Letters to the Editor

Recentl y, Jaffe 1 has suggested, in analogy with lithium solutions, that the eutectic arising from a solution of sodium in ammonia is a compound (possibly Na(NH₃)₃ or perhaps non-stoichiometric) and hence he proposes an alternative explanation for our electrical conductivity measurements on solidified sodium-ammonia solutions.2 Whilst we agree with Jaffe that lithium and ammonia almost certainly do form a compound,3 probably Li(NH₃)₄, at low temperatures, which melts in contact with solid ammonia at −185°C (Jaffe gives −181°C) we do not believe that a compound is formed in the case of sodium. The obviously non-homogeneous mixture of metal and ammonia crystals constituting the solidified sodium-ammonia eutectic differs completely in appearance from the homogeneous lithium compound (and the analogous alkaline-earth metal derivatives).

That super-cooling can occur under favorable conditions is clearly indicated in the absence of a latent heat at −110°C (the m.p. of the sodium-ammonia eutectic) in some of our thermal measurements.2 This is perhaps not so surprising as Jaffe seems to think because the composition of the saturated solution of sodium in ammonia is practically temperature independent, and the vapor-pressure:concentration curve in this region is almost vertical. There should be small. On this view, the role of a super-cooled phase is thus to prevent this cracking, and the decrease in conductivity on warming is due to crystallization of the phase, which proceeds faster at higher temperatures still below −110°C.

A theoretical discussion of the constitution of metal-ammonia solutions and metal-ammoniates is to be published.4


Metal-Ammonia Solutions

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S EVERAL analyses of the vibration spectrum of ozone have been proposed in recent years, 1-4 all of which have been open to serious objection. Either they have failed to account for the observed structure of all the infrared bands, or if consistent with this structure have required an acute angled molecular model which is not in accord with the structure determination by electron diffraction.5 These difficulties appear to have resulted in part from some misconceptions regarding the relative intensities of the ozone bands, but chiefly from the previous failure to recognize the fundamental band of the vibration ν₁.

The spectrum of ozone has recently been re-examined in this laboratory in the region 1.5-15μ, using a Beckman IR-2 spectrophotometer. Particular care was taken to avoid contamination by NO₃ and the possible effects of contamination by this gas, and by CO₂ and other impurities which have been carefully considered. The concentration of ozone in the absorption tube was determined by chemical analysis and the "apparent" extinction coefficient at the maximum of each observed band was determined as shown in Table I.

Because of the limited resolution employed, and the discontinuous character of the absorption, these coefficients are appreciably dependent on pressure, but they approximately represent the pressure dependence of average absorption near the maximum, when the absorption lies between 10 and 30 percent, and they serve to indicate

<table>
<thead>
<tr>
<th>ν (cm⁻¹)</th>
<th>Observed type</th>
<th>Spacing (cm⁻¹)</th>
<th>α</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>705</td>
<td>doublet</td>
<td>~5.7</td>
<td>0.08</td>
<td>ν₁</td>
</tr>
<tr>
<td>1043</td>
<td>Q</td>
<td>~1</td>
<td>0.0</td>
<td>ν₂</td>
</tr>
<tr>
<td>1110</td>
<td>doublet</td>
<td>~5</td>
<td>0.05</td>
<td>ν₁</td>
</tr>
<tr>
<td>1740</td>
<td>Q</td>
<td>~</td>
<td>0.04</td>
<td>ν₁+ν₃</td>
</tr>
<tr>
<td>2105</td>
<td>Q</td>
<td>~1</td>
<td>0.15</td>
<td>ν₁+ν₃</td>
</tr>
<tr>
<td>2800</td>
<td>Q</td>
<td>~</td>
<td>0.005</td>
<td>ν₁+2ν₃</td>
</tr>
<tr>
<td>3050</td>
<td>Q</td>
<td>~</td>
<td>0.015</td>
<td>3ν₂</td>
</tr>
</tbody>
</table>

α (base 10) is expressed as cm⁻¹ of pure ozone at S.T.P.
The new observations make possible the revised vibrational analysis presented in the table, which is in agreement with all observations on the band structures, and supports the approximate analysis of fine structure made by Miss Simpson on the basis of the obtuse angled model. Some previous difficulties in the apparent divergence in band progressions and combination bands are now resolved, and the observed relative intensities of the bands support the proposed analysis.

The more accurate determination of the apex angle and internuclear distances of the ozone molecule must await better resolution of the fine structure of one or more of the $B$ type bands which we propose to attempt in the near future.


**Joshi-Effect**

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In recent years a large number of papers have been published on the Joshi-effect. The effect may be described as follows: An alternating field is applied to gases at low pressures and the gaseous current is measured. It is observed that the gaseous current diminishes when the discharge tube is exposed to light. The diminution in the gaseous current, which is an ionic current, is observed in a number of gases, and with light of different wave-lengths. As the frequency of the incident light is generally not sufficient to produce photoelectrons in the gas, we shall be justified in excluding the photoelectric effect from the plausible agents which could reduce the ionic current. In addition “photo-ionization” or “resonance excitation” leading to ionization may occur. Both these effects will lead to an increase in the gaseous current. Their mechanisms are well known and hence they are not considered here. But it is necessary to remember that unless the experimental conditions are isolated, both these effects are likely to occur along with the Joshi-effect and this may lead to an increase in the current occasionally observed.

It is a well-known fact that the gaseous ionic current can be written as

\[ Q = \Sigma n ev, \]

where \( n \) is the number of charged particles carrying a charge \( e \) and moving with a velocity \( v \). Or it can be written as

\[ Q = \Sigma n ekX, \]

where \( k \) is the ionic mobility and \( X \) the field strength. Joshi and others observe a diminution in \( Q \). From the above equation it can be seen that \( Q \) can be reduced by changing \( n \) or \( e \) or \( k \). That is, a change in the discharge current is

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Relative intensities of the bands. In previous estimations of relative intensity the observations of Hettner, Pohlmann and Schumacher appear to have been misinterpreted. It is now evident that in this earlier investigation about 5 percent of stray light was present at 10\( a \) and that the 1043 cm\(^{-1} \) band is much more intense than was supposed.

The particularly new observation made in the course of this work was the discovery of a new fundamental band with center at about 1110 cm\(^{-1} \), shown in Fig. 1. This band has nearly as great intensity as the fundamental at 705 cm\(^{-1} \). It is suggested in several previously published tracings of the ozone spectrum but has apparently escaped special notice because of its proximity to the extremely intense band at 1043 cm\(^{-1} \). Under conditions suitable for study of the latter band the former may easily escape detection. As shown in the lower tracing the new band shows no suggestion of a \( Q \) branch, but four lines with an average spacing of about 5 cm\(^{-1} \) have been resolved on the long wave-length side of the minimum. Evidently the new band is similar in structure to the fundamental at 705 cm\(^{-1} \), recently investigated by Adel and Dennison, and these two bands are to be described as \( v_1 \) and \( v_2 \), respectively. The extremely intense band at 1043 cm\(^{-1} \) is then evidently the fundamental \( v_3 \). There has been some question as to the structure of this band, and it has been suggested that the observed fine structure is due in part to CO\(_2\) contamination. This may be possible in observations of atmospheric absorption, but our observations indicate that this is most unlikely under the laboratory conditions employed by Gerhardt. The \( Q \) branch of this band is certainly not prominent, but the tracings of Gerhardt strongly suggest its presence, though somewhat displaced and "washed out" by convergence.