free energy of formation of $Cr^{+++}(aq)$ which can then be combined with our free energy of formation of $Cr_2O_7^{=}(aq)$ to give $\Delta F°$ and $E°$ for the $Cr^{+++}/Cr_2O_7^{=}$ couple. Or the heat of reduction of $Cr_2O_7^{=}(aq)$ to $Cr^{+++}(aq)$ can be combined with an estimated entropy of $Cr^{+++}(aq)$, and our entropy of $Cr_2O_7^{=}(aq)$ to give $\Delta F°$ and $E°$ for the $Cr^{+++}/Cr_2O_7^{=}$ couple. Data from the literature for the pertinent heats[3,14] are so unreliable as to make these calculations virtually meaningless.

From the results of the investigation by Davies and Prue[8] of the temperature dependence of the equilibrium constant for reaction 7 we calculate $\Delta S_7^\circ = 8.5$ cal./deg. mole $Cr_2O_7^{=}$ and $\Delta H_7^\circ = 4.64$ kcal./mole $Cr_2O_7^{=}$. These data have been combined with our heat of formation and entropy of $Cr_2O_7^{=}(aq)$ and the National Bureau of Standards values for water to give the heat of formation of $HCrO_4^-(aq)$ as $-205.0$ kcal./mole and the entropy as 47.8 cal. deg./mole. We also have calculated the standard free energy of formation of $HCrO_4^-$ to be $-179.0$ kcal./mole.

## Discussion

Latimer[3] and the National Bureau of Standards[1] have taken the entropy of $HCrO_4^-(aq)$ to be 16.5 cal./deg.mole. Our value (47.8) is much more nearly in accord with what one should expect from comparison with $MnO_4^-$ (45.4),[3] $ReO_4^-$ (48.3),[15] and $ClO_4^-$ (43.2).[3] We also see that the entropy of ionization of $HCrO_4^-$ ($-38.6$) as calculated from our entropy is in accord with the entropies of ionization of $HSO_4^-$ ($-26.2$), $HSO_3^-$ ($-33$), $H_2PO_4^-$ ($-29.9$), $HCO_3^-$ ($-35.4$) as taken from Latimer.[3]

Our heat of solution of $K_2CrO_4(c)$ ($\Delta H_2^\circ$) is in good agreement with the results obtained by earlier workers.[1] Our heat of solution of $K_2Cr_2O_7(c)$ ($\Delta H_4^\circ$) is about 3 kcal./mole more positive than heats reported by earlier investigators.[1] It is impossible to compare our heats of reaction of $K_2CrO_4(c)$ with $H^+(aq)$ ($\Delta H_3^\circ$) and of $K_2Cr_2O_7(c)$ with $OH^-(aq)$ ($\Delta H_5^0$) with the older heats[1,2] because the older work was carried out in relatively concentrated solutions and at temperatures lower than 25°. Our heat of reaction of $CrO_3(c)$ with $OH^-(aq)$ ($\Delta H_9^\circ$) is several kcal./mole more exothermic than earlier heats. We attribute this to the fact that the older work was carried out in more concentrated solutions at temperatures lower than 25° and possibly with less pure $CrO_3$.

**Acknowledgments.**—We are pleased to express our gratitude to Mr. Robert L. Graham for help with some of the calorimetric work and to the Research Corporation for financial assistance.

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[14] M. W. Evans, Paper 3.30 "Nat. Nuclear Energy Series," Vol. 14B, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 282.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

# A Copper Analog of the Alkali Tungsten Bronzes

BY LAWRENCE E. CONROY AND M. J. SIENKO[1]

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Non-stoichiometric solids of the form $Cu_xWO_3$ have been prepared by electrolytic reduction at 800° of molten mixtures of $CuWO_4$ and $WO_3$. Copper content has been varied from $x = 0.26$ to $x = 0.77$. Two kinds of crystals have been found—orthorhombic with $a = 3.88$ Å., $b = 3.73$ Å., and $c = 7.74$ Å., taken from the preparation for which $x = 0.26$, and triclinic with $a = 5.85$ Å., $b = 6.65$ Å., $c = 4.88$ Å., $\alpha = 134°45'$, $\beta = 91°40'$, and $\gamma = 93°37'$, taken from the preparation for which $x = 0.77$. The molar magnetic susceptibility at 26° of the powder for which $x = 0.26$ was observed to be $+34 \pm 1 \times 10^{-6}$. Conductivity measurements from $-160°$ to $+80°$ made on single triclinic crystals taken from the preparation for which $x = 0.77$ showed typical semi-conductor behavior. At 26° the specific resistance was 12.6 ohm-cm. perpendicular to the $c$-axis and 17.2 ohm-cm. parallel to the $c$-axis. Energies of activation for the conduction process were found to be 0.147 and 0.149 electron volt, respectively. Attempts to measure the Hall voltage of a single crystal indicated 13 cc. per coulomb as an upper limit for the Hall constant, from which it is deduced that the minimum concentration of current carriers is $5 \times 10^{17}$ particles per cc. It is proposed that these materials are analogous to the tungsten bronzes.

