^- , I^- or SO_4^{2-} and our results are in good agreement with this two step theory. These data are used to evaluate certain rate and equilibrium constants at $22^\circ C$ and $160^\circ C$. Comparison is also made to similar results that have been obtained by other methods.

I. Introduction

Ion pair formation is to be expected in ionic solutions. In aqueous solutions the cations are heavily solvated so that the anions have to displace water molecules in order to form ion pairs. One possible ion pair is a complex in which the cation largely retains its full solvation sphere although perhaps distorted by the anion. This kind of an ion pair has a large interionic distance and only a small entropy increase due to solvation changes. At the other extreme, ion pairs can be formed in which the solvation sphere is breached and large entropy changes will occur.

Most spectroscopic methods are not sensitive to outer sphere coordination, but the epr spectra of high-spin, S-state, transition metal ions are affected by such coordination. The line widths of these ions are due to a time dependent zero-field splitting which is averaged in solution. While the zero-field splitting may be only slightly increased by the formation of an outer sphere complex its correlation or averaging time is greatly increased over that of the simple hydrated ion. In addition, the inner sphere coordination can cause a large increase in the apparent zero-field splitting and quite broad epr lines.

In a previous publication¹ it was shown that Mn^{2+} in aqueous solution had an epr spectrum which was broadened by Cl^- and SO_4^{2-} . A two step coordination model was proposed to explain this broadening and sets of equations were established which depended upon the rates of formation and dissociation of an outer and inner sphere complex. While all these rates could not be evaluated at that time, a consistent picture was established and a few specific rates were determined from the epr data.

In this paper we have obtained data for the broadening of Mn^{2+} by Cl^- , Br^- , I^- , F^- and SO_4^{2-} . For Cl^- and SO_4^{2-} greater attention was paid to ionic strength than was previously done.¹ We were also able to further justify the pattern of rate constants previously assumed and to firmly establish certain rate and equilibrium constants for Mn^{2+} in aqueous solution.

II. Experimental

As previously done,¹ we measured the first derivative epr line width (ΔH) for the $M_I = + 1/2$ hyperfine component of Mn^{2+} in aqueous solution. This was done both near room temperature and in sealed tubes to above 200°C. Samples were prepared from ordinary, laboratory distilled water and weighed amounts of available salts. Almost all of the solutions were acidified to approximately pH5 with $HClO_4$ to prevent precipitation of $Mn(OH)_2$. Except for solutions containing fluoride ion, acid strength does not seem to affect the results.

The only solutions which were purposely deoxygenated were those used for the sulfate runs. Water for these runs was boiled for some time before use. Other solutions were made with ordinary laboratory distilled water. It is unfortunate that more attention was not given to this detail because dissolved oxygen might be expected to contribute somewhat to line widths.

Other data on vanadyl² and nitrosodisulfonate^{2,3} ions, suggests that the line width contribution due to molecular oxygen might be about 0.3 gauss in a 20° air saturated solution, with slightly increased line width contribution at higher temperatures. The water used could have contained

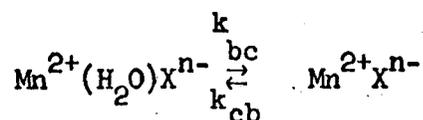
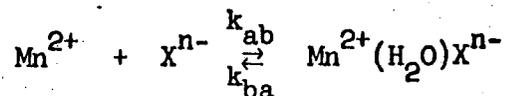
oxygen in varying amounts up to the air saturated concentration, but an examination of the data, particularly that for perchlorate solutions, and including the deoxygenated perchlorate data taken to standardize the sulfate runs shows no oxygen broadening. Even at high temperatures there are no deviations which could not be attributed to experimental error or ionic strength. So it seems that the effect of oxygen on Mn^{2+} is small. It might contribute to small systematic errors or to experimental scatter, but it cannot significantly change the large line width differences which were measured.

The procedure for obtaining accurate line widths at elevated temperatures is described elsewhere.² In this work the data previously presented¹ for the line width of $0.1M Mn(ClO_4)_2$ was used as reference. More precise data were obtained near room temperature, but the previous results for above $80^\circ C$ are quite accurate. The experimental quantity of interest is ΔH_{xs} the excess line width above that of the reference solution. Extensive tables of line widths can also be found elsewhere.²

III. Theory

The following is a brief summary of the theory of Hayes and Myers,¹ including only the elements necessary for an analysis of experimental data. They assume that manganous ions in water solution exist in three forms, isolated ions, ions with an anion in the second coordination sphere, and ions with an anion in the first coordination sphere. These three species could be designated Mn^{2+} , $Mn^{2+}(H_2O)X^{n-}$, and $Mn^{2+}X^{n-}$ respectively, or, for convenience they could be named species a, b, and c. The

following reactions and constants are defined:



$$K_{ab} = \frac{k_{ab}}{k_{ba}} \quad K_{bc} = \frac{k_{bc}}{k_{cb}}$$

$$\tau_a = 1/k_{ab} [\text{X}^{n-}] \quad \tau_{ba} = 1/k_{ba}$$

$$\tau_{bc} = 1/k_{bc} \quad \tau_c = 1/k_{cb}$$

T_{2a} , T_{2b} , and T_{2c} are defined as the epr relaxation times of species a, b, and c which would be observed in these species if each were present during the whole observation period in the indicated form, and T_2 is the net relaxation time for the whole system.

In the case of fast exchange between two species a and b, where $\tau_a \ll T_{2a}$ and $\tau_{ba} \ll T_{2b}$ one can show that if we neglect species c

$$1/T_2 = P_a/T_{2a} + P_b/T_{2b}$$

where P_a and P_b are the mole fractions of a and b. A useful form of the above equation when $T_{2a} > T_{2b}$ and $P_a > P_b$ is:

$$1/T_2 - 1/T_{2a} = P_a K_{ab} [\text{X}^{n-}] (1/T_{2b} - 1/T_{2a}) \quad (1)$$

In the above equation, $1/T_2 - 1/T_{2a}$ is proportional to the excess line width due to the presence of an anion.

At low temperatures, say below 80°C, if K_{bc} is small and $\tau_{bc} \gg T_{2b}$ we may ignore the presence of species c and use the above equation.

These assumptions are justified in the cases of the anions F^- , Cl^- , Br^- and I^- as will be shown in a later section concerned with low temperature results. In favorable cases K_{ab} and T_{2b} can be measured using Equation (1).

If one has the case that $\tau_a > T_{2a}$, $\tau_{ba} > T_{2b}$ and P_b is small, again ignoring species c, then

$$1/T_2 - 1/T_{2a} = 1/\tau_a = k_{ab} [X^{n-}] \quad (2)$$

This condition is satisfied with any anion at infinite dilution and to a fair approximation in the concentrations of sulfate discussed in the results section. Using this equation, k_{ab} can be measured.

