

## METALLIC AMMONIUM

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(Received 1954 February 3)

*Summary*

It has been pointed out by Ramsey that metallic ammonium ( $\text{NH}_4$ ) may be important in determining the properties of Uranus and Neptune. The pressure-density relation for this metal at pressures of importance in this connection is calculated by quantal methods. The transition pressure for the phase transition from mixed crystals of ammonia and hydrogen ( $\text{NH}_3$  and  $\frac{1}{2} \text{H}_2$ ) to ammonium metal is also investigated and found to be almost certainly less than 250 000 atmospheres, so that the metallic phase will persist throughout the bulk of the two planets mentioned.

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*Introduction.*—The importance of allowing for phase changes which occur at high pressures, in determining the constitutions of the planets, has been emphasized by Ramsey (1). Unfortunately the investigation of the conditions under which these phase changes take place is extremely difficult. The transition pressures are usually beyond the reach of available experimental technique, while the processes are usually too complex for theoretical treatment. An exception in the latter respect is the transition from the molecular crystal to the metallic form of hydrogen. This has been treated quite thoroughly theoretically by Wigner and Seitz (2) and by Kronig, de Boer and Korringa (3). Their results, which provide, in numerical form, an equation of state for hydrogen at pressures of the order of those encountered within the major planets, have been applied by Ramsey (4) to the elucidation of the constitution of these planets. He finds that whereas Jupiter and Saturn are predominantly hydrogen, Uranus and Neptune, which have much smaller masses, have lost most of their hydrogen. For these planets the principal constituents are likely to be water, methane and ammonia. This raises an interesting opportunity for further theoretical investigation.

It has long been known that the ammonium ion  $\text{NH}_4^+$  behaves in many ways like an alkali metal ion. The existence of the so-called ammonium amalgam, produced when sodium amalgam is mixed with a solution of ammonium chloride, shows that this similarity persists to some extent into the metallic phase. In other words ammonium metal is probably stable above a comparatively low transition pressure. Ramsey (4) points out that metallic ammonium is therefore likely to be an important constituent of Uranus and Neptune. Owing to the comparatively high symmetry of the molecular structure of the  $\text{NH}_4^+$  ion it is possible to carry out calculations of the properties of metallic ammonium which should be of sufficient accuracy for application to planetary constitution. Apart from this application such calculations are also of interest as providing an estimate of the order of magnitude of the transition pressure for the phase change from the mixed ammonia and hydrogen molecular crystals to the metal.

In this paper we give the results of a theoretical investigation on these lines.

*Calculation of the equation of state of metallic ammonium.*—The basis of the method used is provided by the work of Buckingham, Massey and Tibbs (5) on the properties of methane. They obtained a self-consistent field for this molecule by first averaging the proton distribution over a sphere. The resulting central field problem may then be dealt with by exactly the same methods as for the self-consistent fields of atoms. The results obtained were very encouraging and suggested that, for many purposes, the approximation is quite a satisfactory one. To deal with the ammonium problem the field of the ammonium ion is first obtained as for methane by averaging the tetrahedral distribution of protons over a sphere of radius  $r_0$ . The value of  $r_0$  was chosen from a preliminary investigation (6) carried out by one of us (M. J. M. B.) in which the total energy of the tetrahedral ion was calculated as a function of  $r_0$  by a simple variational procedure. The minimum value of  $r_0$  obtained in this way ( $r_0 = 1.84a_0$ ) was then adopted for the further calculations.

Having chosen  $r_0$ , a self-consistent field for the ion with spherically symmetrical proton distribution was obtained in the usual way. In Table I the self-consistent wave functions and the effective nuclear charges ( $Z_p$ ) for potential are given.

Once the self-consistent wave functions are obtained the usual procedure of the theory of metals (7) may be adopted to calculate the energy of ammonium metal as a function of the nitrogen–nitrogen separation. The metal is divided into polyhedra centred round each nitrogen nucleus, and the ground-state wave function of the metallic electron must contain the correct number of nodes within the polyhedron and have vanishing slope at the boundary walls of the polyhedron. To simplify the calculation it is usual to represent the polyhedra by spheres of radius  $a$ ,  $2a$  being the separation of the nitrogen nuclei. It has been shown by Wigner (8) that the various corrections which should be applied to the results obtained by this simplified procedure are not very significant for the alkali metals. Since ammonium metal is likely to be essentially similar, we have ignored these corrections.

