

# Manganese(III) and its Hydroxo- and Chloro-complexes in Aqueous Perchloric Acid: Comparison with similar Transition-metal(III) Complexes

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At 25°C the formation constant of  $\text{MnCl}^{2+}$  is found by spectrophotometry to be  $13.2 \pm 0.9 \text{ dm}^3 \text{ mol}^{-1}$  at ionic strength  $3.26 \text{ mol dm}^{-3}$ ; for  $\text{MnCl}$  the value is  $1.1 \pm 0.7 \text{ dm}^3 \text{ mol}^{-1}$ . Increase in the number of chloride ions in complexes results in longer wavelengths for the corresponding absorption maxima. In the absence of chloride the hydrolysis constant of  $\text{Mn}^{\text{III}}$  at ionic strength  $5.6 \text{ mol dm}^{-3}$  is found from voltammetry and potentiometry to be  $1.0_5 \pm 0.2_6 \text{ mol dm}^{-3}$ . Aged manganese(III) is found to be 15-25 % polymeric, from both kinetic and e.m.f. measurements. Comparison of formation constants for halogeno- and hydroxo-complexes of  $\text{M}^{3+}$  (first transition series) shows that a combination of charge-transfer, ligand-field and coulomb interactions underlies the observed sequences; the dipole moment of  $\text{OH}^-$  is also a factor.

The extent of interest in halide ( $\text{X}^-$ ) and hydroxo complexes of the trivalent cations  $\text{M}^{3+}$  of the first-row transition metals is evident from the growing number of measurements of stability constants  $K$  collated<sup>1</sup> or being recorded.<sup>2-5</sup> Solutions in quite concentrated  $\text{HClO}_4$  have often to be used; however, at ionic strengths  $I > 0.5 \text{ mol dm}^{-3}$  ionic activity coefficients change but slowly with composition, and for our purposes, comparison of  $\log K$  values in this range, such high electrolyte concentrations present few problems. Some  $K$  values<sup>1</sup> are less well founded than most. That<sup>1</sup> for  $\text{FeI}^{2+}$  cannot be obtained in  $\text{HClO}_4$ , since oxidation of  $\text{I}^-$  occurs by a mechanism which does not give a stability constant from the rate equation.<sup>4</sup> For  $\text{MnCl}^{2+}$  an estimate, from kinetics, of  $8.9 \text{ dm}^3 \text{ mol}^{-1}$  in  $2 \text{ mol dm}^{-3} \text{ HClO}_4$  has been recalculated<sup>5</sup> as  $13.5 \text{ mol dm}^{-3}$ . This revision may well reflect only the uncertainty of the estimate. For  $\text{MnOH}^{2+}$  formation the original<sup>6</sup> spectrophotometric value of the hydrolysis constant  $K_h \approx 4 \text{ mol dm}^{-3}$  in  $I = 6 \text{ mol dm}^{-3}$ , was re-measured<sup>7a</sup> as  $0.93 \text{ mol dm}^{-3}$  in ionic strength  $4 \text{ mol dm}^{-3}$ , and  $0.96 \text{ mol dm}^{-3}$  (at 23°C).<sup>7b</sup> Values of  $K$  for both of these  $\text{Mn}^{\text{III}}$  complexes clearly need to be redetermined, by independent techniques if possible, and in this paper we report such measurements, first of  $K_h$  by electrochemical methods<sup>9</sup> and secondly of  $K_{\text{Cl}}$  for  $\text{MnCl}^{2+}$  by spectrophotometry. Fresh  $\text{Mn}^{\text{III}}$  differs from aged  $\text{Mn}^{\text{III}}$  in that with time, a fraction of the fresh sample forms a polymeric species which reacts slowly in some electron transfer reactions.<sup>8</sup> It is possible to use e.m.f. data<sup>9, 13</sup> to substantiate a kinetic estimate of the fraction polymerised, which has some effect on the  $K$  values. Finally we compare  $K$  values for most of the  $\text{MX}^{2+}$  species, and elicit the major molecular factors governing the values observed.