At high temperatures and high concentrations relaxation proceeds through species c and if $\tau_c > T_{2c}$, every time species c is formed it results in relaxation. With the conditions

$$\tau_a < T_{2a}, \tau_b < T_{2b}, T_{2c} < \tau_c, \text{ and } \tau_{bc} < T_{2b}$$

$$1/T_2 = P_a/T_{2a} + P_b/\tau_{bc}$$

or

$$1/T_2 - 1/T_{2a} = P_a K_{ab} k_{bc} [X^{n-}] \quad (3)$$

These conditions are rather well met by Cl^- , Br^- and I^- ions at high temperatures in high concentrations. The product $K_{ab} k_{bc}$ and its activation energy can be measured. At lower concentrations τ_a becomes comparable to T_{2a} and one must use Equation (2).

If none of these conditions are met then one can use the more general equation, proposed by Pearson and Buch⁴

$$T_2^2 = \left[\frac{T_{2b}(1 + T_{2a}/\tau_a) + T_{2a}(1 + T_{2b}/\tau_b)}{1 + T_{2a}/\tau_a + T_{2b}/\tau_b} \right]^2 - \frac{2 T_{2a} T_{2b}}{1 + T_{2a}/\tau_a + T_{2b}/\tau_b} \quad (4)$$

Unfortunately this equation must be used for our high temperature sulfate data because all terms are of comparable size. In the most general case the lines are not Lorentzian and even Equation (4) is only approximate.

IV. Manganous Halide Solutions

A. Low Temperatures

We shall first consider solutions at low temperatures (5° to 25°C). A natural division is found between calculations and results in this low temperature range and those at higher temperatures (100° to 200°C) which will be discussed later. Low temperatures are characterized by small excess line width, ΔH_{xs} , values which are independent of temperature. At high temperatures ΔH_{xs} is large and a strong function of temperature.

Experimentally the region of 5° to 25° is somewhat difficult because since the intrinsic line width is changing very rapidly with temperature, the temperature must be measured very accurately, or at least precisely in order to get a good measurement of ΔH_{xs} . Every effort was made to achieve high precision. The halide studies used the same equipment, operated in the same way and all data were taken during the short interval of only a few days. The data are expected to be internally consistent so that systematic errors, which could lead to absolute errors of $\pm 1^\circ\text{C}$, can be largely ignored since they will cancel in all comparisons.

A plot of these data in Figure 1 shows how accurately temperature and line width can be measured. They also show the invariance of ΔH_{xs} with temperature. In Figure 1 the quantity .90 gauss has been subtracted from all chloride data. One can see that there is no clear indication of any appreciable activation energy for the processes contributing to chloride ion broadening and that ΔH_{xs} is approximately the .90 gauss subtracted. Over the range of 6° to 22°, if ΔH_{xs} changed by 10%, an activation energy of 1 kcal/mole would be indicated. Clearly the change is not larger than this.

To get data as accurate as possible it is necessary to work at a constant temperature and average a great many runs. This was done for many different samples and at temperatures close to 22°C.

It would be laborious and is unnecessary to adjust temperature to exactly the same value. From Figure 1, the slope of ΔH versus T is known and is about -.45 gauss/degree. Points taken within 1° of 22° were corrected to 22°C and averaged. Each point was already the average of ten measurements and on the basis of 12 points for $0.05M \text{ Mn}(\text{ClO}_4)_2 + 0.50M \text{ NaClO}_4$ we obtained $\Delta H_{22} = 23.58$ gauss with an average deviation of 0.08 gauss. With 9 points for $0.05M \text{ Mn}(\text{ClO}_4)_2 + 0.50M \text{ NaCl}$ we obtained $\Delta H_{22} = 24.52$ gauss with an average deviation of 0.06 gauss. Thus these more precise measurements give much the same excess width as found in Figure 1.

In order to confirm the expected linear dependence of the excess width upon anion concentration we varied the chloride concentration at constant ionic strength. These data are shown in Table I. Within the limits of error this linearity is established. Also given in Table I are data for added NaBr and NaI. The contribution for I^- is close to zero, but Br^- has about one-half of the Cl^- value.

These ions form very weak complexes with Mn^{+2} . Hayes and Myers¹ have estimated values for the lifetimes in Cl^- solutions. The lifetime of the inner-sphere complex (species c) is so long that it can be neglected at low temperatures. For 0.5M solutions of Cl^- with $k_{ab} = 2 \times 10^{10} M^{-1} sec^{-1}$ then $\tau_a = 2.5 \times 10^{-11}$ sec. Combining this with the other estimates of Table I in Reference 1 one can see that our Equation (1) should be applicable to the low temperature Cl^- , Br^- and I^- data.

For F^- we show from our data that $T_{2a}/T_{2b} = 22$ at 22°C. This is close to the estimate¹ of 10 for Cl^- . Since this ratio should be very similar for all halides we shall assume this ratio for Cl^- , Br^- and I^- . With this assumption in Equation (1) we obtain $K_{ab} = 0.09, 0.045$ and < 0.01 for Cl^- , Br^- and I^- , respectively, at 22°C. The small activation energy for the line widths must result from similar activation energies for K_{ab} and T_{2b} . Since we find an activation energy of close to 3 kcal/mole for T_{2a} , as expected on viscosity considerations, we should also expect T_{2b} and hence K_{ab} to have this same activation energy.

For F^- one can anticipate even larger values of K_{ab} . Our results for F^- are given in Table II. Since HF is a weak acid we used solutions with a fixed ratio of HF to F^- and with $NaClO_4$ to keep the $[Na^+]$ also nearly the same. From Table II it can be seen that $\Delta H_{xs}/M(F^-)$ is not exactly constant and that higher $M(F^-)$ leads to smaller ratios. For large values of K_{ab} P_a decreases appreciably as $[F^-]$ increases. The last column in Table I takes the variation of P_a and $[F^-]$ into account assuming that $K_{ab} = 1.5M^{-1}$. If we use this value for K_{ab} we can also separate the two unknowns in Equation (1) for F^- and determine that at 22°C $T_{2a}/T_{2b} = 22$. Since the primary source of activation energy for T_{2a} and T_{2b}

is the viscosity of the water this ratio should not vary much with temperature. However, if as Hayes and Myers postulate, the increase in T_{2b} over T_{2a} is due to an increased correlation time one should find that this ratio is frequency dependent.

Our low temperature data for Cl^- , Br^- , I^- and F^- all can be explained by Equation (1). The derived constants are all reasonable and clearly support the pattern of times that were assumed by Hayes and Myers to explain the low temperature broadening of Mn^{2+} by these anions.

B. High Temperatures

Above 80°C Hayes and Myers observed that Mn^{2+} solutions containing Cl^- have a striking increase in line width. A plot of $\Delta H_{\text{xs}}/[\text{Cl}^-]$ gave an activation energy of 9.35 kcal/mole and this activation energy was ascribed to that of $K_{\text{ab}} k_{\text{bc}}$ in Equation (3). Ionic strength effects were evident from Hayes and Myers¹ data but this was not investigated by them. In our determinations of the line width of Mn^{2+} containing Br^- we went to low ionic strength and the effect of ionic strength became very evident. This is illustrated in Figure 2.