The alkali tungsten bronzes are non-stoichiometric solids of composition $M_xWO_3$, where M is an alkali metal and $x$ can vary from 0 to 1. Although known since their discovery by Wöhler[2] in 1824, it is only recently that these bronzes have been well characterized.[3] The sodium tungsten bronzes, for which the data are most extensive, have been shown to have a cubic perovskite structure[4] if $x$ is greater than about 0.35, a high electronic[5] conductivity which passes through a maximum[6] at $x = 0.75$, and a feeble paramagnetism[7,8] which is independent of temperature.[8] The Hall coefficient is negative, and its magnitude indicates that there is approximately one free electron per sodium atom.[5] Chemically, all the alkali tungsten bronzes are quite inert, being attacked only by strong alkalies.

As discussed in a previous paper,[9] the tungsten

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[1] On leave of absence at the Laboratorie de Chimie Minérale, University of Toulouse, Toulouse, France.

[2] F. Wöhler, *Pogg. Ann.*, **2**, 350 (1824).

[3] G. Hägg, *Z. physik. Chem.*, **B29**, 192 (1935); G. Hägg, *Nature*, **135**, 874 (1935); M. F. Straumanis and S. S. Hsu, THIS JOURNAL, **72**, 4027 (1950); A. Magneli, *Arkiv. Kemi*, **1**, 213 (1949); A. Magneli and B. Blomberg, *Acta Chem. Scand.*, **5**, 377 (1951).

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[9] L. E. Conroy and M. J. Sienko, THIS JOURNAL, **74**, 3520 (1952).

bronzes can best be considered as solutions of M in $WO_3$, in which each M atom is dissociated into $M^+$ and an electron. The cubic bronzes can then be visualized as consisting of a simple cubic arrangement of tungsten atoms with shared oxygen atoms on the cube edges and with vacancies in the cube centers more or less occupied by alkali metal cations. Each alkali metal atom has thus effectively contributed one free electron to the electron gas which permeates the whole lattice. Since Cu(I) has approximately the same ionic radius as the sodium ion, it might be possible to substitute copper cations for sodium cations in the above structure and thereby obtain a $Cu_xWO_3$ analogous to $Na_xWO_3$. In the following, the preparation and properties of $Cu_xWO_3$ are described.

## Experimental Procedure and Results

**Preparation.**—$Cu_xWO_3$ was prepared by electrolytic reduction of fused mixtures of $CuWO_4$ and $WO_3$. The $CuWO_4$ was made by mixing tungstic acid, $H_2WO_4$, and basic copper carbonate, $CuCO_3 \cdot Cu(OH)_2$, in a 2:1 molar ratio and adding enough water to make a thin slurry. The mixture was heated at about 70° for 3 to 4 hr. and the remaining water was then evaporated off at 130° in a drying oven. The product was a green-brown powder melting at about 680°. The $WO_3$ was made as previously described.[9]

To produce $Cu_xWO_3$, mixtures of various proportions of $CuWO_4$ and $WO_3$ were electrolyzed at 800° using platinum electrodes. The applied potential was six volts at the electrodes with a cathode current density of 0.06 to 0.08 amp. per cm.$^2$. Electrolysis was continued for four hours. The cooled melt, on being heated with 5% NaOH solution at 80° overnight, disintegrated into a mixture of black crystals and red $Cu_2O$. After the $Cu_2O$ was removed with concentrated HCl, the remaining crystals were further leached with 5% NaOH for one hour, washed alternately with aqueous HF and $NH_4OH$, and finally rinsed with water. Chemically, the $Cu_xWO_3$ was found to be as inert as the alkali tungsten bronzes.

Three different preparations of $Cu_xWO_3$ were produced, having values of $x$ of 0.26, 0.34 and 0.77. These materials were prepared from melts containing one, two and six moles of $CuWO_4$, respectively, per one mole of $WO_3$.

