

TABLE IV
CONSTANTS AND DATA FOR COMPOUNDS

	HCl (g)	NOCl (g)	CH ₃ OH (g)	CH ₃ ONO (g)
$\Delta F_{298.1}^{\circ}$	-22,740	16,400	-38,870	-100
$\Delta H_{298.1}^{\circ}$	-22,030	12,300	-48,290	-16,750
$\Delta S_{298.1}^{\circ}$	2.38	-13.8	-31.6	-55.9
$S_{298.1}^{\circ}$	44.64	60.3	56.7	64.2

Summary

Quantitative measurements of the light absorption of nitrosyl chloride and methyl nitrite have been made. Measurements of the light absorption due to nitrosyl chloride present in the gas phase equilibrium $\text{CH}_3\text{ONO (g)} + \text{HCl (g)} = \text{CH}_3\text{OH (g)} + \text{NOCl (g)}$ have been made and equilibrium constants calculated for the temperatures of 25 and 50° for both the forward and reverse reactions. The equilibrium is instantly established, is independent of the direction from which it is established and is free from side reactions. The equilibrium constants are $K_{298.1} = 0.521$ and $K_{323.1} = 0.753$. From these values and from thermodynamic data in the literature for hydrogen chloride, nitrosyl chloride and methyl alcohol we have calculated the free energy, the heat and the entropy of formation and the entropy of methyl nitrite.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

REACTION OF GASES WITH INCANDESCENT TANTALUM

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It has been known for many years that tantalum, when heated, absorbs actively such gases as nitrogen and hydrogen, but early experimentation was confined to the comparatively low temperatures obtainable in furnaces, and the pressures were the comparatively large ones measurable with a manometer.¹ With modern methods of vacuum technique, it is possible to study reactions at very low pressures and at temperatures up to the melting point of the material under observation. Tantalum offers a particularly interesting subject for such a study.

The following work was done with tantalum filaments mounted in bulbs on an exhaust system. The system contained a reservoir of the particular gas in use and suitable mercury traps for shutting off known volumes. Pressures were read with McLeod gages.

¹ Von Bolton, *Z. Electrochem.*, **11**, 45 (1905); Sieverts and Bergner, *Ber.*, **44**, 2394 (1911); Balke, *Chem. Met. Eng.*, **27**, 1271 (1922); Borelius, *Metallwirtschaft*, **8**, 105-108 (1929)

Nitrogen.—The tantalum filament was given a preliminary degassing in vacuum at 2400–2500° until the cold resistance had decreased to a constant value and no more gas was evolved. A known pressure of nitrogen was then admitted, the filament run at a constant wattage and the pressure was read at known intervals until the gas had been absorbed to an equilibrium pressure.

If, now, another charge of nitrogen was admitted and the filament again run, absorption took place at a somewhat lower rate than before, and the equilibrium pressure was somewhat greater (see Fig. 1). During the first part of any run, the temperature is uncertain, due to the cooling effect of the gas, but for low equilibrium pressures the temperature at the end of the run is accurate within a few degrees.

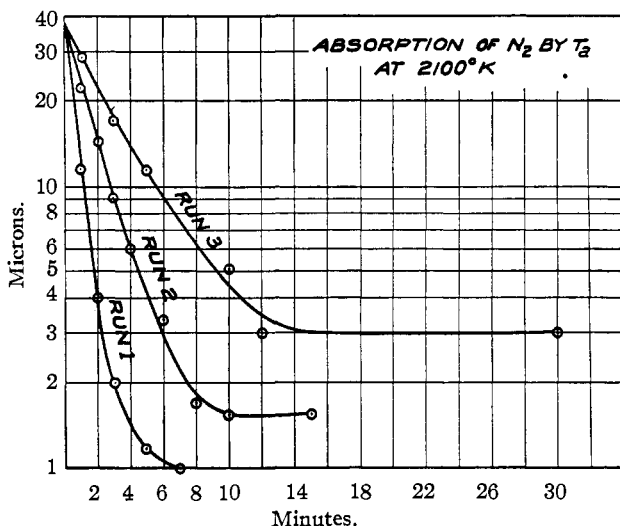


Fig. 1.—Absorption of nitrogen in a volume of 3250 cc. by a 10 mil tantalum filament 20 cm. long at 2100°K. Pressure in system *vs.* time of absorption.