In Figure 2 the bottom three sets of points correspond to the Br^- data taken under conditions similar to Hayes and Myers¹ Cl^- data. The points for lower ionic strength clearly show a higher activation energy and a ΔH_{xs} value which is close to being proportional to $(\text{Br}^-)^{1/2}$. Considering the large change in ionic strength from 0.00125M MnBr_2 to 0.05M $\text{Mn}(\text{ClO}_4)_2 + 0.10\text{M KBr}$ this is not too surprising.

The theories of Debye and Hückel and of Brönsted predict that formation rates of complex ions involving ions of opposite charge will

decrease with increasing ionic strength. If we adapt a commonly used equation to the variation of K_{ab} with ionic strength, I , we predict that

$$\log K_{ab} - \log K_{ab}^{\infty} = -3.65 \times 10^6 z_+ z_- \left(\frac{\rho}{\epsilon^3 T^3}\right)^{1/2} \left(\frac{I^{1/2}}{1+I^{1/2}}\right)$$

where $I = \frac{1}{2} \sum_i m_i z_i^2$, m_i is the molality of the i th component and z_i is its charge. K_{ab}^{∞} is K_{ab} at infinite dilution, ρ is the density of water and ϵ is its dielectric constant. This equation allows an extrapolation to zero ionic strength such as shown in Figure 3. Points for Figure 3 were read from the best set of points of the same concentration shown in Figure 2. At 160° , $\epsilon = 41.87$ and $\rho = .9075^5$ so one expects $(\log K^{\infty}/K) \left(\frac{I^{1/2}}{1+I^{1/2}}\right) = 2.85$. At other temperatures this same quantity was calculated in the same way.

Three temperatures, 140° , 160° , and 190° are represented in Figure 3 and a line corresponding to the theoretical slope is drawn through the point at farthest right on the graph. This point is the specific excess line width of the $.05M \text{ Mn}(\text{ClO}_4)_2$ plus $.10M \text{ KBr}$. It can be seen that this slope comes fairly close to fitting the experimental results. Lines seem to be somewhat wider at low concentrations than predicted by the theory.

Hayes and Myers estimate that at 160°C $k_{ab} = 2 \times 10^{11} \text{ M}^{-1} \text{ sec}^{-1}$ for chloride. Other halide ions would be expected to have almost the same value. If this is the correct value, τ_a should be 4×10^{-9} sec in $.00215M \text{ MnBr}_2$ at 160° . $T_{2a} = 9 \times 10^{-9}$ at this same temperature so the inequality $\tau_a < T_{2a}$ used to derive the excess line width in Equation (3) is not especially good. This could explain the deviation seen in Figure 3 of the points at lowest concentration. At even lower concentrations

than were used τ_a becomes greater than T_{2a} and the specific broadening should become equal to k_{ab} , about 10^4 gauss M^{-1} . The .00125M $MnBr_2$ point is seen to deviate by 220 gauss M^{-1} at 160° . With accurate measurements at lower concentrations it would be possible to directly measure k_{ab} . This could be done with the 100 kc spectrometer which was used for the low concentration sulfate work to be described in the next section.

When bromide specific line widths are extrapolated to zero concentration they indicate an activation energy of 14.5 kcal/mole, considerably higher than the 9.35 kcal/mole found by Hayes and Myers for the most concentrated chloride solutions. Similar results were also obtained for broadening by I^- . These are given in Reference 2. If one corrects for the changes in concentrations brought about by volume expansion at the higher temperatures the activation energy should be increased by about .5 kcal M^{-1} . At high concentrations similar to those used by Hayes and Myers, and without volume correction, $MnBr_2$ and MnI_2 approach the same 9.35 kcal/mole activation energy as the $MnCl_2$ they studied. This indicates that the activation energy is the same for all three ions for K_{ab} k_{bc} .

One can then calculate the difference in entropy, ΔS , for the quantity K_{ab} k_{bc} for Mn^{+2} and the three different halides. Iodide has a ΔS of $.74 \pm .02$ e.u. less than that of bromide. Comparing .05M $MnBr_2$ with line widths of .05M $MnCl_2$ found in Figure 2 of the paper by Hayes and Myers gives ΔS of chloride $.55 \pm .02$ e.u. greater than bromide.

V. Manganous Sulfate Solutions

A. Low Temperatures

Sulfate ions form relatively stable complexes with Mn^{2+} . At $20^\circ C$ $K_1 = (K_{ab} + K_{ac})$ is reported⁶ to be 158 and with a $\Delta H^\circ = 3.37$ kcal/mole. This indicates that a 0.005M $MnSO_4$ solution should be about 35% complex at $20^\circ C$ and that complex formation should increase with temperature. The effects of this complexing were clearly observed by Hayes and Myers. We attempted to unravel the $MnSO_4$ problem by operating with $10^{-3} M Mn^{2+}$ and with added Na_2SO_4 varying from 3×10^{-3} to $5 \times 10^{-4} M$. The ionic strength was kept approximately constant with added $NaClO_4$. The results of our measurements are given in Table III. It can be seen that the excess widths are comparatively large even at rather small sulfate concentrations.

Hayes and Myers estimate $k_{ab} = 2 \times 10^{10} M^{-1} sec^{-1}$ at $20^\circ C$. This value predicts that τ_a is 10^{-7} sec in $5 \times 10^{-4} M$ sulfate and 1.7×10^{-8} sec in $3 \times 10^{-3} M$ sulfate solution. This is to be compared with a T_{2a} at 20° of 2.8×10^{-9} sec. It can be seen that $\tau_a \gg T_{2a}$ and at the same time $\tau_b \sim \tau_a$ so that $\tau_b > T_{2b}$ which indicates that the equation to use to analyze these data is Equation (2). This equation however assumes that P_b is small, but this will only be true at low sulfate concentrations. The extrapolated value of specific broadening at zero sulfate concentration is approximately 1100 gauss M^{-1} and this corresponds to a $k_{ab} = 1.7 \times 10^{10} sec^{-1} M^{-1}$, which is rather close to the value estimated by Hayes and Myers. At higher sulfate concentrations the specific broadening is seen to be falling rapidly, presumably toward a value close to the 100 gauss M^{-1}

found by Hayes and Myers at high concentrations. This decrease however is not easily predicted by even the use of Equation (4). For this equation gives values of T_2 which are usually smaller than T_{2a} but sometimes larger than T_{2a} when $\tau_b \sim \tau_a$ and $T_{2b} < T_{2a}$. Since values of T_2 under these circumstances can never be expected to be larger than T_{2a} , it is clear that Equation (4) is even less satisfactory than Equation (2) when $\tau_a \gg T_{2a}$, $T_{2a} > T_{2b}$ and $P_b \sim P_a$. At least Equation (2) always gives $T_2 \leq T_{2a}$ and smoothly approaches it as a limit.