**Chemical Analysis.**—The products were brought into solution by fusion with a mixture consisting of three parts of $NaNO_3$ to one part of $Na_2CO_3$ by weight. The cooled melt was then dissolved in water. Tungsten was determined as the trioxide by the nitric acid-cinchonine precipitation.[10] Copper was determined (1) electrolytically[11] in ammoniacal solution and (2) polarographically using a dropping mercury electrode. For the latter method, the copper diffusion current of the analysis solution was compared with the copper diffusion current of a standard copper solution containing all other ions in the same concentrations as in the analysis solution. The two methods agreed within 4% of the copper content. Oxygen content, calculated by difference, amounted to 2.9 ± 0.3 gram-atoms per gram-atom of tungsten.

**X-Ray Studies.**—Powder X-ray patterns of the three products prepared were very similar. The lines in all cases were quite diffuse in the high angle region and could not be measured more accurately than 0.1 mm. Indexing the powder pattern lines proved to be a formidable task, so single crystal photographs were taken of two crystals. Crystal I was taken from the preparation having the composition $Cu_{0.26}WO_3$ and crystal II, $Cu_{0.77}WO_3$.

Crystal I was a needle about 0.7 mm. long and 0.08 mm. in diameter. It was mounted for oscillation about the direction of elongation. Fifteen-degree oscillation photographs and zero and first layer Weissenberg photographs were taken using copper K$\alpha$ radiation. The zero layer Weissenberg photograph showed the axes to be orthogonal within 0.2°. This photograph also showed the systematic absence of any spots with indices $l$ odd. The lattice parameters were calculated to be: $a$ = 3.88 Å., $b$ = 3.73 Å., and $c$ = 7.74 Å. The zero and first layer Weissenberg photographs about the $b$-axis showed no other special extinctions. Since photographs were not taken about the other axes, the crystal symmetry could be classified only as far as orthorhombic.

Crystal II was a needle about 0.9 mm. in length and 0.07 mm. in diameter. This crystal was mounted for oscillation about the elongation direction, and 15° oscillation photographs were taken. The layer line spacings indicated an interplanar spacing of 4.90 Å. Zero layer and first layer equi-inclination Weissenberg photographs were taken about the same axis. It was found that two series of spots could be indexed on these photographs, indicating that the crystal was twinned. The apparent presence of a symmetry plane led us at first to the erroneous assumption that the symmetry was monoclinic. Further studies[12] on other crystals of this preparation, however, have shown that the symmetry is actually triclinic. The lattice parameters of the "best" primitive cell have been taken as: $a$ = 5.85 Å., $b$ = 6.65 Å., and $c$ = 4.88 Å. with $\alpha$ = 134°45′, $\beta$ = 91°40′, and $\gamma$ = 93°37′. The needle axis is always in the direction of $c$, and the crystals are twinned about $a$. (The proximity of $\beta$ to 90° was responsible for our original assumption of monoclinic symmetry.) The space group is either P1 or P1.

**Magnetic Susceptibility.**—The molar magnetic susceptibility of a powder sample having the composition $Cu_{0.26}WO_3$ was determined by the Gouy method using the apparatus and the procedure previously described.[9] The observed susceptibility at 26° for a mole of $Cu_{0.26}WO_3$ was found to be $+34 \pm 1 \times 10^{-6}$ c.g.s. units. Furthermore, using 3 cm. radiation, there was no detectable paramagnetic resonance absorption in magnetic fields ranging from zero to 9000 oersted, either at 26° or at liquid nitrogen temperature.

**Electrical Conductivity.**—The electrical conductivity of some apparently single crystals of $Cu_{0.77}WO_3$ was measured as a function of temperature over the range 110 to 350°K. The crystals used were of the triclinic form and were 2 to 3 mm. long and 0.5 to 1 mm. in diameter. They were cleaved approximately perpendicular to the long axis and were mounted in a brass crystal holder between indium-faced pressure contacts by means of a micromanipulator. The potential drop across the crystal was measured with a Leeds and Northrup type K-2 potentiometer. The current flowing through the crystal was measured by noting the potential drop across a standard resistor in series with the crystal. The crystal holder itself was mounted on a Plexiglas rod support and enclosed in a silvered Dewar flask by a Plexiglas cover sealed with a rubber O-ring. The gas pressure in the Dewar jacket could be varied through a side-arm and stopcock. The temperature of the crystal was measured by a copper–constantan thermocouple mounted on the brass crystal holder with the junction in contact with one of the pressure contacts which held the crystal.

