

as 1% (300 keV), 19% (927 keV) and 76% (1064 keV) feeding the 768, 137 and 0 keV levels and the internal conversion coefficients to be equal, the relative intensities of gamma transitions are obtained as 137 keV 19.6%, 630 keV 0.6% and 738 keV 0.4% which normalized to 10% intensity for 137 keV transition are given in Table I.

Rotational levels of even nuclei have been treated<sup>10</sup> under the assumption that the nuclei possess equilibrium shapes which are not axially symmetric. The transverse deformation parameter for Os<sup>186</sup> is 16.5°. The ratio of reduced transition probabilities is obtained as

$$\frac{B(E_2; 2_2^+ \rightarrow 2_1^+)}{B(E_2; 2_1^+ \rightarrow 0^+)} = 3.188.$$

In the Unified model<sup>20</sup> the same ratio is predicted as 1.43. In the asymmetric rotor model the ratio varies with the transverse deformation parameter ( $\gamma$ ), at  $\gamma = 0^\circ$ , the ratio is 1.43 and at  $\gamma = 30^\circ$ , it is infinite. In general, the experimental values of this ratio are found to lie in between these two theories. In the transitional region, however, the Davydov and Fillippov model is more successful in predicting this ratio. The experimental ratio in the case of Os<sup>186</sup> is

$$\frac{B(E_2; 2_2^+ \rightarrow 2_1^+)}{B(E_2; 2_1^+ \rightarrow 0^+)} = 3.83.$$

The experimental value shows better agreement with the asymmetric rotor model than with the vibrational model.

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## CHELATING TENDENCIES OF FERRON WITH SOME BIVALENT METAL IONS\*

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**8-HYDROXY** quinoline and its derivatives are of unusual importance in analytical chemistry. Ferron, 7-iodo 8-hydroxy quinoline 5-sulphonic acid has been widely recognised as a specific reagent for the spectrophotometric estimation of ferric iron.<sup>1</sup> Further, ferron has been used by Van Zijp<sup>2</sup> as a sensitive micro-chemical reagent in the detection of barium and strontium. Recently, Nasanen and Ekman<sup>3</sup>

have studied calcium-ferron chelate system as regards its stoichiometry and stability constant. However, the chelating tendencies of ferron with many other metal ions have not been investigated. The present communication describes a physico-chemical study of certain bivalent metal ions, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup>, and Zn<sup>2+</sup>-ferron systems with a view to determine their stoichiometries and stability constants. Further, it has also been aimed to compare these bivalent metal ion-ferron chelate stability constants with those reported values<sup>4</sup> of 8-hydroxy quinoline and 8-hydroxy quinoline 5-sulphonic acid chelates.

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The experimental method consisted of pH titrations of the free ligand, in the absence of and in the presence of the metal ion being investigated. The ionic strength was maintained constant by using a medium containing 0.10 M  $\text{KNO}_3$  and low concentrations ( $1.0 \times 10^{-3}$  M) of the ligand and the metal ion. The pH titrations were carried out by introducing free ligand as well 1:1 and 1:2 ratios of metal ion to ligand concentration into a titration cell. The pH readings were then taken after the addition of small increments of 0.10 M carbon-dioxide-free KOH solutions.

The chemicals employed were all of Analar grade and Leeds and Northrup pH meter (Cat. 7666) with glass and calomel electrodes was employed for the pH measurements.

The required first and second dissociation constants of ferron were calculated from the pH titration curves by an adaptation of Bjerrum's method as followed by Chaberek and Martell<sup>5</sup> using the final equation