It was mentioned by Hayes and Myers that under some circumstances when $P_b \sim P_a$ a line shape function will be obtained which deviates a great deal from Lorentzian. In this case there is no easy way to correlate T_2 with a line width measurement. In particular, the derivative method of measuring line width tends to favor the species present with the larger T_2 value, which in our case is uncomplexed Mn^{2+} . It is quite possible that the drop in specific line width shown in Table III is due to deviation from a Lorentzian line shape function but this was not investigated.

B. High Temperatures

At higher temperatures broadening by sulfate is rather more complicated. In Figure 4 we present data taken near $160^\circ C$. Hayes and Myers estimate that at $160^\circ C$ $k_{ab} = 2 \times 10^{11} \text{ sec}^{-1} M^{-1}$. Then by calculation at $160^\circ C$ τ_a varies from 10^{-8} to 1.7×10^{-9} sec in sulfate solutions of between 5×10^{-4} and $3 \times 10^{-3} M$. At this same temperature the minimum line width is about 7 gauss so $T_{2a} = 9 \times 10^{-9}$ sec and $\tau_a \approx T_{2a}$. No simplified equation is applicable here because Equation (1) requires that $\tau_a \ll T_{2a}$ and Equation (2) requires $T_{2a} \ll \tau_a$.

All three species contribute to the line widths shown in Figure 4, but at a single temperature the relative contributions of species b and c are constant since the reaction converting b to c is first-order. At 160°C and relatively high sulfate concentrations Hayes and Myers observed a line width of about 20 gauss independent of the excess sulfate concentration. If we take this as the 160°C value for T_{2b} in Equation (4) including relaxation by species c and if we also assume Hayes and Myers¹ estimate for k_{ab} then we find these values suitable for Equation (4): $T_{2a} = 9.5 \times 10^{-9}$ sec, $T_{2b} = 2.5 \times 10^{-9}$ sec and $k_{ab} = 2 \times 10^{11} \text{ M}^{-1} \text{ sec}^{-1}$. The best fit to the observed line widths with Equation (4) is obtained with $\tau_{ba} = 1.25 \times 10^{-9}$ sec where it predicts $\Delta H_{xs}/[\text{SO}_4^{2-}]$ equal to 3080, 3070, 2685 and 2410 gauss M^{-1} for $[\text{SO}_4^{2-}]$ equal to 5×10^{-4} , 10^{-3} , 2×10^{-3} and $3 \times 10^{-3} \text{ M}$, respectively. The experimental values shown in Figure 4 at 160°C for $\Delta H_{xs}/\text{M}(\text{SO}_4^{2-})$ are 2800 gauss M^{-1} for the three lower concentrations and 2500 gauss M^{-1} for $\text{M}(\text{SO}_4^{2-})$ equal to 3×10^{-3} . Corrections for the amount of sulfate complexed, as was done in Table III, would be expected to make the experimental line widths even closer to that calculated by Equation (4).

Since $K_{ab} = k_{ab} \tau_{ba}$ these values would predict that $K_{ab} = 250 \text{ M}^{-1}$ at 160°C. Extrapolation of the zero ionic strength value for total complexing by sulfate⁶ indicates the $K_{ab} + K_{ac}$ should be close to $1,000 \text{ M}^{-1}$ at 160°C. Ionic strength effects in our solutions would be expected to lower this to close to 500 M^{-1} . This value is consistent with our estimates since it is expected that $K_{ab} \sim K_{ac}$.

VI. Discussion

Table IV summarizes the measured constants. For the halides we know of no previous values for K_{ab} . For Cl^- attempts⁶ have been made to measure K_1 and the few reported values are reasonably close to our K_{ab} value. There appears to be no previous work on F^- and Mn^{2+} , although its K_1 values should be large enough to measure by several techniques.

Our values for K_{ab} k_{bc} at 160°C have been extrapolated to zero ionic strength. The Cl^- value determined by Hayes and Myers was for $I \sim 0.5$ and due to ionic strength effects it had only a 9.35 kcal/mole activation energy. If their value and ours are extrapolated to 25°C then for $\log(K_{ab} k_{bc})$ after correcting for volume expansion we get 7.1 and 6.75, respectively. Our $I \sim 0.5$ value for K_{ab} for Cl^- can then be applied to the Hayes and Myers value so that $\log k_{bc} = 8.1$. Since k_{bc} should be little affected by ionic strength our zero ionic strength value should also be close to this. It is reasonable since K_{ab} might be expected to increase by about a factor of three in going to zero ionic strength.

While we have had to make a considerable extrapolation from 160°C to 25°C our value for k_{bc} is about a factor of four larger than the Swift and Connick⁷ value for the k_{bc} for H_2O and Mn^{2+} . The considerably smaller K_{ab} value for I^- indicates that its k_{bc} value could be close to the water value. One could hypothesize that the larger I^- can only occupy the first coordination sphere after an H_2O has left while the smaller Cl^- seems to be able to make a place for itself faster than an H_2O normally takes to leave.

At the present time there is more uncertainty for SO_4^{2-} . The original sound absorption work by Eigen and Tamm⁸ has been revised by Atkinson and Kor⁹ but still defended by others.¹⁰ The major difference between these workers is whether the sound absorption data can be resolved into two or three curves. As a result the two groups obtain quite different values for K_{bc} and for k_{bc} . For MnSO_4 solution Eigen and Tamm get 6.6 for $\log k_{bc}$ while Atkinson and Kor get 7.68. This last value is quite close to the Swift and Connick H_2O value. Hayes and Myers evaluated a k_{bc} value at 160°C of $5 \times 10^8 \text{ sec}^{-1}$ and with an activation energy of only 2.8 kcal/mole. If this is extrapolated to 25°C with a volume correction one obtains that $\log k_{bc} = 7.9$, a value close to Atkinson and Kor. However, in another paper Atkinson and Kor¹¹ determined that k_{bc} has an activation energy of 10.4 kcal/mole . If this larger activation energy is used then $\log k_{bc}$ is reduced to about 6.3, a value close to that of Eigen and Tamm.

It seems clear that the Hayes and Myers activation energy for k_{bc} is too low, but the fact that they got such a low value at all opens their 160°C evaluation of k_{bc} to question. There does not seem to be any doubt that by making the proper measurements on the epr of MnSO_4 solutions a good value for k_{bc} can be obtained even at 25°C . The MnSO_4 case is a good example of how the choice of solution concentration and conditions are very important for making a really satisfactory interpretation of epr data.