Before each set of conductivity measurements, the Dewar containing the crystal was flushed for 30 min. with dried argon or oil-pumped nitrogen. For the low temperature measurements, dry air was let into the Dewar jacket and the Dewar and contents immersed in liquid nitrogen. The Dewar jacket was then pumped out and the liquid nitrogen-bath removed. Readings were then taken as the crystal slowly warmed to room temperature. For temperatures above room temperature the Dewar was immersed in a heated water-bath.

A typical crystal had a resistance of 2 to 3 thousand ohms, so that the current through the crystal from a 6-volt dry cell source was a few milliamperes. Using this apparatus, the conductivity curve for a given crystal could be reproduced to within the precision of the thermocouple reading (*ca.* 0.5%). Reversal of the polarity of the imposed potential produced no detectable change in the conductivity. For specific resistivity values the crystal dimensions were measured with a microscope, using a micrometer eyepiece. The data obtained for several crystals are represented in Fig. 1 as a plot of the logarithm of the specific resistivity against the reciprocal of the absolute temperature. At 26° a typical crystal showed a specific resistivity of 12.6 ohm-cm. perpendicular to the crystal elongation axis ($c$-axis) and 17.2 ohm-cm. parallel to the same axis. Assuming an exponential form of the dependence of resistivity on the reciprocal of the absolute temperature, we obtain for

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(10) F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1937, p. 226.

(11) Ref. 10, p. 68.

(12) R. E. Hughes and H. Katz, private communication. Detailed structure studies are now in progress.

the energy of activation of the process 0.147 electron volt for conductance perpendicular to the $c$-axis and 0.149 e.v. for conductance parallel to the $c$-axis. Measurements using sputtered contacts in place of the pressure plates give essentially the same values.

**Measurement of the Hall Coefficient.**—A three-probe method was used. One probe was mounted on one side of the crystal; the other two were connected through a 100,000 ohm helipot and were in contact with the opposite side of the crystal. With the center tap of the helipot connected to the voltage-measuring apparatus, the $IR$ drop between the probes in the direction of the current in the crystal could be balanced out by obtaining a minimum voltage reading with current flowing in the crystal in the absence of a magnetic field. Any change in the voltage when the magnetic field was applied must then be due solely to the magnetic field. The probes were 10 mil diameter tungsten wires, sharpened by dipping repeatedly in molten potassium nitrite. The magnetic field was supplied by a small magnetron magnet with half-inch diameter pole faces rated at 7500 gauss.

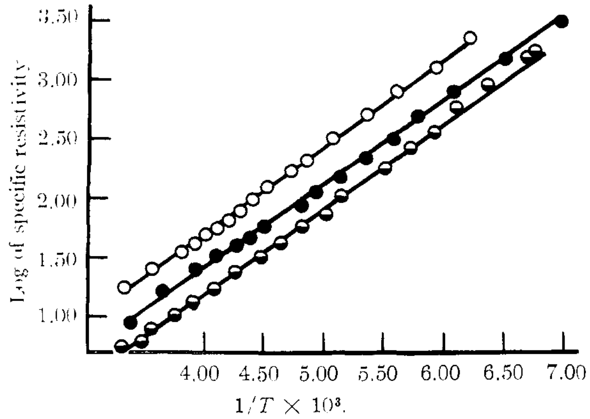

Fig. 1.—Logarithm of the specific resistivity *vs.* reciprocal temperature of three different crystals of $Cu_{0.77}WO_3$.

Attempts to measure the Hall voltage using direct current through the crystal did not give reproducible results. An alternating current method, using a 50-cycle square wave of 10 milliamperes through the crystal and a narrow-band amplifier tuned to 50 cycles at the output of the Hall probes, indicated that there was no Hall voltage measurable above the noise level of the equipment. Thus, it was possible to set only an upper limit on the Hall voltage of 0.25 millivolt, which was the limit of sensitivity of the apparatus.

## Discussion

Compared to the sodium tungsten bronzes, in which the magnetic susceptibility and conductivity behavior are typically metallic, the substances $Cu_xWO_3$ offer a contradiction in these properties. Their low magnetic susceptibility can be interpreted in terms of an electron gas, but such an electron gas structure would suggest fairly high conductivity. In fact, the conductivity of $Cu_xWO_3$ is low and increases with temperature, a behavior more representative of a typical semi-conductor. It is true that many semi-conductors show also a low magnetic susceptibility but this in general is due to the low concentration of impurity centers. In $Cu_xWO_3$, which may be considered as solutions of impurity copper in $WO_3$, the concentration of impurity centers is large enough to be expected to produce an easily detected paramagnetism.