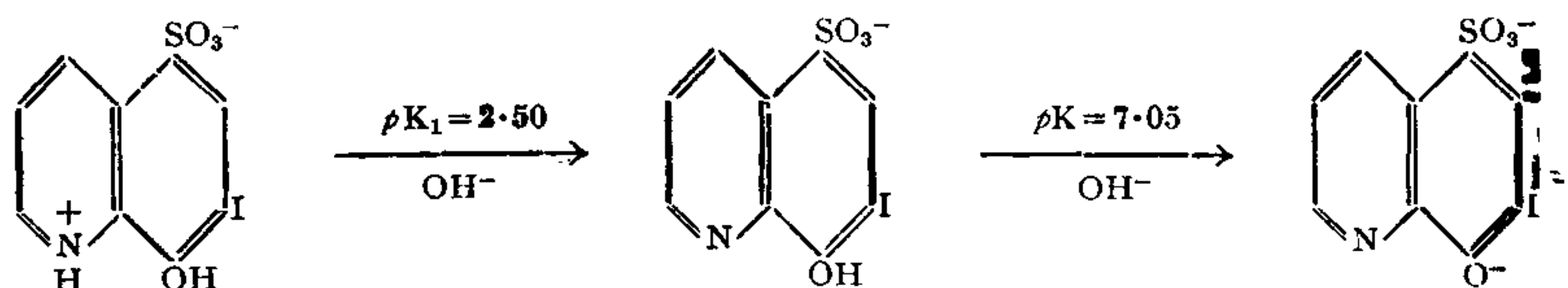
$$\bar{n} = (\text{HA}^-) + 2(\text{H}_2\text{A})/C_A$$

$\text{H}_2\text{A}$  = Concentration of ferron,

$C_A$  = total concentration of ligand species.

The values of  $\text{pK}_1$  and  $\text{pK}_2$  for ferron have been found out to be 2.50 and 7.05 respectively ( $\mu = 0.10$  M  $\text{KNO}_3$  and  $t = 28^\circ \text{C}$ ). These values are in fair agreement with those reported by Nasanen *et al.*<sup>6</sup> ( $\text{pK}_1 = 2.51$ , and  $\text{pK}_2 = 7.41$ ).

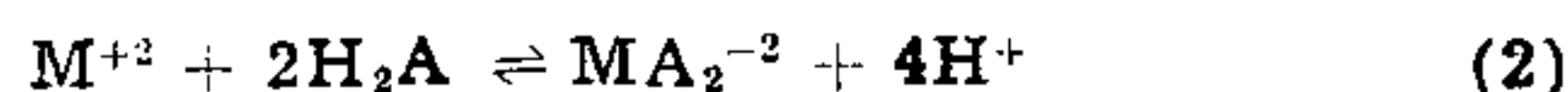
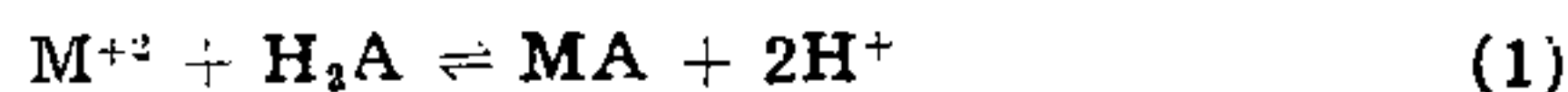
The pH titrations of ferron produces two sharp inflections which probably correspond to the separate neutralisation reactions



The  $\text{pK}$  values of 2.50 and 7.05 may be compared to the corresponding values of 3.84 and 8.35 obtained for 8-hydroxy quinoline 5-sulphonic acid by Martell *et al.*<sup>4</sup> The lower basicity of ferron may be considered as the result of the inductive effect of the iodide group in 7 position due to which the sulphonic and phenolic protons become much more easily ionisable causing the lowering of  $\text{pK}$  values.

The 1:1 metal-ligand titration curves showed a definite inflection at two moles of base per mole of metal ion while 1:2 metal-ligand titration curves showed a strong inflection at four moles of base per mole of metal ion indicating the formation of both 1:1 and

1:2 chelates. The chelate formation may be expressed by the equations (1) and (2)



The first and second chelate stability constants were calculated from 1:2 titration curves by an adaptation of Bjerrum's method as followed by Chaberek and Martell<sup>5</sup> employing the final equation

$$\bar{n} = \frac{1}{C_M} \left[ C_A - \left( \frac{(\text{H}^+)^2}{K_1 K_2} + \frac{(\text{H}^+)}{K_2} + 1 \right) (A^{-2}) \right]$$

where

$C_M$  = total concentration of metal ion species

$C_A$  = total concentration of the ligand species

$K_1, K_2$  = first and second dissociation constants of ligands.