VII. Acknowledgments

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References

1. R. G. Hayes and R. J. Myers, *J. Chem. Phys.* 40, 877(1964).
2. D. C. McCain, Doctoral Thesis, Univ. of California, Berkeley, August 1966; also available as Lawrence Radiation Laboratory Report, UCRL-17064.
3. M. T. Jones, *J. Chem. Phys.* 38, 2892(1963).
4. R. G. Pearson and T. Buch, *J. Chem. Phys.* 36, 1277(1962).
5. G. C. Akerlof and H. I. Oshry, *J. Am. Chem. Soc.* 72, 2844(1950).
6. L. G. Sillén, Stability Constants of Metal-Ion Complexes, Chemical Society Special Publication No. 17, London (1964).
7. T. J. Swift and R. E. Connick, *J. Chem. Phys.* 37, 307(1962).
8. M. Eigen and K. Tamm, *Z. Elektrochem.* 66, 107(1962); M. Eigen and R. G. Wilkins in Mechanisms of Inorganic Reactions, R. F. Gould, Ed., Adv. in Chem. Series, No. 49, Am. Chem. Soc., Washington, D.C. 1965).
9. G. Atkinson and S. K. Kor, *J. Phys. Chem.* 69, 128(1965).
10. L. J. Jackopin and E. Yeager, *J. Phys. Chem.* 70, 313(1966); G. Atkinson and S. K. Kor, *J. Phys. Chem.* 70, 314(1966).
11. G. Atkinson and S. K. Kor, *J. Phys. Chem.* 71, 673(1967).

Table I.
 Low Temperature Line Widths and Excess Line Widths
 of Cl^- , Br^- and I^- Solutions

At 22°C			
Solution ^(a)	$\Delta H_{22}^{(b)}$ gauss	$(\Delta H_{22})_{\text{xs}}^{(c)}$ gauss	$\frac{(\Delta H_{22})_{\text{xs}}}{[\text{X}^-]}$ gauss M^{-1}
.125M NaCl+.375M NaClO ₄	23.84±.03 ^(d)	.26±.05	2.08±.40
.250M NaCl+.250M NaClO ₄	24.05±.02	.47±.04	1.88±.16
.375M NaCl+.125M NaClO ₄	24.15±.04	.57±.06	1.52±.16
.50 M NaCl ^(e)	24.52±.02	.94±.04	1.88±.08
.50 M NaBr	24.03±.02	.45±.04	.90±.08
.50 M NaI	23.58±.04	0±.06	0±.12
At 10°C			
Solution ^(a)	$\Delta H_{10}^{(f)}$	$(\Delta H_{10})_{\text{xs}}$	$\frac{(\Delta H_{10})_{\text{xs}}}{[\text{X}^-]}$
.50 M NaCl	30.83±.03	.87±.06	1.74±.12
.50 M NaBr	30.39±.02	.43±.05	.86±.10
.50 M NaI	30.11±.03	.15±.05	.30±.12

- (a) Includes $.05M \text{ Mn}(\text{ClO}_4)_2$. pH = 5
 - (b) Corrected to 22°C from data taken at $22 \pm 1^\circ$.
 - (c) $(\Delta H_{22})_{\text{xs}} = \Delta H_{22} - 23.58 \pm .02$ gauss.
 - (d) All limits of error are the average deviation divided by the square root of the number of observations.
 - (e) Includes some $.50M \text{ LiCl}$ data.
 - (f) $(\Delta H_{10})_{\text{xs}} = \Delta H_{10} - 29.96 \pm .03$ gauss.
-
-

Table II.

Fluoride Ion Data at 22°C

Sample	ΔH_{22}	$(H_{22})_{xs}^{(a)}$	$\frac{(\Delta H_{22})_{xs}}{M(F^-)}$	$P_a \frac{(\Delta H_{22})_{xs}^{(b)}}{[F^-]}$
.2M F ⁻ , .01M Mn ⁺⁺ (c)	28.16±.03	4.60±.05	23.0±.3	33.3±.4
.1M F ⁻ , .01M Mn ⁺⁺ (d)	26.21±.10	2.63±.12	26.3±1.2	31.4±1.4
.1M F ⁻ , .05M Mn ⁺⁺ (e)	26.26±.03	2.68±.05	26.8±.5	33.9±.6
.05M F ⁻ , .05M Mn ⁺⁺ (f)	25.01±.03	1.43±.05	28.6±1.0	33.2±1.1
.0404M F ⁻ , .05M Mn ⁺⁺ (g)	24.78±.01	1.20±.03	29.7±.8	34.0±.9
.0202M F ⁻ , .05M Mn ⁺⁺ (h)	24.09±.02	.51±.04	25.2±2.0	27.9±2.2
.30M F ⁻ , .001M Mn ⁺⁺ (i)	30.45±1.0	6.87±1.0	22.9±3.0	33.2±3.0
.40M F ⁻ , satd. Mn ⁺⁺ (j)	31.88±1.5	8.30±1.5	20.7±4.0	33.1±4.0

(a) $(\Delta H_{22})_{xs} = \Delta H_{22} - 23.58 \pm .02$

(b) Calculated by assuming that the reaction $Mn^{2+} + F^- = Mn^{2+}H_2O F^-$ has $K_{ab} = 1.5 M^{-1}$ and with $P_a = \frac{[Mn^{2+}]}{[Mn^{2+}][Mn^{2+}H_2O F^-]}$

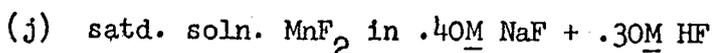
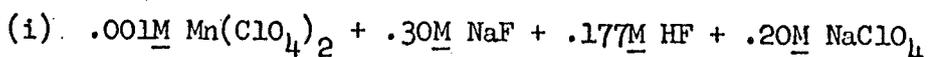
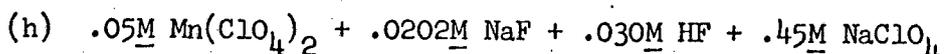
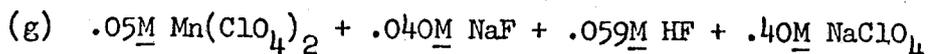
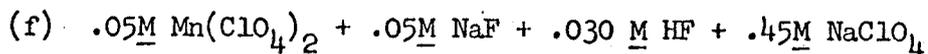
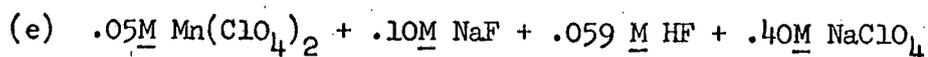
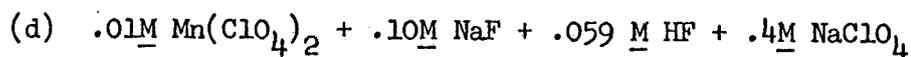
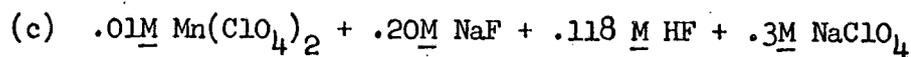


Table III.