The equation for the wave function  $P/r$  of the metallic electron is, in atomic units,

$$P''(r) + 2[\epsilon - (V + r^{-1}Z_{\text{eff}})]P(r) - \lambda_{1s}P_{1s}(r) - \lambda_{2s}P_{2s}(r) \\ = -2\sum_{nl} (2l+1) \left[ r^{-l-1} \int_0^r P_{nl}(r_1)P(r_1)r_1^l dr_1 + r^l \int_r^a P_{nl}(r_1)P(r_1)r_1^{-l-1} dr_1 \right] \\ P_{nl}(r), \quad (1)$$

where  $V$  is the potential due to the nitrogen nucleus and proton distribution

$$V = -\frac{7}{r} - \frac{4}{r_0}, \quad r \leq r_0, \\ = -\frac{11}{r}, \quad r \geq r_0,$$

$r^{-1}P_{nl}$  are the normalized  $\text{NH}_4^+$  wave functions (the values of  $P_{nl}$  given in Table I are not normalized), and  $Z_{\text{eff}}$  is the effective central charge of the  $\text{NH}_4^+$  electrons

$$Z_{\text{eff}} = 2Z_p(1s) + 2Z_p(2s) + 6Z_p(2p),$$

where  $Z_p(1s)$ ,  $Z_p(2s)$  and  $Z_p(2p)$  are given in Table I.

