

resistance of the crystal to be a linear function of the time. This is confirmed by experiment. For example, Fig. 1 shows the resistance-time relation found during the quenching of a specimen by infrared light at  $-196^{\circ}\text{C}$ . It is seen that within the limits of experimental uncertainty the relation is linear.

It is interesting to note that phosphorescence decay data for zinc-blende obtained recently by Antonow-

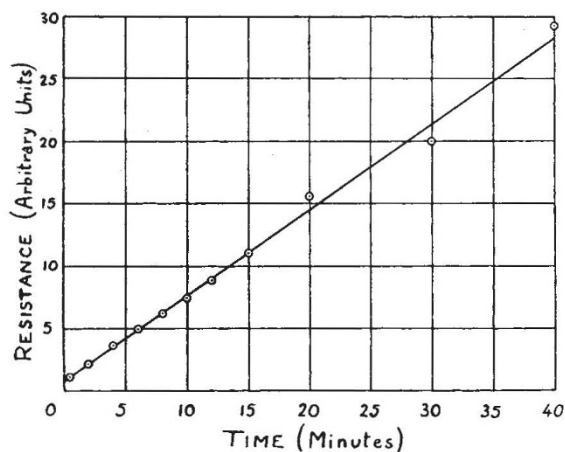


Fig. 1.

Romanowsky<sup>2</sup> are in full accord with these results, in that they show that the phosphorescence is due to a bimolecular reaction. It is easily seen that on the assumption that the intensity of phosphorescence,  $p$ , is proportional to the rate of recombination of electrons with holes,  $p^{-1/2}$  should vary linearly with time. Plots of  $p^{-1/2}$  against  $t$ , obtained from Antonow-Romanowsky's data, show that this is,

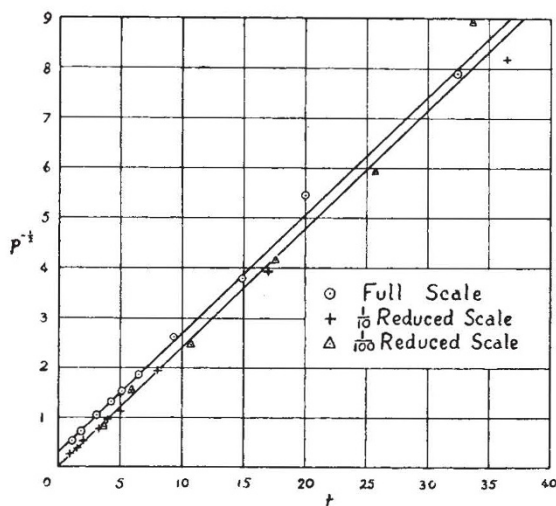


Fig. 2.

indeed, the case. An example of such a plot is given in Fig. 2, in which the lower line is to be regarded as a continuation of the upper one, representing the points on the two reduced scales.

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### Phosphine and Arsine Derivatives of the Group I(b) Metals: Volatile Derivatives of Gold

WE have shown that the trialkyl phosphine and arsine derivatives of cuprous iodide, previously considered to be  $R_3P(\text{As})\text{CuI}$ , have a fourfold macromolecule<sup>1</sup>,  $[R_3P(\text{As})\rightarrow\text{CuI}]_4$ , and are therefore tetraakis-[iodo-trialkylphosphine (or arsine)-copper]. A complete X-ray examination of the triethyl-arsine member,  $[\text{Et}_3\text{As}\rightarrow\text{CuI}]_4$ , showed that the four copper atoms occupy the apices of a regular tetrahedron; the iodine atoms are situated each above the central point of one face of this tetrahedron, so that they also form a tetrahedron external to that of the copper atoms. Beyond each copper atom is an arsenic atom lying on the elongation of the axis joining the centre of the inner tetrahedron to the copper atom. The iodine atoms are thus 3-covalent, each being joined to the three neighbouring copper atoms apparently by one covalent and two co-ordinate links: if this is so, the stereochemistry of the 3-covalent iodine atom must be similar to that of 3-covalent sulphur, and the iodine atom can be regarded as occupying one apex of a tetrahedron with its valencies directed towards the other three apices.

The corresponding silver compounds have now been examined, and prove also to have the fourfold molecule,  $[R_3P(\text{As})\rightarrow\text{AgI}]_4$ . These silver compounds have, moreover, the same constitution as the cuprous compounds, since  $[n\text{Pr}_3\text{As}\rightarrow\text{AgI}]_4$  is strictly isomorphous with  $[\text{Et}_3\text{As}\rightarrow\text{CuI}]_4$ . This is a remarkable example of isomorphism, the effect of the replacement of the copper by silver atoms being compensated by the replacement of the ethyl by the  $n$ -propyl groups. It follows that both the 4-covalent cuprous and argentous atoms have a tetrahedral configuration, in confirmation of the results obtained by Cox, Wardlaw and Webster<sup>2</sup>.

The aurous compounds,  $[R_3P(\text{As})\rightarrow\text{AuX}]$ , where X is a chloride, iodide or thiocyanate radical, prove, however, to be monomolecular, and the gold thus shows a true co-ordination number of 2. The phosphine compounds,  $[R_3P\rightarrow\text{AuX}]$ , where X is Cl or I, possess remarkable stability, and can be freely distilled under reduced pressure. The compound  $[n\text{Bu}_3\text{P}\rightarrow\text{AuCl}]$  can be volatilized even at atmospheric pressure, and the vapour, if passed through a heated tube, deposits a fine film of gold. There are thus two distinct chemical methods of producing gold films, the first having been recently described by Prof. C. S. Gibson in NATURE of August 14 (p. 279).

It is noteworthy that, whilst the copper and silver atoms both acquire 7 electrons in the above compounds and thus attain the electronic structure of the next inert gas, the gold atoms acquire only 3 electrons and thus remain 4 short of the radon structure. The gold in these compounds, however, falls in line with mercury, which acquires 2 electrons in compounds such as  $\text{HgR}_2$  and  $\text{Hg}(\text{SR})_2^3$ , and with thallium, which acquires 1 electron in compounds such as  $[\text{TlR}_2]\text{X}$ , a group of 4 shared electrons in the sixth quantum group allowing considerable stability in all three cases.

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<sup>1</sup> Mann, Purdie and Wells, *J. Chem. Soc.*, 1503 (1936).

<sup>2</sup> Cox, Wardlaw and Webster, *J. Chem. Soc.*, 775 (1936).

<sup>3</sup> Mann and Purdie, *J. Chem. Soc.*, 1549 (1935); Wells *Z. Krist.* 96, 435 (1937).

<sup>1</sup> Gudden, B., "Lichtelektrische Erscheinungen" (Springer, 1928).  
<sup>2</sup> Antonow-Romanowsky, W. W., *Sov. Phys.*, 7, 366 (1935).