Manganous Line Widths for Various Concentrations of Sulfate Ion at 20°C

$M(\text{SO}_4^{2-})$	$\Delta H_{20}^{(a)}$	$(\Delta H_{20})_{xs}^{(b)}$	$\frac{(\Delta H_{20})_{xs}}{M(\text{SO}_4^{2-})}$	$\frac{(\Delta H_{20})_{xs}}{[\text{SO}_4^{2-}]}$
0 (d)	$23.80 \pm .04$	--	--	--
5.0 ± 10^{-4} (e)	$24.24 \pm .08$	$.44 \pm .12$	880 ± 240	1020 ± 270
1.00 ± 10^{-3} (f)	$24.76 \pm .04$	$.96 \pm .08$	960 ± 80	1110 ± 90
2.00 ± 10^{-3} (g)	$25.00 \pm .04$	$1.20 \pm .08$	600 ± 40	675 ± 45
3.00 ± 10^{-3} (h)	$25.38 \pm .07$	$1.58 \pm .11$	530 ± 40	585 ± 40

(a) Data are for points within .5° of 20°C, and with values corrected to 20°. Limits of error are the average deviation divided by square root of number of observations.

(b) $(\Delta H_{20})_{xs} = \Delta H_{20} - 23.80 \pm .04$.

(c) Calculated by assuming that the reaction $\text{Mn}^{2+} + \text{SO}_4^{2-} = \text{MnSO}_4$ has a $K = 158$.

(d) $6.0 \times 10^{-3} \text{M NaClO}_4$. This and all other solutions contain $1.0 \times 10^{-3} \text{M Mn}(\text{ClO}_4)_2$ and $2.0 \times 10^{-4} \text{M HClO}_4$.

All solutions were deoxygenated.

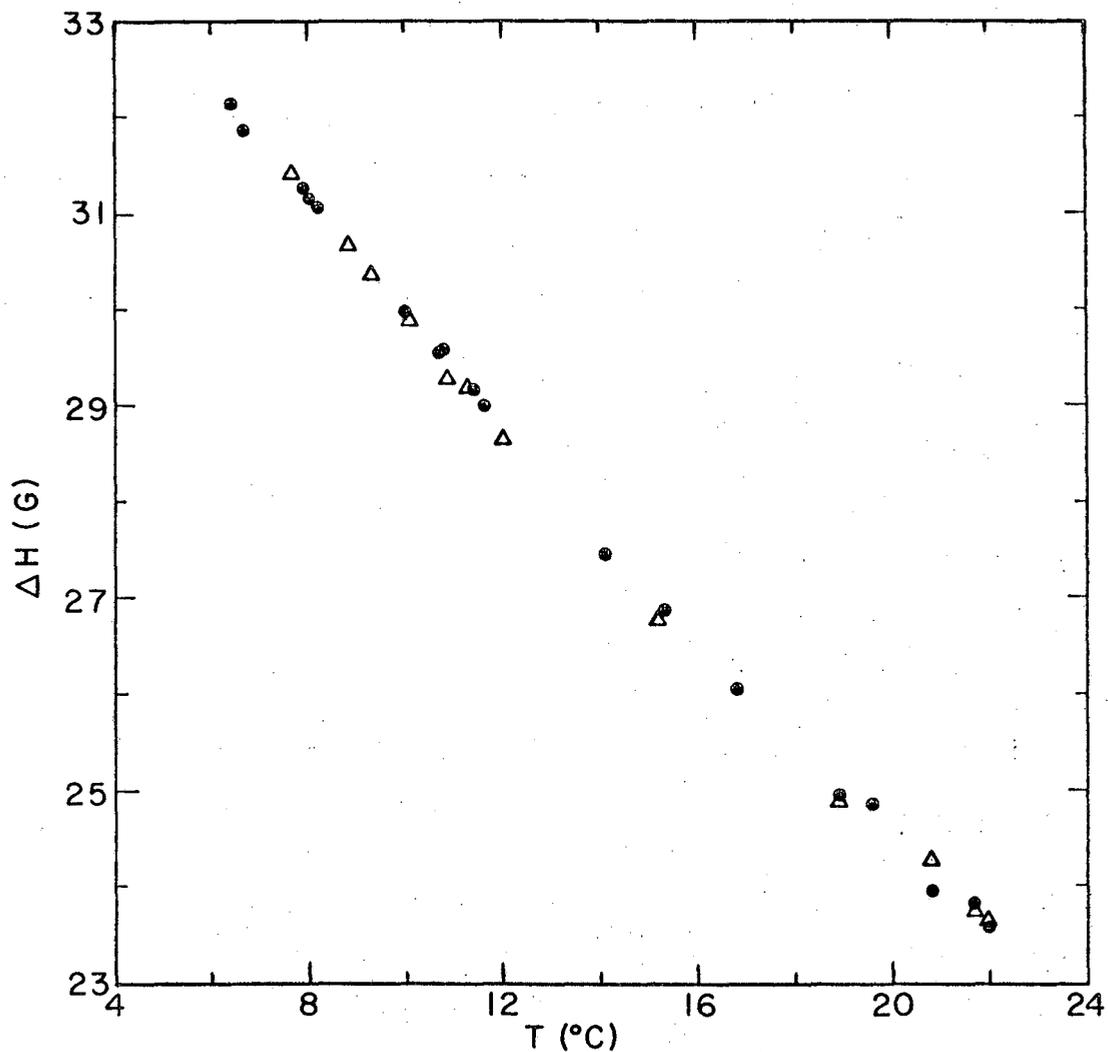
- (e) $.50 \times 10^{-4} \text{ M Na}_2\text{SO}_4 + 5.0 \times 10^{-3} \text{ M NaClO}_4$
(f) $1.00 \times 10^{-3} \text{ M Na}_2\text{SO}_4 + 4.0 \times 10^{-3} \text{ M NaClO}_4$
(g) $2.00 \times 10^{-3} \text{ M Na}_2\text{SO}_4 + 2.0 \times 10^{-3} \text{ M NaClO}_4$
(h) $3.00 \times 10^{-3} \text{ M Na}_2\text{SO}_4$
-

Table IV.

Summary of Results for Manganese Complexes

Measured Constants		
Anion	22°C	160°C
F ⁻	$K_{ab} = 1.5 \text{ M}^{-1}$ $T_{2a}/T_{2b} = 22$	--
Cl ⁻	$K_{ab} = 0.09 \text{ M}^{-1}$ ^a	$K_{ab} k_{bc} = 1.4 \times 10^{10} \text{ sec}^{-1} \text{ M}^{-1}$ ^b
Br ⁻	$K_{ab} = 0.045 \text{ M}^{-1}$ ^a	$K_{ab} k_{bc} = 1.1 \times 10^{10} \text{ sec}^{-1} \text{ M}^{-1}$ ^b
I ⁻	$K_{ab} < 0.01 \text{ M}^{-1}$ ^a	$K_{ab} k_{bc} = 0.8 \times 10^{10} \text{ sec}^{-1} \text{ M}^{-1}$ ^b
SO ₄ ⁼	$k_{ab} = 1.7 \times 10^{10} \text{ sec}^{-1} \text{ M}^{-1}$ ^c	$k_{ba} = 8 \times 10^7 \text{ sec}^{-1}$ $k_{bc} = 5 \times 10^8 \text{ sec}^{-1}$ ^d

- (a) With T_{2a}/T_{2b} assumed equal to 22 and for $I \sim 0.5$.
- (b) For $I = 0$ and with activation energy = 14.5 kcal/mole.
- (c) For I close to 0.5×10^{-2} .
- (d) From the measurements of Hayes and Myers.