TABLE I

*Self-consistent wave functions and  $Z_p$  values for  $NH_4^+$* 

$r$	$P(1s)$	$P(2s)$	$P(2p)$	$Z_p(1s)$	$Z_p(2s)$	$Z_p(2p)$	$2Z_{\text{eff}}$
0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.02	0.1739	0.1737	0.0022	0.1318	0.0193	0.0159 <sub>5</sub>	0.7957
0.04	0.3028	0.3012	0.0084	0.2563	0.0383	0.0319 <sub>1</sub>	1.5614
0.06	0.3956	0.3905	0.0177	0.3698	0.0569	0.0478 <sub>6</sub>	2.2811
0.08	0.4598	0.4487	0.0295	0.4705	0.0750 <sub>5</sub>	0.0638 <sub>1</sub>	2.9478
0.10	0.5014	0.4813	0.0433	0.5582	0.0927	0.0797 <sub>5</sub>	3.5605
0.12	0.5252	0.4930	0.0587	0.6334	0.1099 <sub>5</sub>	0.0956 <sub>9</sub>	4.1219
0.14	0.5353	0.4877	0.0753	0.6974	0.1268	0.1116 <sub>1</sub>	4.6361
0.16	0.5348	0.4686	0.0929	0.7512	0.1433	0.1275 <sub>1</sub>	5.1083
0.18	0.5262	0.4384	0.1111	0.7962	0.1596	0.1433 <sub>7</sub>	5.5436
0.20	0.5116	0.3993	0.1298	0.8336	0.1756 <sub>5</sub>	0.1592	5.9472
0.24	0.4708	0.3015	0.1679	0.8899	0.2073 <sub>5</sub>	0.1907 <sub>1</sub>	6.6774
0.28	0.4219	0.1869	0.2060	0.9278	0.2387 <sub>5</sub>	0.2219 <sub>6</sub>	7.3296
0.32	0.3709	0.0639	0.2433	0.9530	0.2700 <sub>5</sub>	0.2528 <sub>6</sub>	7.9263
0.36	0.3214	-0.0616	0.2791	0.9695	0.3013 <sub>5</sub>	0.2833 <sub>4</sub>	8.4837
0.40	0.2753	-0.1853	0.3130	0.9804	0.3326	0.3133 <sub>4</sub>	9.0119
0.44	0.2337	-0.3043	0.3448	0.9874	0.3638 <sub>5</sub>	0.3427 <sub>7</sub>	9.5184
0.48	0.1969	-0.4166	0.3743	0.9920	0.3948 <sub>5</sub>	0.3715 <sub>9</sub>	10.0064
0.52	0.1649	-0.5210	0.4014	0.9949	0.4256	0.3997 <sub>4</sub>	10.4788
0.56	0.1373	-0.6168	0.4262	0.9968	0.4560	0.4271 <sub>6</sub>	10.9370
0.60	0.1139	-0.7037	0.4486	0.9980	0.4857 <sub>5</sub>	0.4538 <sub>3</sub>	11.3809
0.64	0.0941	-0.7817	0.4688	0.9987	0.5148 <sub>5</sub>	0.4797 <sub>2</sub>	11.8111
0.72	0.0638	-0.9119	0.5031	0.9995	0.5706 <sub>5</sub>	0.5290 <sub>8</sub>	12.6296
0.80	0.0429	-1.0105	0.5301	0.9998	0.6226 <sub>5</sub>	0.5751 <sub>2</sub>	13.3914
0.88	0.0287	-1.0816	0.5508	0.9999	0.6704 <sub>5</sub>	0.6178 <sub>3</sub>	14.0956
0.96	0.0194	-1.1294	0.5663	1.0000	0.7139	0.6572 <sub>6</sub>	14.7426
1.04	0.0134	-1.1580	0.5774		0.7529	0.6935 <sub>1</sub>	15.3337
1.12	0.0097	-1.1709	0.5849		0.7877	0.7266 <sub>8</sub>	15.8709
1.20	0.0078	-1.1711	0.5893		0.8184	0.7569 <sub>4</sub>	16.3569
1.28		-1.1611	0.5911		0.8454	0.7844	16.7944
1.44		-1.1179	0.5879		0.8893	0.8318	17.5388
1.60		-1.0528	0.5766		0.9219	0.8700	18.1276
1.76		-0.9725	0.5572		0.9457	0.9005	18.5888
1.92		-0.8808	0.5295		0.9626 <sub>5</sub>	0.9244 <sub>5</sub>	18.9440
2.08		-0.7835	0.4952		0.9745 <sub>5</sub>	0.9430	19.2141
2.24		-0.6872	0.4573		0.9828	0.9572 <sub>3</sub>	19.4180
2.40		-0.5962	0.4182		0.9884 <sub>5</sub>	0.9680 <sub>6</sub>	19.5705
2.56		-0.5127	0.3795		0.9923	0.9762 <sub>5</sub>	19.6842
2.72		-0.4377	0.3421		0.9948 <sub>5</sub>	0.9824	19.7683
2.88		-0.3714	0.3066		0.9966 <sub>5</sub>	0.9870 <sub>1</sub>	19.8307
3.04		-0.3135	0.2736		0.9978	0.9904 <sub>4</sub>	19.8765
3.20		-0.2634	0.2431		0.9985 <sub>5</sub>	0.9929 <sub>9</sub>	19.9101
3.36		-0.2204	0.2152		0.9990 <sub>5</sub>	0.9948 <sub>7</sub>	19.9346
3.52		-0.1837	0.1894		0.9994 <sub>4</sub>	0.9962 <sub>4</sub>	19.9524
3.68		-0.1525	0.1671		0.9996	0.9972 <sub>6</sub>	19.9655
3.84		-0.1261	0.1467		0.9997 <sub>5</sub>	0.9980 <sub>1</sub>	19.9751
4.00		-0.1038	0.1284		0.9998 <sub>5</sub>	0.9985 <sub>5</sub>	19.9820
4.16		-0.0857	0.1120		0.9999	0.9989 <sub>5</sub>	19.9870
4.48		-0.0581	0.0848		0.9999 <sub>5</sub>	0.9994 <sub>5</sub>	19.9933
4.80		-0.0391	0.0638		1.0000	0.9997 <sub>2</sub>	19.9966
5.12		-0.0262	0.0476			0.9998 <sub>6</sub>	19.9983
5.44		-0.0174	0.0353			0.9999 <sub>3</sub>	19.9992
5.76		-0.0115	0.0261			0.9999 <sub>7</sub>	19.9996
6.08		-0.0076	0.0192			0.9999 <sub>8</sub>	19.9998
6.40		-0.0050	0.0141			0.9999 <sub>9</sub>	19.9999
6.72		-0.0033	0.0103			1.0000	20.0000
7.04		-0.0021	0.0075				

$$\left. \begin{aligned} N(1s) &= 12.35788 \\ N(2s) &= 0.500120 \\ N(2p) &= 1.450171 \end{aligned} \right\} \{N(nl)\}^2 \int_0^\infty \{P(nl)\}^2 dr = 1$$