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## EXPERIMENTAL

The voltammetric cell for measuring the variation of exchange current, and of e.m.f., with  $[H^+]$  was used<sup>9</sup> in the determination of transfer coefficient  $\alpha$  and rate constant in 3 mol  $dm^{-3}$   $HClO_4$  for the electrode reaction  $Mn^{III} + e_{Pt} \rightarrow Mn^{2+}$ . The ionic strength was now made 5.6 mol  $dm^{-3}$  in  $HClO_4 + NaClO_4$  so as to accommodate a sufficiently large change of  $[H^+]$ , from the minimum commensurate with the stability of  $Mn^{III}$ , 0.75 mol  $dm^{-3}$ , to 5.3 mol  $dm^{-3}$ . The solution was made 0.1 mol  $dm^{-3}$  in  $Mn(ClO_4)_2$  to suppress the disproportionation of  $Mn^{III}$ , the concentration of which was kept at  $1.89 \times 10^{-4}$  mol  $dm^{-3}$  throughout. The  $Mn^{III}$ , at near this concentration, was prepared at room temperature by the reaction<sup>8, 9</sup>  $4 Mn^{II} + Mn^{VII}$ , and aged for  $> 36$  h, at which time after a prolonged period of decrease the absorbance at 470 nm remained constant.  $Mn^{III}$  was standardised by amperometric titration<sup>8</sup> with iron(II).

To determine the  $MnCl^{2+}$  stability constant at ionic strength 3.26 mol  $dm^{-3}$  (a value chosen in connection with other work<sup>8</sup>) twenty four solutions of  $4 \times 10^{-4}$  mol  $dm^{-3}$   $Mn^{III}$ , 3 mol  $dm^{-3}$   $HClO_4$  and 0.05 mol  $dm^{-3}$   $Mn(ClO_4)_2$  containing 0.01-0.2 mol  $dm^{-3}$   $Cl^-$ , were examined at 25.0°C in 0.2-4 cm cells being Unicam SP500 spectrophotometer over the wavelength range 230-400 nm, where neither  $Mn^{II}$  nor  $Cl^-$  absorb. Enhancements of absorbance occurred, which were checked with doubled  $[Mn^{III}]$  at the two extreme  $[Cl^-]$  values. For both  $[Cl^-]$  values the enhancements were doubled, indicating that the absorbing complex(es) were monatomic in  $Mn^{III}$ . Further elaboration depended on assumptions regarding  $K_h$ .

## RESULTS AND DISCUSSION

## HYDROXO-COMPLEX

The value of the exchange current<sup>9</sup>  $i_0$  and the e.m.f.  $E$  at 25°C are given in table 1 for five different solutions at compositions differing only in  $[H^+]$  and  $[Na^+]$ , with  $[H^+] + [Na^+]$  constant. Notably, the transfer coefficient  $\alpha$  is identical for both acidities, strongly implying constancy of electroactive species.<sup>9</sup> The relationship between  $i_0$  at 5.3 mol  $dm^{-3}$   $H^+$  and at 0.75 mol  $dm^{-3}$   $H^+$  is

$$\log\{i_0(5.3)/i_0(0.75)\} = (1 - \alpha) \log\{5.3[(K_h/\text{mol } dm^{-3}) + 0.75] / 0.75[(K_h/\text{mol } dm^{-3}) + 5.3]\}.$$

TABLE 1.—VOLTAMMETRY AND POTENTIOMETRY ON  $Mn^{III}$  SOLUTIONS AT TWO DIFFERENT ACIDITIES

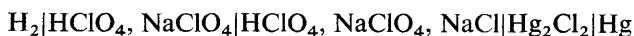
$[Mn^{III}] = 1.89 \times 10^{-4}$  mol  $dm^{-3}$ ,  $[Mn^{II}] = 0.1$  mol  $dm^{-3}$ ,  $I = 5.60$  mol  $dm^{-3}$ , 25°C