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Figure 1. The black dots represent an average of ten measurements for the line width of the $M_I = +1/2$ component for $0.05M \text{ Mn}(\text{ClO}_4)_2 + 0.50M \text{ NaClO}_4$. The triangles are similar data for $0.05M \text{ Mn}(\text{ClO}_4)_2 + 0.50M \text{ NaCl}$ where 0.90 gauss is subtracted to make the points all fall on the same line.

Figure 2. The high temperature data for broadening by Br^- . Comparison should be made to Figure 2 of Reference 1. The greater range of ionic strengths shown in our data make evident both a displacement and a change in slope for the lines.

- 0.05 M MnBr_2
- 0.01 M MnBr_2
- 0.005 M MnBr_2
- ▽ 0.0025 M MnBr_2
- ▼ 0.00125 M MnBr_2
- 0.05 M $\text{Mn}(\text{ClO}_4)_2$ + 0.05 M KBr
- △ 0.05 M $\text{Mn}(\text{ClO}_4)_2$ + 0.1 M KBr

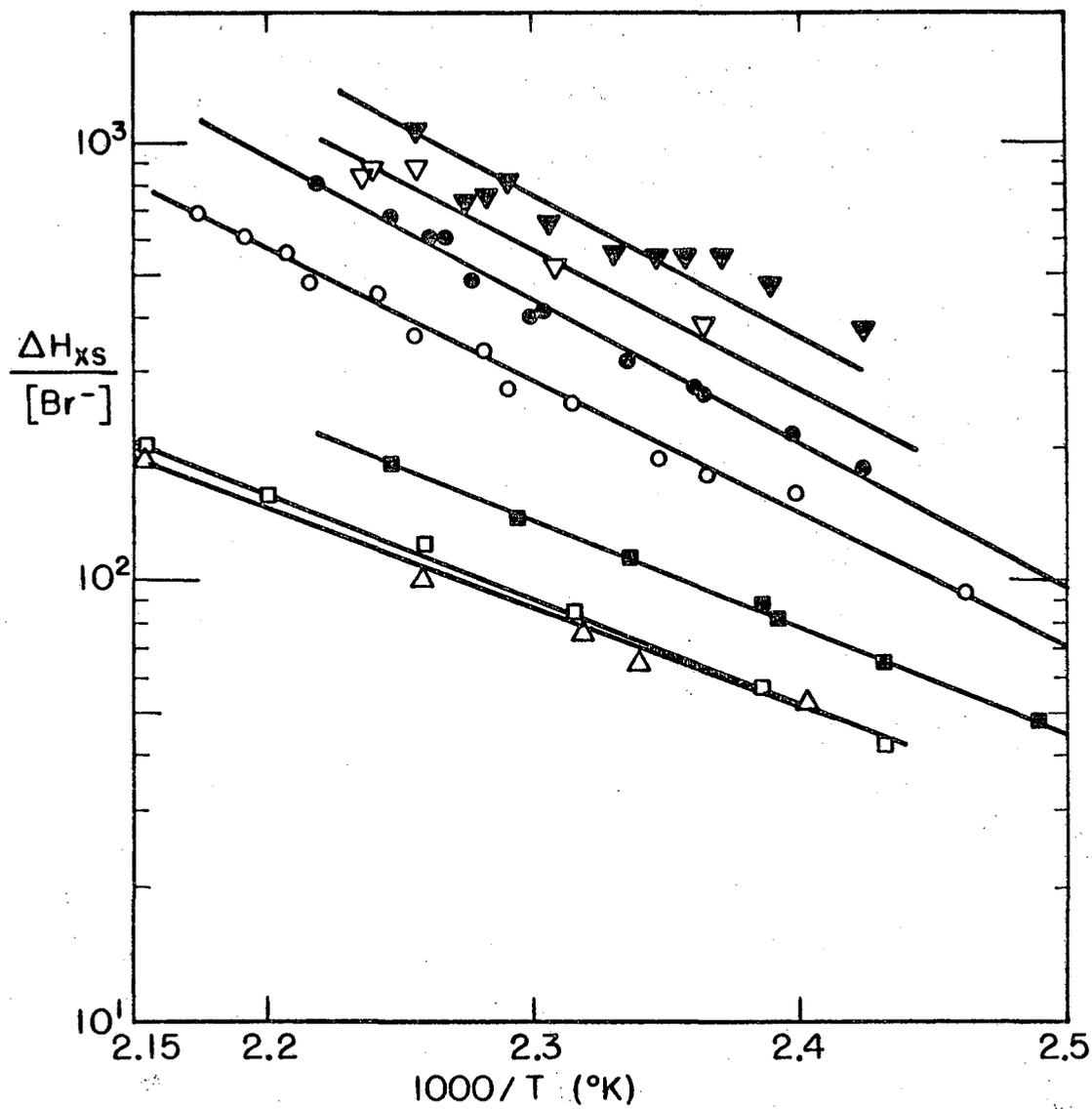
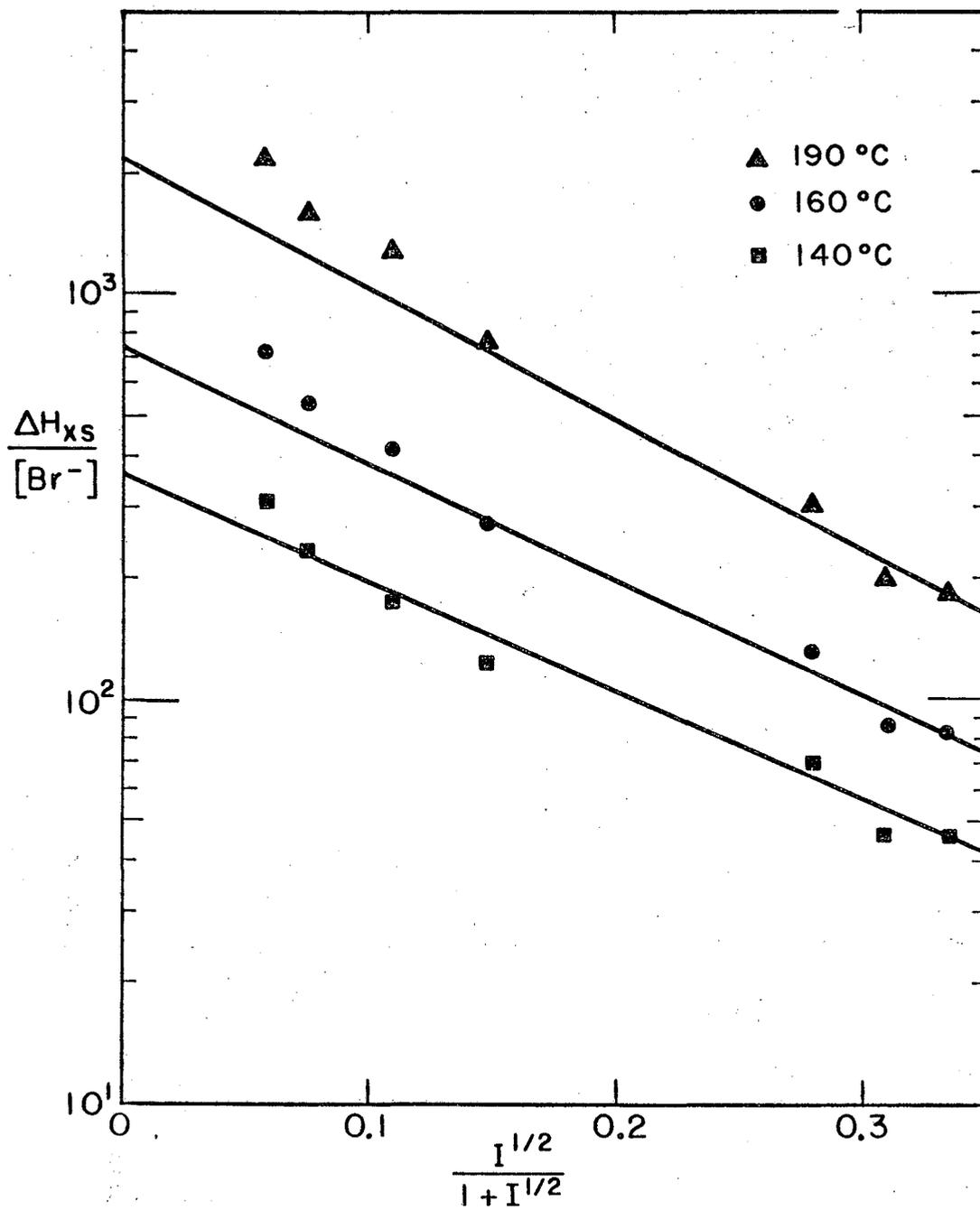