The parameters  $\lambda_{1s}$  and  $\lambda_{2s}$  are adjusted so that  $r^{-1}P$  is orthogonal to  $r^{-1}P_{1s}$  and  $r^{-1}P_{2s}$ .

The terms on the right-hand side represent the exchange interaction. Strictly speaking the core functions  $P_{nl}$  should be determined from equations of the same form as (1), in which the effect of interaction with the metallic electron is included. This effect is likely to be very small and has been ignored throughout. Furthermore in (1) the contribution from terms involving the  $1s$  electron is also very small and has been neglected.

The function  $P/r$  is of  $3s$  type.  $\epsilon$  must therefore be determined so that  $P$  has two nodes between  $r=0$  and  $r=a$  and  $d/dr(P/r)$  vanishes at  $r=a$ .

The numerical calculations were carried out by an iterative procedure which converged quite quickly. Numerical solutions were first obtained with the exchange terms in (1) ignored. For a particular value of  $a$ , the function  $P_0$  obtained in this way was substituted in the right hand-side of (1). The resulting equation was solved with  $\lambda_{1s}$  and  $\lambda_{2s}$  put equal to zero, to obtain a new approximation  $P_1$ ,  $\epsilon_1$  to  $P$  and  $\epsilon$ , for this value of  $a$ . This approximation does not satisfy the orthogonality condition but it is not difficult to guess a modified function  $P_1 + \eta P_{2s}$  which does satisfy it, at least approximately. This function is then substituted for  $P$  on the right-hand side of (1) and further approximate solutions for  $P$  and  $\epsilon$  obtained. It was found from experience that this approximation is accurate enough for the present calculations.

Fig. 1 illustrates the variation of  $\epsilon$  with  $a^3$  obtained in this way. The considerable importance of the exchange interaction may be seen by comparison of curve I, obtained by neglect of exchange, with curve II, in which it is included.

So far the calculations have referred only to the lowest level in the conduction band of the metal. The actual energy per polyhedron relative to the gaseous ion is obtained by adding the mean Fermi energy. For alkali-like metals this is given quite closely (7) by

$$\epsilon_F = \frac{3}{10} \left( \frac{9\pi}{4} \right)^{2/3} \frac{h^2}{4\pi^2 m a^2} = \frac{1.10}{a^2} \text{ atomic units if } a \text{ is also measured in atomic units.}$$

This energy is represented as a function of  $a^3$  by curve III in Fig. 1. The final calculated variation of the electronic energy with the volume per nitrogen atom in the metal is then represented by curve IV in Fig. 1. This gives the amount per nitrogen atom by which the energy of the metal falls below that of the free ion  $\text{NH}_4^+$ . The equation of state of the metal at 0 deg. K may now be obtained from the relation

$$p = \frac{3}{4\pi} \frac{\partial \epsilon}{\partial a^3}, \quad (2)$$

$p$  being the pressure when the volume per ion is  $\frac{4}{3}\pi a^3$ .

Table II gives the pressure-density relation obtained in this way for a range of pressures of interest in connection with the constitution of Uranus and Neptune. It remains to consider what can be said about the transition pressure for the phase change to the metallic state.

*The transition pressure.*—To calculate the transition pressure the energy-volume relation for the mixed molecular ammonia-hydrogen crystal and for the metal must be available, both of course calculated from the same zero. The slope of the common tangent to the two curves then gives the transition pressure at 0 deg. K.