$[H^+]/\text{mol } dm^{-3}$	$E/V$	$-\log(i_0/A)$	$\alpha$
0.75	1.008	6.993	0.249
	1.006	6.998	0.255
	1.010	6.976	0.257
	1.009	6.994	0.256
	1.008	6.957	0.248
	mean:	$1.008 \pm 0.002$ [0.3657] <sup>a</sup>	$6.977 \pm 0.016$
5.30	1.052	6.794	0.251
	1.056	6.731	0.248
	1.057	6.781	0.250
	1.055	6.745	0.253
	1.056	6.777	0.258
	mean:	$1.055 \pm 0.001$ [0.2877] <sup>a</sup>	$6.767 \pm 0.021$

<sup>a</sup>  $E$  for  $H_2|HClO_4, NaClO_4, NaCl|Hg_2Cl_2|Hg$ ; 0.01 mol  $dm^{-3}$   $NaCl$ .

This expression follows irrespective of whether  $\text{Mn}^{3+}$  or  $\text{MnOH}^{2+}$  is assumed to be reduced, as it is kinetically impossible to identify the electroactive species. Indirect arguments from the mechanism<sup>9</sup> invoked to explain the low value of  $\alpha$  suggest that it is  $\text{Mn}^{3+}$ . From table 1 the left side of the equation is  $0.210 \pm 0.037$ , whence the value of  $K_h$  is  $0.95 \pm 0.35 \text{ mol dm}^{-3}$ .

The  $E$  values were combined with those for a cell



([NaCl] small), to give at the two  $[\text{H}^+]$  employed,  $E'$  values for the cell,



with  $I = 5.6 \text{ mol dm}^{-3}$  throughout ( $[\text{Mn}^{2+}]$  small). Hence  $(E')_{5.3} - (E')_{0.75} = RT/F \ln\{[(K_h/\text{mol dm}^{-3}) + 0.75]/[(K_h/\text{mol dm}^{-3}) + 5.30]\}$  which was  $1.374 \pm 0.002 - (1.342 \pm 0.001) \text{ V}$  or  $-32 \pm 3 \text{ mV}$ , giving  $K_h = 1.1 \pm 0.20 \text{ mol dm}^{-3}$ .

Preliminary measurements were carried out with calomel electrodes having electrolyte which differed in composition from that of the  $\text{Mn}^{3+}$ ,  $\text{Mn}^{2+}$  and hydrogen electrodes. The liquid junctions introduced slightly irreproducible error; nevertheless, the current against voltage curves (with  $\alpha$   $0.249 \pm 0.005$  and  $0.255 \pm 0.004$  at 0.75 and  $5.3 \text{ mol dm}^{-3} \text{ H}^+$ ) gave a  $K_h$  of  $1.05 \pm 0.30 \text{ mol dm}^{-3}$ , and from  $E'$  differences,  $-31 \pm 2 \text{ mV}$ , a  $K_h$  of  $1.1 \pm 0.20 \text{ mol dm}^{-3}$ . Since the additional uncertainty is only slight, we include all these values to obtain a mean of  $K_h = 1.0_5 \pm 0.2_6 \text{ mol dm}^{-3}$ . While a different ratio of activity coefficients is implicitly assumed constant in going from  $i_0$  to  $E$  to calculate  $K_h$ , the consequence is clearly within the experimental error of either method. The agreement of our value with the 0.93 obtained in a predominantly  $\text{Mn}(\text{ClO}_4)_2$  medium at  $I = 4 \text{ mol dm}^{-3}$  is satisfactory considering the difficulties of electrometry with this reactive ion, and the problems of extrapolation to zero time (to correct for polymer formation) involved in the spectrophotometry.<sup>7</sup> We have hitherto considered  $\text{Mn}^{\text{III}}$  monomeric: taking account of the polymeric fraction (below) shows that the high side of the quoted limits should be emphasized for the truly mononuclear equilibria.