If, after absorbing nitrogen, a filament is run in an evacuated bulb, it will evolve gas until an equilibrium pressure is again reached. For a given concentration of gas in the metal, the equilibrium at any given temperature is the same whether obtained by absorption or evolution. If the filament is heated while the gas evolved is steadily pumped away, it will lose all the nitrogen it has absorbed and return to its original degassed condition. In this process there is no loss of tantalum.

These results prove that, at least in low concentrations, nitrogen goes into tantalum by solution, not by the formation of a compound. Were a compound formed, the equilibrium pressure (or decomposition pressure) would be constant during absorption at any given temperature, inde-

pendent of the amount absorbed, until all the metal had been converted to the compound.

Figure 2 shows a composite curve of the logarithm of the equilibrium pressure *versus* the logarithm of the concentration of nitrogen in the filament at 2240°. The concentration is given as the volume (at N. T. P.) of gas absorbed divided by the volume of the filament, that is, the number of times its own volume absorbed by the filament. It should be noted that the slope is about 1:2, or that the pressure varies as the concentration squared. This agrees with results obtained by Sieverts and Bergner on the

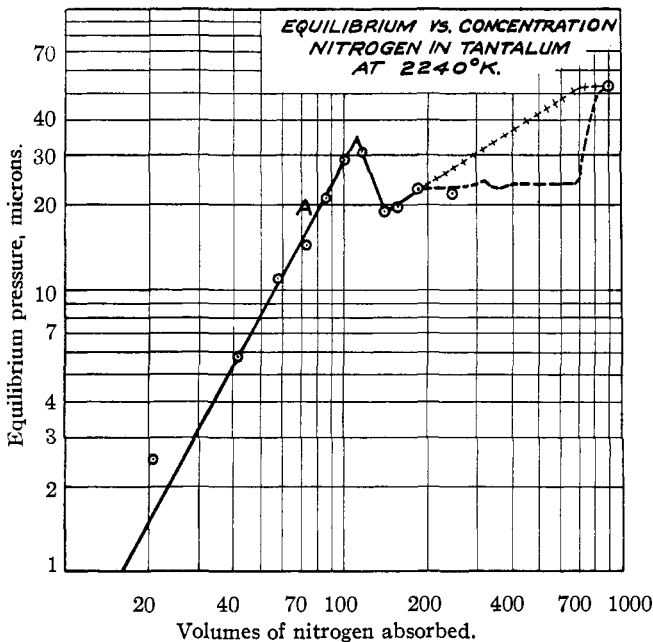


Fig. 2.—Equilibrium pressure *vs.* concentration of nitrogen in tantalum at 2240°K.

solubility of *hydrogen* in tantalum, and indicates that the gas is absorbed in the atomic state. At a concentration of about a hundred volumes, which would give a composition corresponding to Ta₁₀N, this curve shows a sudden break in such a direction that by increased concentration of nitrogen in the filament the equilibrium pressure is lowered. Dr. W. P. Davey very kindly took x-ray photographs of two samples of nitrogen-charged tantalum, one of which contained about fifty volumes of nitrogen, the other about two hundred volumes. The first filament showed only the tantalum structure, but the second, more highly charged filament, showed, besides the tantalum structure, an entirely different crystal form. It is not known whether this is the structure for tantalum nitride or whether the

strain produced by the absorbed gas causes the metal to go into a new form in which nitrogen is more soluble. If the change is to the nitride structure, one would assume that the decomposition pressure of the compound was about that at the point A (Fig. 2) and that the metal in absorbing nitrogen became supersaturated and then suddenly reacted to form the nitride with the excess gas, both within and without the metal. This would explain the shape of the curve at higher concentrations quite nicely, the level part at more or less constant equilibrium pressure being the range through which nitride is being formed. There are, however, objections to this theory. First, it is possible to produce this maximum not only through absorption, but also in the opposite direction by evolution of gas from the filament. For instance, a filament which had absorbed 275 volumes of nitrogen was heated at 2200°K. in an evacuated system of known volume so that it evolved gas until an equilibrium pressure was reached. Gas was pumped out and equilibrium again obtained by evolution from the filament. The following shows the maximum pressure obtained at 112 volumes of nitrogen in the filament

Vol. of N ₂ in filament.....	200	175	112	70
Equilibrium pressure, microns.....	23	22	35	26

If the peak were due to supersaturation, it should not appear when the gas is removed. Moreover, the electrical resistance at room temperature, which increases almost linearly with the concentration of nitrogen, shows no break at this critical concentration, such as would be expected if a compound were being formed [see Fig. 4].