To carry out this procedure it is necessary to determine the difference in energy between the two phases when each is in its lowest state. We have, per nitrogen atom, denoting the energy per molecule of a compound XY by [XY],

$$\begin{aligned} [\text{NH}_4, \text{metal}] &= [\text{NH}_3, \text{gas}] - \text{Proton affinity of NH}_3 + (\epsilon + \epsilon_F)_0, \\ [\text{NH}_3, \text{crystal}] + \frac{1}{2} [\text{H}_2, \text{crystal}] &= [\text{NH}_3, \text{gas}] - I_{\text{H}} - \frac{1}{2} D(\text{H}_2) \\ &\quad + \epsilon(\text{NH}_3, \text{crystal}) + \frac{1}{2} \epsilon(\text{H}_2, \text{crystal}) \\ &\quad + \epsilon_{12}. \end{aligned} \quad (3)$$

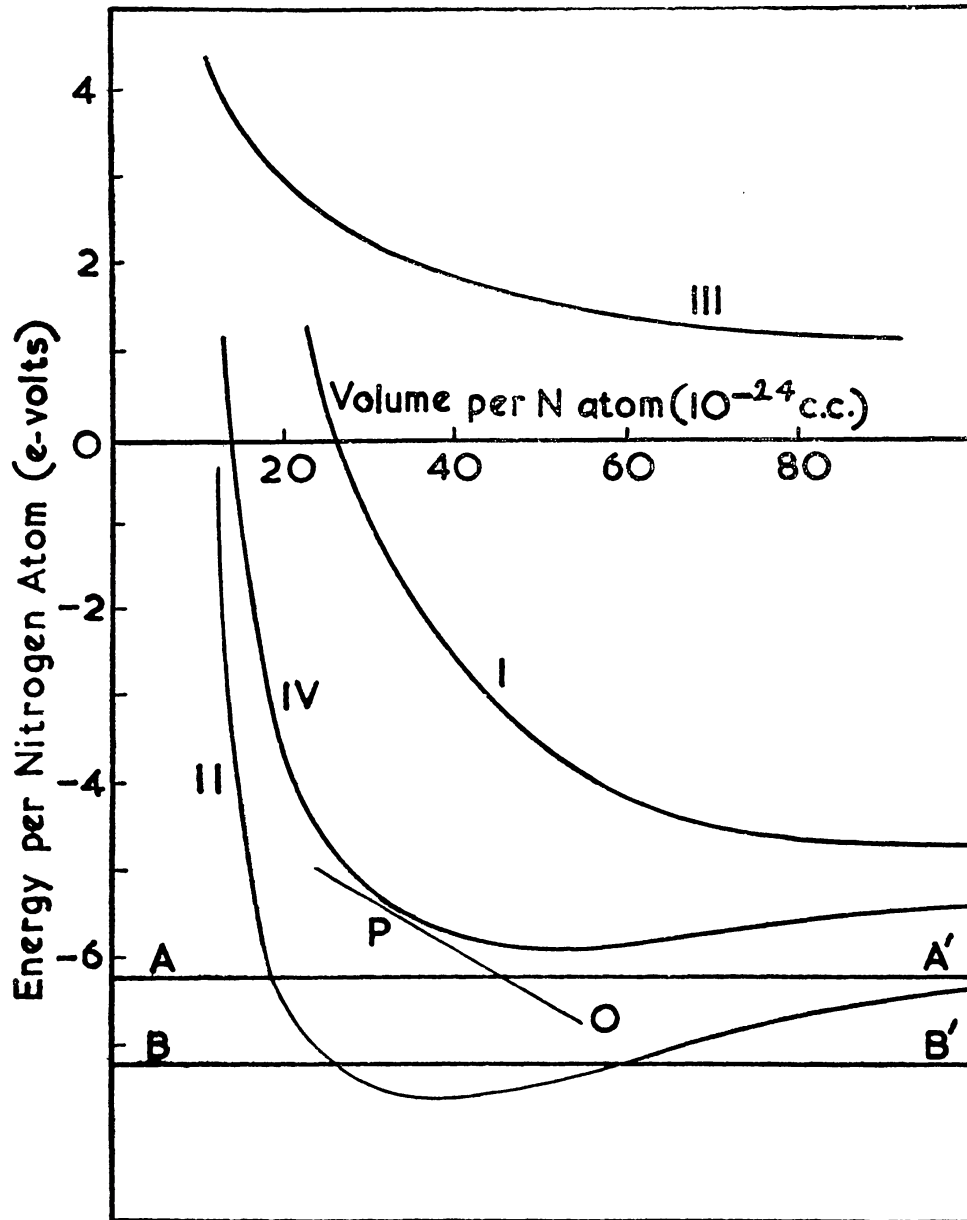


FIG. 1.—Calculated energy-volume relations at 0 deg. K for metallic ammonium.