#### CHLORO-COMPLEXES

By straightforward use of Beer's law and including an appropriate value of  $K_h$ , a three stage computation was employed. First it was assumed that  $\text{MnCl}^{2+}$  is the only chloro-complex. Then these initial  $K_{\text{Cl}}$  values obtained from 230-290 nm data

TABLE 2.—VALUES OF  $K_{\text{Cl}}$  FOR  $\text{Mn}^{3+} + \text{Cl}^- \rightleftharpoons \text{MnCl}^{2+}$  AT VARIOUS WAVELENGTHS

$\lambda/\text{nm}$	$K_{\text{Cl}}/\text{dm}^3 \text{ mol}^{-1}$	$\lambda/\text{nm}$	$K_{\text{Cl}}/\text{dm}^3 \text{ mol}^{-1}$
230	12.9	255	12.5
235	15.8	265	14.7
240	12.2	270	12.4
245	12.6	275	12.7
250	12.9	mean	$13.2 \pm 0.9$

$$K_h = 1.0 \text{ mol dm}^{-3} \text{ assumed}$$

were used to estimate  $K_{2\text{Cl}}$  for  $\text{MnCl}^{2+} + \text{Cl}^- \rightleftharpoons \text{MnCl}_2^+$ , which is invoked to account for the higher-wavelength absorption. This gave a small  $K_{2\text{Cl}}$  and a large  $\epsilon(\text{MnCl}_2^+)$  which justify the original assumptions and support the actual values of  $K_{\text{Cl}}$  initially obtained (table 2). Finally a complete Beer's law expression for the total absorbance gave better values of  $K_{2\text{Cl}}$ , see table 3. The algebra, straightforward but cumbersome,

is detailed elsewhere,<sup>10</sup> as are all individual measurements. Because the value of  $K_{Cl}$  depends on the value assumed for  $K_h$ , the calculation was repeated for a range of  $K_h$ , which established (table 4) that the dependence is not oversensitive, and is small enough to ensure that any further uncertainty introduced is smaller than that already inherent (table 2) in the parameter fitting. The  $K_h$  range almost certainly encompasses the true value for this medium.

TABLE 3.—APPROXIMATE VALUES OF  $K_{2Cl}$  FOR  $MnCl^{2+} + Cl^- \rightleftharpoons MnCl_2^+$  AT VARIOUS WAVELENGTHS

$\lambda/nm$	$K_{2Cl}/dm^3\text{ mol}^{-1}$
300	0.8
320	0.3
340	1.6
360	0.5
380	2.3

mean  $1.1 \pm 0.7\text{ dm}^3\text{ mol}^{-1}$ , with  $K_{Cl} = 13.2\text{ dm}^3\text{ mol}^{-1}$

The spectra observed and calculated are shown in fig. 1. If we add the longest wavelength maximum observed<sup>11</sup> in  $10\text{ mol dm}^{-3}$  HCl, which presumably indicates an even higher complex, the following sequence of absorbance maxima is seen:

species	$Mn^{3+}$	$MnCl^{2+}$	$MnCl_2^+$	$MnCl_n^{(3-n)+}$
$\lambda_{max}/nm$	210	240	300	550.

It is thus possible that the absorption bands are due to ligand-to-metal ion charge transfer. Our spectrophotometry results agree satisfactorily with earlier qualitative observations.<sup>12</sup> Again as with  $MnOH^{2+}$  the upper limits of  $K_{Cl}$  ( $13.2 \pm 0.9\text{ dm}^{-3}$

TABLE 4.—DEPENDENCE OF DERIVED  $K_{Cl}$  ON ASSUMED VALUES OF  $K_h$

$K_h/mol\text{ dm}^{-3}$	$K_{Cl}/dm^3\text{ mol}^{-1}$
0.6	12.8
0.93	13.0
1.0	13.2
1.20	14.0

$mol^{-1}$ ) are to be emphasized when the fraction of hydrolytic polymer present is allowed for. It is unlikely that the  $I = 2\text{ mol dm}^{-3}$  value,  $13.5\text{ dm}^3\text{ mol}^{-1}$  is truly coincident with our  $I = 3.26\text{ mol dm}^{-3}$  value of  $13.2\text{ dm}^3\text{ mol}^{-1}$ , especially in view of the variation<sup>1</sup> of the  $FeCl^{2+}$  value with  $I$ ,  $5.0$  and  $7.8\text{ dm}^3\text{ mol}^{-1}$  at  $I = 2$  and  $3\text{ mol dm}^{-3}$  respectively. As we are quite certain of our limits, this conclusion reflects the uncertainty in the indirect kinetic measurement mentioned in the introduction.