As for the shape of the pressure-concentration curve obtained at the higher concentrations (shown as a broken line in Fig. 2), it may have to be altered considerably because above a concentration of about 200 volumes the emissivity of the surface appears to increase gradually, the color going to a dull gray. As no allowance was made for this change, in the wattages used, the filament temperature undoubtedly fell considerably through the range 200 to 700 volumes concentration. Above seven hundred volumes the equilibrium pressure appears to increase rapidly, but because at these high concentrations the filament becomes very brittle, few measurements could be made. A concentration of 900 volumes would correspond to complete conversion of the metal to TaN. It seems probable, therefore, that at about the concentration of 700 volumes this compound begins to form with a resulting sintering of the surface and a rise of the temperature to something much closer to the original value. If this is so the equilibrium curve should follow, at constant temperature, the cross-hatched line shown in Fig. 2.

As the temperature of the metal is increased, the rate of solution increases, but the solubility decreases, *i. e.*, the equilibrium pressure for any

given concentration increases. Absorptions were made from 1600 to 2400°K. Figure 3 shows the equilibrium pressures for constant nitrogen content in the wire, plotted as the logarithm of the pressures against the inverse of the temperature. From the slope of these lines, the heat of solution is calculated to be 102,000 calories. This value may be somewhat in error due to the necessary correction made for the cooling effect of the gas on the filament at the higher temperatures and pressures.

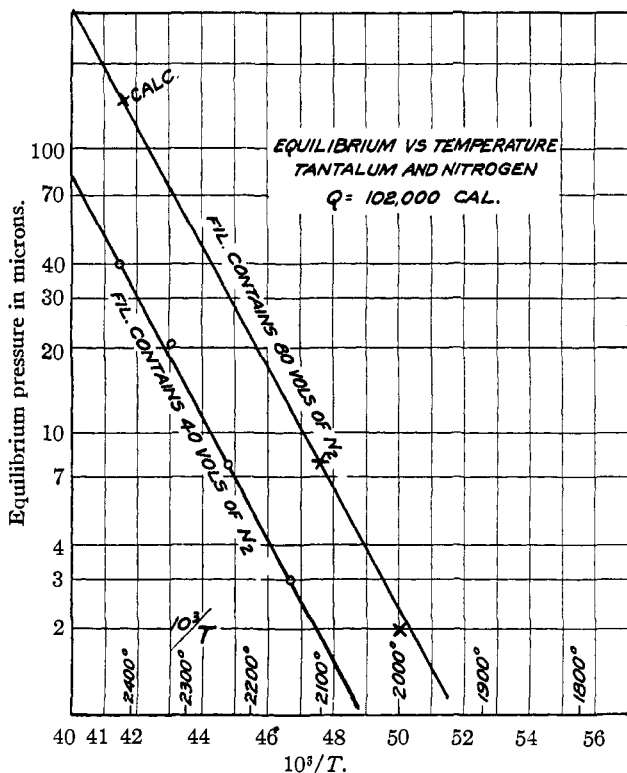


Fig. 3.—Equilibrium pressure vs. temperature at constant concentration of nitrogen. Lower curve: filament contains 40 volumes of nitrogen. Upper curve: filament contains 80 volumes of nitrogen.

Oxygen.—Oxygen is absorbed by tantalum in a somewhat different manner than nitrogen. Whereas nitrogen is taken up very slowly below 1600°, oxygen is absorbed quite readily at 1000°K. and with extreme rapidity at 1800°. Absorption is quite complete up to twenty volumes, the residual pressures being negligible. Further absorption at 1800° (which takes place with great rapidity) leads to the formation of a compound. This is shown by the variation of the resistance with gas content.

(See the oxygen curve in Fig. 4.) The cold resistance increases rapidly with concentration up to twenty volumes and then much more slowly. There appears to be a slight supersaturation just before the oxide begins to form. Not enough work has been done in the absorption of oxygen to show whether the solubility, at the point at which compound formation begins, varies with temperature.