- Curve I. Ground-state energy calculated neglecting exchange.  
 Curve II. Ground-state energy calculated with inclusion of exchange.  
 Curve III. Mean Fermi energy.  
 Curve IV. Calculated total energy.

The energy zero is that of a free  $\text{NH}_4^+$  ion.

The point O is the estimated equilibrium point for mixed crystals ( $\text{NH}_3 + \frac{1}{2}\text{H}_2$ ). OP is the estimated common tangent to the curves for the metallic and mixed crystal phases. The uncertainty in the energy of the mixed crystal relative to the metal due to the uncertainty of the proton affinity of ammonia is indicated by the lines AA', BB' respectively.

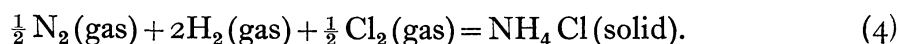
$I_H$  is the ionization energy of atomic hydrogen and  $D(H_2)$  the energy of dissociation of  $H_2$ ;  $-\epsilon(NH_3, \text{crystal})$  and  $-\epsilon(H_2, \text{crystal})$  denote the binding energies per molecule in the respective crystals.  $\epsilon_{12}$  is the energy per  $NH_3$  molecule arising from mixing the two molecular crystals.

TABLE II

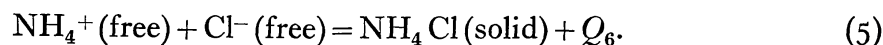
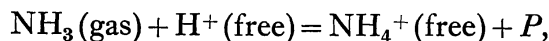
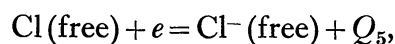
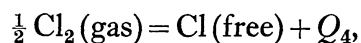
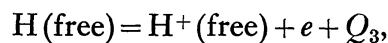
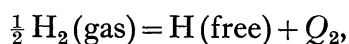
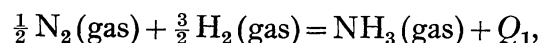
*Pressure-density relation for metallic ammonium at 0 deg. K*

Pressure ( $10^{12}$ dyne/cm <sup>2</sup> )	Density (g cm <sup>-3</sup> )
4.0	2.70
3.5	2.64
3	2.55
2.5	2.44
2	2.28
1.5	2.09
1.0	1.80
0.8	1.66
0.6	1.50
0.4	1.28

To determine the difference between the metal and molecular crystal energies we still need to know the proton affinity of  $NH_3$  and the molecular crystal binding energies. The proton affinity of  $NH_3$  is large and must be known with reasonable accuracy for present purposes. It cannot be calculated directly but may be determined in principle as follows (9). Let  $Q$  be the heat evolved in the reaction



This reaction may be regarded as equivalent to the successive reactions



Hence

$$Q = Q_1 + Q_2 + Q_3 + Q_4 + Q_5 + P + Q_6, \quad (6)$$

where the  $Q$ 's are the heats evolved in each reaction and  $P$  is the required proton affinity. All of the  $Q$ 's in (6) are known from direct measurement except  $Q_6$ . This must be obtained from the heat of sublimation of  $NH_4Cl$  by the method of Born and Mayer (10).

This procedure can be applied equally well to the other ammonium halides and the spread in the resulting values of  $P$  gives some indication of the accuracy of its determination. In electron-volts we find  $P = 9.55, 9.11, 8.94$  and  $8.72$  from the fluoride, chloride, bromide and iodide respectively. This suggests that  $P = 9.06 \pm 0.5$  eV but the uncertainty may be even larger than this.