If we assume that the copper atoms in $Cu_xWO_3$ are dissociated into $Cu^+$ ions and free electrons, then we would have in $Cu_{0.26}WO_3$ 0.26 mole of free electrons. Using the free electron model described in a previous paper,[9] we would calculate $-12 \times 10^{-6}$ for the molar susceptibility of $Cu_{0.26}WO_3$. If the electrons are not free but are bound singly, as for example to tungsten atoms so that formally some of the W(VI) of $WO_3$ is converted to W(V), then we would calculate a value of $+218 \times 10^{-6}$ for one mole of $Cu_{0.26}WO_3$. These values are to be compared with the experimentally observed susceptibility of $+34 \times 10^{-6}$. Evidently, the experimental value is closer to the electron gas model than to the W(V) model. The discrepancy between $-12 \times 10^{-6}$ and $+34 \times 10^{-6}$ could be accounted for qualitatively by assuming that the electrons are not absolutely free as in an ideal electron gas but are feebly bound to some centers in the lattice. Even feeble binding would tend to make the spin paramagnetism of the electrons start to appear.

However, feeble binding of the electrons implies that the electrons are rather free to move through the lattice, a prediction contradicted by the observed low conductivity. Therefore, in spite of the support offered by the low magnetic susceptibility, the free electron gas model does not seem applicable to $Cu_xWO_3$ as it is to the sodium tungsten bronzes.

What is the alternative? To account simultaneously for the low conductivity and the low susceptibility, it is necessary to assume that the odd electron of each copper atom is bound in the lattice not singly but is paired with another electron. There are several mechanisms by which this pairing could occur. An electron could be physically transferred from one copper atom to another, so that the material might consist of a solution of $Cu^+$ and $Cu^-$ ions in a $WO_3$ lattice. Alternatively, the odd electron could be localized on a copper atom but coupled by an exchange interaction with an electron on a neighboring copper atom. There might even be coupling by superexchange through the intermediacy of an intervening oxygen atom. A third possibility would be for the electron of each copper atom to be transferred to the $WO_3$ network with subsequent coupling of neighboring W(V) states by superexchange through intervening oxygen atoms. In any case, the spin paramagnetism of the odd electron of the copper would have to be cancelled to agree with experimental observations. Localization of the electrons would have to be assumed, to agree with the low conductance observed.

Although the measurement of the Hall effect described above is inconclusive, there are some inferences which can be drawn from it. If we set the upper limit of the Hall voltage at 0.25 millivolt, then by using the relation

$$R_H = \frac{10^8 V_H t}{IH}$$

where $V_H$ is the Hall voltage in volts, $t$ is the thickness of the crystal in cm., $I$ is the current in amperes, and $H$ is the magnetic field in gauss, we calculate 13 cc. per coulomb as an upper limit for the Hall constant, $R_H$. According to theory,[13] if conduction is by electrons, the Hall constant is in-

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(13) See, for example, W. Shockley, "Electrons and Holes in Semiconductors," D. Van Nostrand Co., Inc., New York, N. Y., 1950, p. 211.

versely proportional to the density of conducting electrons. Using

$$R_H = -\frac{1}{ne}$$

where $n$ is the number of conduction electrons per cc. and $e$ is the electronic charge in coulombs, we find $5 \times 10^{17}$ as a lower limit for the number of free electrons per cc. This figure is in substantial agreement with the number $10^{18}$ absorbing centers per cc. deduced from very crude measurements of the intensity of infrared absorption by powdered $Cu_xWO_3$.