The 1:1 copper-ferron stability constant could not be calculated by the Bjerrum's method from 1:2 titration curves. This constant was calculated from the 1:1 titration curve by the algebraic method.<sup>5</sup>

In Table I the relative values of stabilities of various bivalent metal-ferron chelates are presented and also compared with corresponding values for stabilities of 8-hydroxy quinoline 5-sulphonic acid and 8-hydroxy quinoline chelates reported in literature.<sup>4</sup> It is evident from the data that the relative values of the stability constants follow the natural order as proposed by Irving-Williams,  $\text{Mn} < \text{Co} < \text{Ni} < \text{Cu} > \text{Zn}$ . And also as was observed by

TABLE I

Stability constants of bivalent metal ion-ferron and related ligand chelates

( $\mu = 0.10$  M  $\text{KNO}_3$ ;  $t = 28^\circ \text{C}$ .)

$\text{M}^{+2}$	Ferron		Log $K_1 K_2$ of		
	Log $K_1$	Log $K_2$	Ferron	8-hydroxy quinoline 5-sulphonic acid	8-hydroxy quinoline
Cu	8.33	8.25	16.58	21.87	29.00
Ni	7.70	6.26	13.96	16.77	22.05
Co	6.70	4.17	10.87	15.06	20.81
Mn	4.95	3.15	8.10	11.72	..
Zn	7.25	6.15	13.40	14.32	20.81



Calvin et al.<sup>7</sup> that the plot of  $\log K_1 K_2$  of the above bivalent metal ion-ferron chelates against the second ionisation potential of the metal ions yields a straight line with the exception of  $Zn^{+2}$ . Further, the data reveal the fact that as the basicity of the ligand decreases in the order of ferron < 8-hydroxy quinoline 5-sulphonic acid < 8-hydroxy quinoline, the values of stability constants also correspondingly decrease. Thus the lower basicity of the ligand is reflected in a correspondingly lower stability of the metal chelates of ferron.

Further details of these investigations will be published subsequently.

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## A GRAPHIC APPROACH IN PALAEOMAGNETIC ANALYSIS

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**I**N studies in structural petrology the use of equal-density contour lines has long been familiar. Density diagrams thus prepared on the basis of a scatter-diagram in which the individual observations are plotted on a stereographic projection (Wulff net) or on an area true projection (Lambert's equal area projection commonly known as Schmidt net) render it easy to visualize fully the pattern of dispersion of the observations.<sup>1</sup> A similar application can as well be extended to the treatment of the palaeomagnetic directions.

The basis of palaeomagnetism is that the magnetic vector in a rock is directionally oriented and this direction carries the magnetic history of the rock itself. The basic factors determined in palaeomagnetic studies are, therefore, the declination and the inclination values. Since this datum is three-dimensional it is customarily presented in a two-dimensional form by making use of a Wulff net or a Schmidt net. On this net unit vectors representing the individual directions are plotted, no weight being given to the varying intensity of magnetisation values. A 'pole diagram' is thus prepared. While a close grouping of these point-projections of the palaeomagnetic directions obtained from the same hierarchical level is always indicative of the reliability of the observations these directions never agree exactly. Instead, a cluster of directions is normally observed. This means that in palaeomagnetic studies, as in structural petrology, a

scatter of observations projected as points on the net in the form of a pole diagram is encountered. The distribution of the individual points in the pole diagram and their dispersion about the mean value, therefore, need to be summarised by some means in order to evaluate a clear picture of the dispersion trends.

Customarily the palaeomagnetic data obtained from a rock unit are analysed statistically following the treatment evolved by R. A. Fisher<sup>2</sup> and the mean declination and inclination values for that particular rock unit are thus estimated. However, the distribution of the points in a pole diagram can also be appreciated if a density diagram is contoured after the manner usually adopted, as mentioned earlier, in structural geology. Since the directions obtained from the same rock unit only approximate a preferred direction (i.e., they would form a coherent distribution if the data is reliable) this preferred direction can be treated as the mean value for the observed unit.

Figure 1 A shown here is a pole diagram of the palaeomagnetic directions of 230 Deccan Trap specimens collected from the neighbourhood of Gulbarga.<sup>3</sup> A density diagram corresponding to this data has also been prepared (Fig. 1 B). In a density diagram an area enclosed by a contour line labelled 'x%' means that 'x%' of the total points used in the pole diagram lie within 1% of the total surface area of the net. Thus the areas between two different contours indicate the