The molecular crystal binding energies are of the order 2 kilocalories per mole or 0.1 eV. This is considerably smaller than the uncertainty in the proton affinity and can therefore be ignored. We now have

$$\begin{array}{rcl}
 \text{Proton affinity of NH}_3 & = & 9.06 \text{ eV} \\
 -(\epsilon + \epsilon_F)_0 & = & 5.84 \text{ eV} \\
 \hline
 & & 14.90 \text{ eV}
 \end{array}
 \qquad
 \begin{array}{rcl}
 \text{Ionization energy of H} & = & 13.54 \text{ eV} \\
 \frac{1}{2} \text{ Dissociation energy of H}_2 & = & 2.22 \text{ eV} \\
 \hline
 & & 15.76 \text{ eV}
 \end{array}$$

The minimum energy per nitrogen atom of the metal is clearly quite close to that of the mixed molecular crystal. The above calculation shows it to be only 0.86 eV larger. On the other hand, the uncertainty in the proton affinity indicated above is as much as  $\pm 0.5$  eV and other uncertainties arising from the approximations made in the calculation are likely to be comparable. This makes a reasonably accurate determination of the transition pressure difficult.

The equilibrium volume in the mixed crystal is not known from direct observation, but for present purposes it will suffice to suppose that the  $\text{NH}_3\text{-NH}_3$  and  $\text{H}_2\text{-H}_2$  separations remain the same as in the separate molecular crystals.

The densities of these crystals are 0.82 and 0.087 g cm<sup>-3</sup> respectively. It follows that the mean volume per nitrogen atom in a stoichiometric mixture is  $53.9 \times 10^{-24}$  cm<sup>3</sup>. This is indicated in Fig. 1 in relation to the equilibrium volume per nitrogen atom in the metal ( $47 \times 10^{-24}$  cm<sup>3</sup>).

In this figure the energy level of the equilibrium state of the mixed crystal is indicated, together with the uncertainty in this arising from the estimated uncertainty in the proton affinity alone.

To complete the estimation of the transition pressure it would seem necessary to know also the shape of the energy-volume curve for the mixed crystal near the equilibrium volume. Fortunately this is not really required. Reference to Fig. 1 shows that the slope of the common tangent to the equation of state curves for the two phases is very nearly that of the tangent to the metal curve from the equilibrium point of the mixed crystal curve. Taking the energy difference per nitrogen atom between the phases as 1.35, 0.85 and 0.35 eV, the range indicated from uncertainty in the proton affinity only, the transition pressure is found to be 140 000, 100 000 and 60 000 atmospheres respectively. It must be remembered that the uncertainty in this estimate is greater than indicated by this range. A transition pressure considerably less than 60 000 atmospheres is certainly not excluded. On the other hand, it is extremely probable that it is so low that metallic ammonium is the most stable phase throughout the main bulk of the planets such as Uranus and Neptune. Thus the calculated cohesive energy of metallic ammonium is not likely to be too large by as much as 0.5 eV as judged from comparison of the calculated and observed cohesive energy of the metallic sodium. In fact the calculated value is more likely to be too small, so decreasing the critical pressure. It is also likely, from comparison with sodium, that the equilibrium separation in the metal is overestimated in the calculation. This would also lead to an overestimate of the transition pressure. However, even if the energy difference per nitrogen atom were increased to 1.85 eV (assuming 0.5 eV overestimate of the cohesive energy and the lowest estimate of the proton affinity) the transition pressure would not exceed 250 000 atmospheres.

Although the foregoing theory cannot yield very accurate results it establishes that there is only a comparatively small energy difference per mole between the

metallic and mixed crystal phases. It is just possible that the transition pressure is low enough to be attained in the laboratory, but the difficulty of carrying out an experiment to produce the metal from the mixed crystal is so great that effort in this direction hardly seems justified at present.

*Acknowledgments.*—We are indebted to Dr W. H. Ramsey for drawing our attention to the possible importance of metallic ammonium in the structure of Uranus and Neptune, and for stimulating us to carry out these calculations. We were assisted in some of the numerical calculations by Miss J. Turner and have had the benefit of discussion with Dr R. A. Buckingham on various matters relating to self-consistent field calculations. The work was greatly assisted by a Special Research Grant from the Department of Scientific and Industrial Research.

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