The size of the error limits calls for comment. For  $K_h$  and  $K_{Cl}$  these are about five times larger than is commonly quoted, and they arise from the highly reactive nature of the cation.  $Mn^{III}$  reacts, albeit slowly, *ca.* 1 % per day, with the solvent, and it partially polymerises (below). For  $K_h$  the effect being measured, while unambiguous, is not so large as to diminish these errors to the ordinary level of parameter fitting. For  $K_{Cl}$  the  $MnCl_2^+$  equilibrium is a marginal complication, but the effect measured is much larger, so diminishing, relatively, the errors resulting from the nature of  $Mn^{III}$ . ( $Ce^{IV}$  and  $Co^{III}$  present comparable problems.<sup>16, 17</sup>)

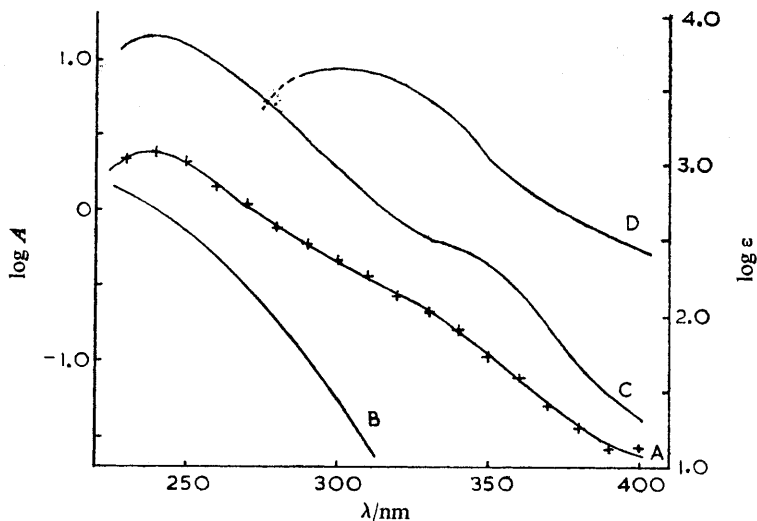


FIG. 1.—A, Calculated (+) and observed (—) values of logarithm of absorbance,  $A$ , for  $0.15 \text{ mol dm}^{-3} \text{ Cl}^-$  solution;  $[Mn^{III}] = 4.00 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[Mn^{II}] = 0.05 \text{ mol dm}^{-3}$ ,  $[HClO_4] = 3 \text{ mol dm}^{-3}$   $25.0^\circ\text{C}$ ; B,  $\log A$  for  $Mn^{III}$  without  $Cl^-$ , otherwise as A; C,  $\log(\epsilon_{MnCl_2^+}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$ ; D,  $\log(\epsilon_{MnCl_2^+}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$ .

#### MANGANESE(III) IN PERCHLORIC ACID

In the chloride catalysed oxidation of  $Tl^I$  by  $Mn^{III}$  with  $10^{-4} \text{ mol dm}^{-3} < [Mn^{III}] < 10^{-3} \text{ mol dm}^{-3}$ , it was found that a multi-step mechanism could explain the observations up to *ca.* 70 or 80 % consumption of  $Mn^{III}$ , but thereafter the rate plots were curved. The plots could be made linear by assuming that about 10-20 %  $Mn^{III}$  was present as unreactive polymer. There is clear evidence for some hydrolytic polymerisation in the marked spectral changes occurring in  $Mn^{III}$  for more than 24 h after preparation. Therefore in the spectrophotometric  $K_h$  determination, readings had to be extrapolated to zero time (see above). Further evidence comes from e.m.f. measurements. All our observations in this and preceding papers have been made on aged  $Mn^{III}$ , and our <sup>9</sup> conditional ( $3 \text{ mol dm}^{-3} \text{ HClO}_4$ ) standard e.m.f. was found to be  $1.535 \pm 0.003 \text{ V}$ , while for fresh  $Mn^{III}$  the value was  $1.541 \text{ V}$ .<sup>13</sup> If the difference  $6 \pm 3 \text{ mV}$  is attributed to the presence of polymer in the former, the fraction of polymer is  $25 \pm 14 \%$ . Combining the kinetic and the e.m.f. estimated values leads to the conclusion that  $\sim 15\text{-}25 \%$  of the  $Mn^{III}$  is polymeric. The precise amount is determined by preparative conditions, since such hydrolytic equilibria are often extremely sluggish.