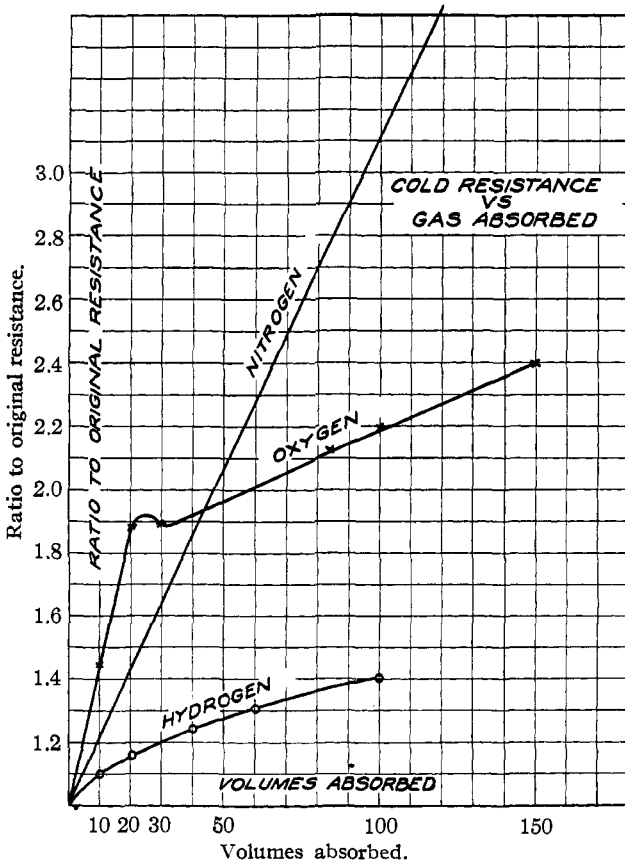


Fig. 4.—Resistance at room temperature *vs.* gas content. Resistance given as the ratio to the resistance of the gas-free filament.

A filament containing twenty volumes of oxygen was examined by Dr. Davey with the x-ray spectrograph. It showed the tantalum structure, but the lattice was stretched, apparently somewhat more in one direction than in the others. This would be exactly what might be expected from a solution of gas in the metal.

Microphotographs were taken of longitudinal sections of a filament that had absorbed 500 volumes of oxygen. The filament was very badly

crinkled and the surface under the microscope looked cracked and scaly (see Fig. 5). The photographs show that penetration takes place most freely along grain boundaries so that the oxide forms in streaks and thin sheets. A concentration of 500 volumes is about one-fifth that necessary to form Ta_2O_5 , and the photographs suggest that nearly this fraction of the metal has reacted.

At the point at which the oxygen compound is first formed, the filament begins to turn dark, so that temperatures were quite uncertain at higher concentrations.

The dissolved oxygen, *i. e.*, the first twenty volumes absorbed can be re-evolved if the filament is run in vacuum at 2200–2300°. There is no appreciable loss of metal in the process. If a filament containing a greater amount of oxygen is heated to such a temperature, some metal is vaporized and deposits as a black film on the bulb wall.

Hydrogen.—The absorption of hydrogen offers an interesting study. At the pressures used, 50 microns or less, no hydrogen was absorbed when the tantalum was heated in the gas; but if an auxiliary filament of tungsten was run in the same bulb at a high temperature so as to dissociate some of the hydrogen and the tantalum filament was run at the same time at 800 to 1200°, hydrogen was absorbed

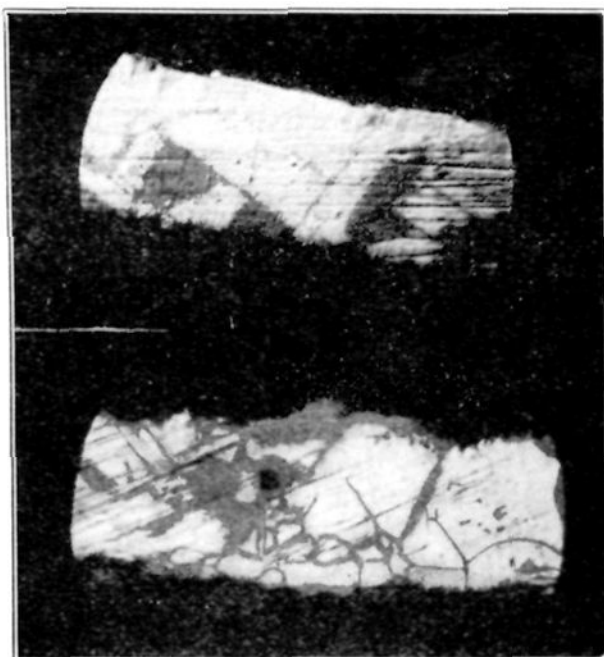


Fig. 5.—Photomicrographs of tantalum filament which has absorbed 500 volumes of oxygen.