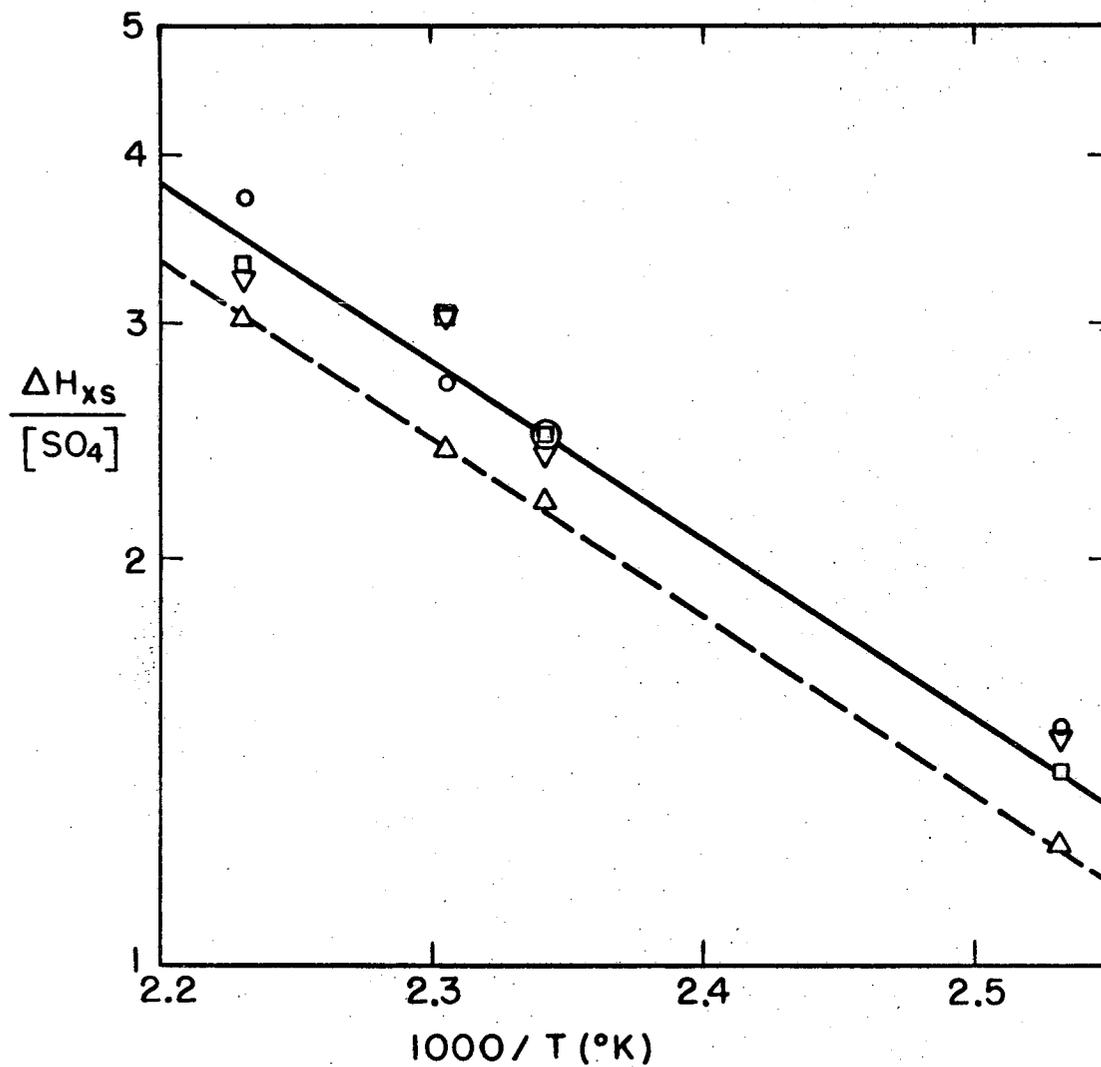


Fig. 2

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Figure 3. The extrapolation of the Br^- data to zero ionic strength. The lines are drawn with a theoretical slope through the points for 0.05 M $\text{Mn}(\text{ClO}_4)_2$ + 0.10 M KBr. Some of the deviation at low ionic strength is probably due to the failure of Equation (3) since it is expected that $\tau_a > T_{2a}$ for dilute solutions.





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Figure 4. The results for the solutions used in Table III from 120° to 175°C. □ 5×10^{-4} M, ▽ 1.0×10^{-3} M, ○ 2.0×10^{-3} M and △ 3.0×10^{-3} M in added Na_2SO_4 . The values for $\Delta H_{xs}/M(\text{SO}_4^{2-})$ are equal within experimental error for the three lowest concentrations of added sulfate. Points at $1000/T = 2.31$ were calculated as described in the text.

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