The conditional e.m.f. values quoted here are for  $Mn^{III}$ ,  $3 \text{ mol dm}^{-3} \text{ HClO}_4$ , without account of the first hydrolysis. Inclusion of  $K_h \approx 1 \text{ mol dm}^{-3}$ , as the value appropriate for  $I = 3 \text{ mol dm}^{-3}$ , gives as the conditional ( $3 \text{ mol dm}^{-3} \text{ HClO}_4$ ) standard e.m.f. for  $Mn^{3+}(\text{unhydrolysed}) + e = Mn^{2+}$  the value  $1.559 \text{ V}$  calculated from the fresh  $Mn^{III}$  measurement.<sup>13</sup>

#### COMPARISON OF $MX^{2+}$ FORMATION CONSTANTS OF FIRST TRANSITION SERIES METAL IONS $M^{3+}$

Values are tabulated in table 5 for perchlorate solutions between  $0.5 \text{ mol dm}^{-3}$  and  $2 \text{ mol dm}^{-3}$  in ionic strength; most have  $I = 1 \text{ mol dm}^{-3}$ ,  $MnOH^{2+}$  has  $4 \text{ mol dm}^{-3}$ . Hydrolysis constants have been converted for comparative purposes to formation

constants by subtraction of  $\log K_w$  at the appropriate ionic strength. Neglecting the only slight irregularities introduced by  $I$  variations, we can immediately make two generalisations which are in almost complete accord with earlier views<sup>6, 14</sup> on the bonding in  $\text{MOH}^{2+}$  and  $\text{MF}^{2+}$ . First, the decrease, with only one minor deviation,

TABLE 5.—SELECTED VALUES<sup>a</sup> OF LOGARITHMS OF FORMATION CONSTANTS FOR  $\text{M}^{3+} + \text{X}^- \rightleftharpoons \text{MX}^{2+}$  IN PERCHLORATE SOLUTION OF IONIC STRENGTH USUALLY<sup>b</sup> 1 mol  $\text{dm}^{-3}$  AT 25°C

	OH	F	Cl	Br	I	$E^\circ(\text{M}^{3+,2+})/V$
Sc	8.84	6.19	1.07) <sub>0.5</sub>	1.21	—	—
Ti	11.7	—	0.34) <sub>0.5</sub>	—	—	-1.29
V	11.1	—	—	—	—	-0.26
Cr	9.8	4.36) <sub>0.5</sub>	-0.65	-2.67) <sub>2</sub>	-5.0 <sup>c</sup>	-0.41
Mn	13.7) <sub>3</sub>	5.63	0.95) <sub>2</sub>	—	—	1.56
Fe	11.0	5.06	0.56 <sup>e</sup>	-0.25	—	0.77
Co	<11.8 <sup>d</sup>	—	1.49) <sub>1.5</sub>	—	—	1.85

<sup>a</sup> from ref. (1) unless otherwise indicated;  $\log(K_X/\text{dm}^3 \text{ mol}^{-1})$  given. <sup>b</sup> Other ionic strengths given in mol  $\text{dm}^{-3}$  as subscripts. <sup>c</sup> T. W. Swaddle and G. Guestalla, *Inorg. Chem.*, 1968, 9, 1915. <sup>d</sup> G. Davies and B. Warnquist, *Coord. Chem. Rev.*, 1970, 5, 349. <sup>e</sup> Ref. (1), and J. K. Rowley and N. Sutin, *J. Phys. Chem.*, 1970, 74, 2043. <sup>f</sup> Ref. (3).