by the tantalum. Solubility was greater at the lower temperatures. At any given temperature absorption would take place until an equilibrium was established. Addition of more hydrogen caused increased absorption. The action was exactly similar to the absorption of nitrogen except that equilibrium was established between the dissolved hydrogen and the external pressure of *atomic* hydrogen. That is, if equilibrium was established with the tungsten filament running at a constant temperature, say 2400°K., and the tantalum also constant, at say 1000°K., and the temperature of the tungsten filament was then increased, to, say, 2600°, thus increasing the fraction of the hydrogen dissociated, the tantalum absorbed hydrogen further until a new equilibrium was established. If the tungsten filament was lowered in temperature, the tantalum would immediately evolve gas to

establish again an equilibrium, or if the current was taken off the tungsten filament, the tantalum one being left at 1000°K ., gas would be evolved from the tantalum until practically all that had been absorbed had reappeared.

The hydrogen curve in Fig. 4 shows that the resistance at room temperature rises less rapidly with hydrogen concentration than for either oxygen or nitrogen. It can be assumed that this is due to the small atomic volume of the hydrogen, so that a given number of molecules dissolved in the metal would strain the lattice less than larger atoms. There was no evidence of any compound up to the maximum concentrations of hydrogen reached.

Water Vapor.—One or two experiments were made on the reaction between water vapor and hot tantalum. Above 1400°K . the water is decomposed with absorption, by the filament, of the oxygen and evolution of the hydrogen. At 1200° the reaction is negligibly slow.

It was observed in the absorption of both nitrogen and hydrogen that the rate of absorption was much less when a new filament was used than it was after the filament had absorbed gas and had been degassed. Rates were never constant, however. This suggests that diffusion of these two gases as well as of oxygen takes place along grain boundaries and that gassing and degassing helped to open up the structure so that diffusion was more rapid than when the filament was new.

Hydrocarbons.—When heated between 2000 and 2800°K . in low pressures of hydrocarbon vapors, such as benzene or naphthalene, tantalum can form two carbides. The first one to form, *i. e.*, the one of lowest decomposition pressure, is silvery-gray and has a chemical composition of Ta_6C_5 . The electrical resistivity of this carbide is about twelve times that of pure tantalum, or 180×10^{-6} , and the temperature coefficient of resistance is very low. Our measurements do not permit of great accuracy in this determination since by complete conversion to this compound the filament is often warped and sometimes shows longitudinal cracks, but the above figure should be accurate to within 20%. This value agrees with the resistivity and temperature coefficient reported by Friedrich and Sittig,² and copied elsewhere for the compound TaC.

If the filament is heated further in hydrocarbon vapor, the electrical resistance decreases due to the formation of the compound TaC. This has a resistivity about 120% that of pure tantalum, or a specific resistivity of 17 to 18×10^{-6} . TaC has a brilliant golden-yellow color when in the dense crystalline form and shows a metallic luster equal to that of well-crystallized metals. Both carbides have high melting points, certainly above 3800°K ., but no determinations of the two in the pure state have been made here. It would appear, however, from the color and electrical resistivity of their material that Friedrich and Sittig² found the melting point of Ta_6C_5 (rather than TaC as they report) to be 4000 – 4100°K . The

² Friedrich and Sittig, *Z. anorg. allgem. Chem.*, **144**, 169–189 (1925).

material used by Agte,³ which he found to have a melting point of $4150 \pm 150^\circ\text{K}$., was almost certainly TaC at the start and probably suffered only superficial decarbidization during the melting point determination.

When formed from metal by diffusion of carbon inward, as when a tantalum filament is heated in hydrocarbon vapor, the rate of formation is very much less than is the case when tungsten is carbidized in the same way. The time necessary to convert a 10 mil tantalum filament to the first carbide, Ta_6C_5 at 2600°K ., for instance, is fully ten times as great as that for conversion of a similar filament of tungsten to the carbide W_2C . Like the two carbides of tungsten, both tantalum carbides are brittle. They have been prepared also in powder form by the well-known method of heating mixtures of tantalum oxide and carbon in hydrogen protected by graphite boats. The products agree in composition with those formed by carbidizing metallic filaments. The colors of the powdered materials are, for Ta_6C_5 , a dark gray, and for the TaC a yellowish-brown.

