MetalAmmonia Solutions

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Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the first of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($4.00 per page) will not be made and no reprints will be furnished free.

Metal-Ammonia Solutions

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RECENTLY Jaffe[1] has suggested, in analogy with lithium solutions, that the eutectic arising from a solution of sodium in ammonia is a compound (possibly $Na(NH_3)_5$ or perhaps non-stoichiometric) and thence 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 $Li(NH_3)_4$, 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 a saturated solution of sodium in ammonia is practically temperature independent, and the vapor-pressure:concentration curve in this region is almost vertical. There should thus be less tendency for either of the solid components (Na, NH_3) to separate from the saturated solution on cooling than in more familiar types of solution. Whether in fact at the very low temperatures (ca. $-183°C$) the super-cooled phase is a mobile liquid or a glass (i.e. a solid solution perhaps corresponding to Jaffe's non-stoichiometric compound) seems to us a distinction without a difference; the observed phenomenon is that a continuous network of conducting material is maintained. The contraction on slow cooling, and subsequent cracking with rupture of conducting material is due to the fact that metal-ammonia solutions have a far greater volume than their components, rather than to normal thermal contraction which would

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]

[1] H. Jaffe, J. Chem. Phys. (to be published).
[2] A. J. Birch and D. K. C. MacDonald, Trans. Faraday Soc. 43, 792 (1947).
[3] A. J. Birch and D. K. C. MacDonald, Nature 159, 811 (1947); Trans. Faraday Soc. (to be published).
[4] A. J. Birch and D. K. C. MacDonald, Oxford Science (to be published).

A Reinvestigation of the Vibration Spectrum of Ozone

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SEVERAL analyses of the vibration spectrum of ozone have been proposed in recent years,[1-5] all of which have been open to serious objection. Either they have failed to account for the observed structure of all the infra-red 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.[6] 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 ν_1.

The spectrum of ozone has recently been re-examined in this laboratory in the region $1.5-15\mu$, using a Beckman IR-2 spectrophotometer. Particular care was taken to avoid contamination by N_2O_5, and the possible effects of contamination by this gas, and by CO_2 and other impurities 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 I. Extinction coefficients[a] and assignments of the observed ozone bands.

ν (cm^{-1})	Observed type	Spacing (cm^{-1})	α	Assignment
705	doublet	~5.7	0.08	ν_2
1043	Q	~1	6.0	ν_3
1110	doublet	~5	0.05	ν_1
1740	?	—	0.04	$\nu_2+\nu_3$
2105	Q	~1	0.15	$\nu_1+\nu_3$
2800	?	—	0.005	$\nu_1+2\nu_3$
3050	Q	—	0.015	$3\nu_3$

[a] α (base 10) is expressed as cm^{-1} of pure ozone at S.T.P.
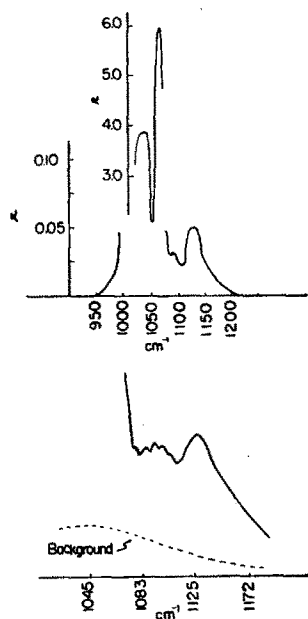
FIG. 1. Ozone bands near 1100 cm⁻¹.

relative intensities of the bands. In previous estimations of relative intensity the observations of Hettner, Pohlmann and Schumacher[2] appear to have been misinterpreted. It is now evident that in this earlier investigation about 5 percent of stray light was present at 10μ 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 ν_1, and ν_2, respectively. The extremely intense band at 1043 cm⁻¹ is then evidently the fundamental ν_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.[1] 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.

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.[7] 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.

[1] S. L. Gerhardt, Phys. Rev. 42, 622 (1932).
[2] G. Hettner, R. Pohlmann, and H. J. Schumacher, Zeits. f. Physik. 91, 372 (1934).
[3] W. G. Penney and G. B. B. M. Sutherland, Proc. Roy. Soc. A156, 654, 678 (1936).
[4] D. M. Simpson, Trans. Faraday Soc. 41, 209 (1945).
[5] A. Adel and D. M. Dennison, J. Chem. Phys. 14, 379 (1946).
[6] W. Shand and R. A. Spurr, J. Am. Chem. Soc. 65, 179 (1943).
[7] D. M. Simpson, J. Chem. Phys. 15, 846 (1947).

Joshi-Effect

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IN recent years a large number of papers have been published on the Joshi-effect.[1] 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 wavelengths. 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[2] 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.[3]

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

$$Q = \Sigma nev,$$

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

$$Q = \Sigma nekX,$$

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