from  $\text{OH}^-$  and  $\text{F}^-$  to  $\text{I}^-$  can be attributed to the decreases in coulomb interaction and in the  $\text{X}^-$  ligand field stabilisation parameter. Very low values probably indicate outer sphere association. Secondly, in the variation with  $\text{M}$ , considering the Sc, Cr and Fe complexes for which the data are most complete, the Cr values always fall low

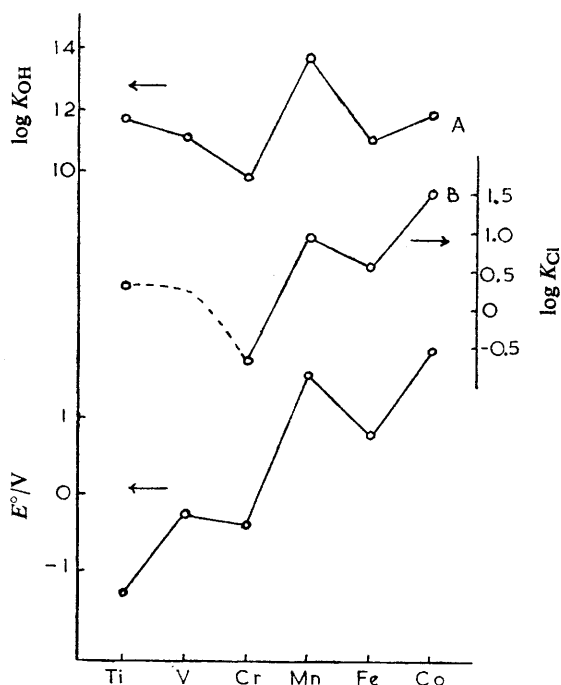


FIG. 2.—Approximate parallelism of trends in  $\log K_X$  for  $\text{MX}^{2+}$  and  $E^\circ(\text{M}^{3+,2+})$ . Data from table 5. at 25°C. A,  $\log K_{\text{OH}}$ ; B,  $\log K_{\text{Cl}}$ ; C,  $E^\circ$ .

n a plot of  $\log K$  against the M atomic number, which supports the view that charge transfer interaction is important. This follows from the fact that of the three  $E^\circ(M^{3+,2+})$  values, that for Cr is negative.  $Mn^{3+}$  has the second highest, positive,  $E^\circ$  and, again in agreement, the  $K$  values fall *high* relative to the Sc-Fe line. These trends are illustrated in fig. 2. The detailed dependences on ionic properties further involve the effect of replacing the originally co-ordinated  $OH_2$  by  $X^-$ , and the variation of dielectric saturation with  $M^{3+}-X^-$  separation in the coulomb interaction. These variables apart from charge transfer are amenable to quite exact theoretical treatment, which however we do not pursue here.

We note that the earlier<sup>14</sup> coincidence, of  $F^-$  and  $OH^-$  complexing dependences on  $M^{3+}$ , arose from the use of Latimer's outdated quantities for fluorine reactions, and  $OH^-$  complexes turn out to be more stable than  $F^-$  complexes by an amount which cannot be explained solely by easier charge transfer<sup>14</sup> from  $OH^-$ . (The anion radii are nearly identical.) However, this excess stability is readily understood as arising from the fact that  $OH^-$  is  $O^{2-}$  with an attached  $H^+$ , and a large part of the interaction is  $M^{3+}O^{2-}$ ; put alternatively,  $OH^-$  has a large dipole moment, absent in  $F^-$ , which enhances  $M^{3+}-OH^-$  interactions. (A similar enhancement of interaction arising this time within the cation is found<sup>15</sup> in  $[NO_2Co^{III}(NH_3)_5]^{2+} SO_4^{2-}$  ion association, which greatly exceeds that for e.g.  $Co^{2+}SO_4^{2-}$  by virtue of the *cationic* dipole moment in the former. Further examples are available,<sup>15</sup> e.g.  $VO^{2+}$  cf.  $Fe^{2+}$ , where the dipole moment in the  $V^{IV}$  cation is evident in relative rate and equilibrium effects.)

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