When a filament of the yellow TaC is heated to 2500°K . or more in vacuum or in a neutral gas, such as argon, it loses carbon at a rate depending on the temperature and gas pressure. If the heating is interrupted from time to time to measure the cold resistance, the latter is found to increase very greatly until it has reached the resistance of the compound Ta_6C_5 . On further heating, if this be kept below the temperature at which metallic tantalum melts, the loss of carbon continues and the resistance decreases until that of a pure tantalum filament is reached. If the temperature of the carbidized filament is above the melting point of tantalum, fusion occurs as soon as an appreciable amount of the Ta_6C_5 has lost carbon to form a small amount of tantalum, and the filament burns out immediately. In the decomposition of TaC to Ta_6C_5 even at temperatures of 3000 to 3400°K . there is no appreciable evaporation of the tantalum, or of the carbides.

In conclusion I take this opportunity for thanking Dr. Saul Dushman for his interest and advice and Mrs. Donald McLeod for her assistance in making these investigations.

Summary

A study has been made of the behavior of filaments of tantalum when heated in low pressures of nitrogen, hydrogen, oxygen or hydrocarbons. In nitrogen, absorption increases with increased pressure until about 100 volumes are absorbed. At this point the equilibrium pressure drops as absorption increases. Absorption can take place to the formation of TaN. In hydrogen, the amount absorbed depends on the concentration of atomic hydrogen in the gas. In oxygen, absorption followed by oxide formation

³ Agte, Dissertation, Technische-Hochschule zu Berlin, April 8, 1931. Agte and Alterthum, *Z. anorg. allgem. Chem.*, **144**, 169-189 (1925).

occurs. In hydrocarbons, two carbides may be formed— Ta_6C_6 and TaC . These both have very high melting points. The former has a specific resistance of about 180×10^{-6} , the latter of about 18×10^{-6} .

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

ELECTRIC MOMENT AND MOLECULAR STRUCTURE. VII. THE CARBON VALENCE ANGLE

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The experimental examination of the angle between the valences of the carbon atom may seem an attempt to prove the obvious, but the calculations of Slater¹ and of Pauling² by means of wave mechanics that the angle is the regular tetrahedral valence angle, 109.5° , and the evidence as to the angle given by x-ray³ and electron scattering⁴ in gases make it desirable to extend the preliminary application of electric moments which has been made in the study of the problem.⁵ This preliminary application was made in the case of the moments of the halogenated methanes. Rough kinetic theory diameters were calculated for chlorine, bromine and iodine by comparison with the dimensions of the corresponding inert gas structures and used as the internuclear distances of the halogens in the methylene halides. The assumption of these distances, when used with the carbon-halogen nuclear separations obtained by Pauling,⁶ necessitated a widening of the angle between the C-X valences to 124° in methylene chloride, 120° in methylene bromide and 135° in methylene iodide. When the C-X dipole moments were resolved at these angles, the resultants agreed so well with the experimentally determined moments of the molecules that the moments were regarded as indicating these values for the angles between the C-X valences. However, it was stated that the disregard of the inductive effects of the dipoles as well as the speculative nature of the treatment of the atomic dimensions rendered the excellence of the agreement between the observed and the calculated values of the moments somewhat fortuitous. As the inductive action of each C-X dipole in the methylene halide lowers the moment of the other C-X dipole in the molecule, it is evident that the angle calculated between the dipoles without regard for this effect is too large, although it is interesting to note that the recent calculation by Bewilogua³ from the results of x-ray scattering also

¹ Slater, *Phys. Rev.*, **37**, 481 (1931); *ibid.*, **38**, 1109 (1931).

² Pauling, *THIS JOURNAL*, **53**, 1367 (1931).

³ Debye, *Z. Elektrochem.*, **36**, 612 (1930); Bewilogua, *Physik. Z.*, **32**, 265 (1931).

⁴ Wierl, *Ann. Physik*, [5] **8**, 521 (1931).

⁵ Smyth and Rogers, *THIS JOURNAL*, **52**, 2227 (1930).

⁶ Pauling, *Z. Krist.*, **67**, 377 (1928).