In view of the crudity of our Hall voltage measurement, only qualitative significance can be given to the numerical comparison offered above. We are now in the process of refining our measurements to make the comparison more meaningful. In addition, we are extending our investigations to newly prepared $Pb_{0.4}WO_3$, which seems to be typically metallic, and to $Ag_{0.4}WO_3$, which is apparently semi-conducting.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

# Free Energy Change and the Electron Electrode in Liquid Ammonia

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The standard free energy change for the reaction $Na_{(s)} \rightarrow Na^+_{(NH_3)} + e^-_{(NH_3)}$ has been determined experimentally by combining measurements on two types of galvanic cells: Na | NaI in liquid ethylamine | Na amalgam, for which the standard e.m.f. was found to be 0.828 ± 0.000 and 0.835 ± 0.001 volt at −50 and −70°, respectively, and Na amalgam | NaI in liquid ammonia ‖ Na in liquid ammonia | inert metal, for which the standard e.m.f. was found to be −0.933 ± 0.020 volt at −50° and −0.947 ± 0.020 volt at −70°. These results have been used to obtain directly an experimental value for the solvation free energy of sodium ion in ammonia. Measurements are also reported for the distribution of sodium between mercury and liquid ammonia.

The existence of ion-like electrons in sodium–liquid ammonia solutions[2] suggests the possibility of constructing a galvanic cell which would give directly the free energy change for the reaction

$$Na_{(s)} \longrightarrow Na^+_{(NH_3)} + e^-_{(NH_3)}$$

The most obvious design—solid sodium as one electrode and an inert metal as the other, both immersed in the same solution of sodium in liquid ammonia—gives no useful information because the over-all cell reaction shown above comes to equilibrium as a dissolution equilibrium at the solid sodium–liquid ammonia interface. To bypass this difficulty, we have constructed two cells—in one of which the dissolution equilibrium was completely suppressed by amalgamation of the sodium and in the other of which the effect of such amalgamation on the voltage was determined. The two types of cells and their designations in this paper are

Cell I $Na_{(s)}$ | NaI in $EtNH_2$ | $Na_{(Hg)}$

Cell II $Na_{(Hg)}$ | NaI in $NH_3$ ‖ Na in $NH_3$ | inert metal

Before describing the structure and operation of these cells, we note two problems that arose in the course of this research. In order to choose an amalgam concentration that would be sufficient to repress the sodium dissolution equilibrium, it was necessary that we investigate the distribution of sodium between mercury and liquid ammonia. The second problem dealt with the choice of metal to use as an inert "electron electrode" in liquid ammonia. Kraus[3] in his work on transference numbers and Laitinen and Nyman[4] in their polarographic work with the "electron electrode" used platinum as the inert conductor. For ease in constructing the complicated closed systems of glass required to keep the sodium–ammonia solutions away from air, we used tungsten. However, since tungsten does not give reproducible results when used as an electrode in aqueous solutions, it was necessary that we show for ammonia solutions that platinum and tungsten electrodes give substantially equivalent results.

## Experimental Procedure

**Preparation of Materials.**—All procedures were carried out in a high vacuum chain capable of producing pressures less than $1 \times 10^{-6}$ mm. Degassing and baking out were carried out where needed. Ammonia, obtained from Matheson as anhydrous 99.9% pure, was triply distilled from its solutions with sodium before use. Sodium, obtained from Mallinckrodt, was purified by the method of Watt and Sowards.[5] Ethylamine, obtained from Eastman Kodak as a 33% solution in water, was first concentrated by distilling it off from a slurry of calcium oxide and then purified by redistilling it from its solution of lithium metal. Sodium iodide, Baker and Adamson reagent grade, was used directly without further purification except for drying. Mercury for the amalgams was scrubbed in a mercury oxifier, washed with nitric acid and triply distilled before use.

**Distribution Experiments.**—The distribution of sodium between mercury and liquid ammonia was determined in an all-glass system with a built-in pipet which served both to introduce gas for stirring the liquid ammonia solutions and to take samples of the solutions for analysis. In operation, a sodium–ammonia solution was formed in an outer jacket and a weighed amount of mercury dropped in through a ball-and-socket valve manipulated from the outside. Prepurified hydrogen bubbled through the pipet tip served to mix the solution. A pair of tungsten electrodes sealed through the outer jacket wall enabled concentration changes in the solution to be followed from measurements of the a.c. electrical resistance. After distribution equilibrium had been established, hydrogen pressure could be applied to force a sample of the ammonia solution into the pipet. Distribution experiments were also performed in which

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[1] On leave of absence at the Laboratoire de Chimie Minérale, University of Toulouse, Toulouse, France.

[2] See, for example, W. N. Lipscomb, *J. Chem. Phys.*, **21**, 52 (1953).

[3] C. A. Kraus, THIS JOURNAL, **36**, 864 (1914).

[4] H. Laitinen and Ç. Nyman, *ibid.*, **70**, 3002 (1948).

[5] G. W. Watt and D. M. Sowards, *ibid.*, **76**, 4742 (1954).