SPORADIC E LAYER OVER TIRUPATI

Tirupati is a low latitude station (latitude 13° 40' N, longitude 79° 27' E, geomagnetic latitude 3° 45' N.) situated in Andhra Pradesh. Observations on the characteristics of Sporadic E layer of the ionosphere at this station have been reported since 1960.

This report deals with some observations made during December 1968 to April 1969 on the Sporadic E layer. The Sporadic E critical frequencies ($f_{E_s}$) were scaled manually on vertical incidence ionosphere sounding equipment at regular intervals of one hour during the daytime from 0900 hr to 1700 hr. From these frequencies the hourly median values of $f_{E_s}$ for the entire period of five months and for each month were obtained. The diurnal variations of $f_{E_s}$ for the period under investigation as well as for the month of December 1968 are shown in Fig. 1. It can be inferred from this that the ionization increases with the hour of the day, reaches a maximum at about local noon and then decreases. This is a typical characteristic behaviour of Sporadic E's. However, a second maximum which is not very pronounced is observed at 1400 hr. Looking at the diurnal variation of $f_{E_s}$ for the month of December 1968, this second maximum is pronounced compared to other months. This particular feature has been observed at this station for over a number of years, right from 1959. However, this observation of ours is not in agreement with that of Rangarajan (Station: Kodaikanal, geomagnetic latitude 0° 44' N.). A careful study over an extended period is probably necessary to elucidate this point.

![Fig. 1. Diurnal variations of $f_{E_s}$.](image)

The cumulative distribution of $f_{E_s}$ with frequency for the five months under study is shown in Fig. 2. Phillips has shown that this semi-logarithmic plot should be a straight line for Sporadic E. However, the observed distribution (Fig. 2) deviates from linearity below $4 \text{Mc/s}$, and it will be noticed that in this range the per cent of times $f_{E_s}$ is greater than the abscissa frequency, rising sharply to 100%, instead of remaining round about 60 to 70%.

![Fig. 2. The cumulative distribution of $f_{E_s}$ with frequency.](image)

We are grateful to Prof. J. Bhimsenachar for his guidance and encouragement.


FORMATION OF LOWER OXIDE OF SULPHUR BY SOLID STATE REACTION

A sulphur rich oxide is formed when sulphur is allowed to combine with a limited supply of oxygen. It is now observed that disulphur monoxide or its polymer is obtained by the solid state reaction between a metal sulphide and the metal (1) oxide, (2) sulphate, (3)
sulphite and (4) thiosulphate. The results of a few representative experiments are reported in this short communication.

When a mixture of finely divided powders of copper sulphide and copper oxide (5 : 1 by weight) is heated at 325-350°C under vacuum, gaseous products are released which on cooling in a trap maintained at -184°C condense in the form of cherry to orange-red solid. The solid gives off sulphur dioxide on warming leaving a residue of elemental sulphur.

Analytical results indicate that the yield of the lower oxide depends on several experimental conditions. The lower oxide is identified to be the Disulphur Monoxide by the methods described earlier. The fact that the reaction between copper sulphide and copper oxide takes place well below the decomposition temperature of both the sulphide and oxide lends support to the view that this is a solid state reaction.

Similar reaction is observed to occur at about 400°C between the following systems with the release of the lower oxide: (1) copper sulphide-copper sulphate, (2) copper sulphide-copper sulphide, (3) copper sulphide-copper thiosulphate and (4) copper sulphide-copper chromate. Experiments with other metal sulphides such as of nickel, cobalt and iron also yielded the lower oxide in good yield. Further work is in progress.


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**CONDUCTOMETRIC STUDY OF SOME COBALTICYANIDES**

**ABSTRACT**

The stoichiometric relationship and the solubility of zinc cobalticyanide and the dissociation constant of ion-pair have been studied from conductivity measurements.

The conductivity bridge employed in this study has been described earlier.1 Zinc sulphate, copper sulphate, nickel sulphate (E. Merck, G.R.) and potassium cobalticyanide (B. D. H.) recrystallised from a water-dioxane mixture were used for preparing stock solutions with conductivity water.

**Zinc Cobalticyanide System.**—Conductometric (both forward and reverse) titrations of zinc sulphate (Fig. 1 and Table I) with potassium cobalticyanide revealed an inflection point at 1:5 indicating the formula of the complex to be $\text{Zn}_3\left(\text{CO(CN)}_6\right)_2$.

**TABLE I**

<table>
<thead>
<tr>
<th>Conductometric titrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_3\left(\text{CO(CN)}_6\right) = 5 \times 10^{-2}$ M</td>
</tr>
<tr>
<td>Volume $= 15.6$ ml.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Zn$^{2+}$ ml.</th>
<th>$K_3 \text{CO(CN)}_6$ ml.</th>
<th>Ratio of Zn$^{2+}$ to CO(CN)$^-_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>0.415</td>
<td>1.45</td>
</tr>
<tr>
<td>1.0</td>
<td>0.65</td>
<td>1.54</td>
</tr>
<tr>
<td>1.5</td>
<td>0.98</td>
<td>1.63</td>
</tr>
<tr>
<td>(Direct titration)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.75</td>
<td>0.5</td>
<td>1.50</td>
</tr>
<tr>
<td>1.05</td>
<td>0.7</td>
<td>1.50</td>
</tr>
<tr>
<td>(Reverse titration)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For conductivity measurements, zinc cobalticyanide, prepared by precipitation, was filtered, washed well and kept suspended in conductivity water for several days. The sample was filtered and dried in vacuo. The resistance of solutions at different concentrations of zinc cobalticyanide was measured. A plot of $\Lambda$ vs. $\sqrt{C}$ (Fig. 2), as compared with the theoretical Onsager curve, was similar to that of a weak electrolyte which could be explained on the basis of ion-pair formation. The dissociation constant of the ion-pair $[\text{Zn CO(CN)}_6]^-$ was calculated from the measured conductances.

The Onsager's equations for complete dissociation and dissociation to ion-pair are

$$\Lambda_1 = 151.7 - 362.97 \sqrt{I}$$
$$\Lambda_2 = 85.67 - 123.5 \sqrt{I}$$

The ionic strength, $I$, can be calculated from

$$I = C(2.5 - 2a)$$

where $C$ is the concentration in g. eq./litre. The measured equivalent conductance, $\Lambda$, can therefore be written as

$$\Lambda = 151.7 - 362.97 \sqrt{I - a} (123.1 - 320.15 \sqrt{I})$$

from which $a$, the degree of dissociation of ion-pair can be calculated by successive approximation. The thermodynamic dissociation constant can then be calculated from

$$\log K = \log \frac{C(1.5 - a)}{3a} - 6.108 I$$

The calculated values of $a$ and $K$ are given in Table II. An average value of $3.6 \times 10^{-4}$