crystals; thus the data of Fig. 5 allow an estimate of the D.C. specific resistivity of D.P.P.H. at 69 °C as $3 \cdot 10^{10}\,\Omega$ cm., before admission of any hydrogen sulphide.

The parahydrogen conversion observed here at low temperatures occurs by the paramagnetic mechanism and establishes the presence of free valencies at the surface of the D.P.P.H. crystals. The observed rate of conversion at 20 °C is $3.3 \cdot 10^{12}$ molecules $cm^{-2}\,sec^{-1}$, which divided by a collision number of $0.72 \cdot 10^{22}$ gives a collision yield of $4.6 \cdot 10^{-10}$. This may be compared with a collision yield of 10^{-10} for crystalline haemin[21]). Uncertainty in the surface areas precludes a further discussion of these figures. The small negative temperature coefficient of the conversion on D.P.P.H. is analagous to the case of haematin, rather than haemin where the temperature coefficient is zero[21]). The collision yield is about one hundred-fold that observed for gaseous molecules such as oxygen, which arises from the relatively long residence-time of the hydrogen molecules in the surface, as pointed out by Harrison and McDowell[12]).

The absence of the hydrogen deuteride reaction, and the failure to observe any effect of hydrogen on the conductivity of the cell Al/D.P.P.H./Al, shows that these free valencies are unreactive in the sense that they will not dissociate molecular hydrogen. Similarly the absence of conductivity changes for oxygen and nitrogen probably exclude chemisorption of these gases. Oxygen gives rise to characteristic resistance changes when chemisorbed on metals[15]) and metal oxides[14]). The design of the sandwich cell left an adequate area of D.P.P.H. film for direct access of gas by bombardment from the gas phase, and there was no question of exclusion of gas from the D.P.P.H. by the upper electrode. The positive result associated with hydrogen and the cell Al/D.P.P.H./Pd must be associated with dissociation of molecular H_2 and the formation of H atoms within the Pd electrode. These atoms will diffuse through the Pd and the results indicate that on arrival at the surface of the D.P.P.H. they immobilize its conduction electrons. Chemically, we shall expect the formation of a covalent link, i. e. formation of a surface layer of $\alpha\alpha'$-diphenyl β-picryl hydrazine molecules. The complete transfer of an electron with the formation of an H^- ion at the surface is chemically quite unlikely in this system. Similarly, the increase in resistance observed when molecular H_2 is admitted to specially clean metal films is to be taken as evidence for the formation of covalently bound H, rather than H^- ions[22]). The evidence for covalency in chemisorption is very widespread[23]).

The energetics of the above process may be discussed in terms of Paulings bond energies, using the revised table published by Pitzer[24]). For the above process

$$-\Delta H = E(\text{N—H}) - \frac{1}{2}E(\text{H—H}) - \text{R}$$
$$= 92.2 - 51.6 - \text{R} = 40.6 - \text{R}.$$

Here R is the lowering of the (N–H) bond energy due to the resonance energy of the free valency on the resultant radical. If we approximate this by the value for triphenyl methyl, namely 20 k.cal/mole[25]), we expect a $-\Delta H$ for chemisorption of 20.6 k.cal/mole. This is rather lower than the heats of adsorption on transition metals, e. g. nickel, 30 k.cal/mole where adsorption of hydrogen is very rapid[26]), but is still much higher than sp metals such as copper, 8 k.cal/mole, where adsorption is very slow at room temperature[27]). The spacing between free radical electrons in adjacent molecules in the exposed surface is unknown, but it might possibly be about 3.5 A, the interplanar spacing in aromatic compounds. If so, this would be suitable since early calculations for two carbon atoms gave 3.5 A as the optimum spacing for dissociative adsorption of an H_2 molecule[28]), and a similar result might hold for two nitrogen atoms. It seems possible that, since the heat of reaction and lattice spacing factor may be favourable for a rapid dissociation of molecular H_2, the failure to achieve this (in the absence of Pd catalyst) may point to the need for a low-lying empty orbital for a rapid chemisorption, as in the role postulated by Dowden for d-orbitals on transition metals[29]). It is clear that further information should enable us to make these arguments more definite in future.

The effect of H_2S is to increase the DC conductivity of D.P.P.H. crystals as shown in Fig. 4. The concept of a co-ordinate link between a sulphur atom and a transition metal surface, as $H_2S \rightarrow$ Pd, is now accepted, and there is magnetic evidence for this type of surface bond[30]). It is also reasonable to postulate a co-ordinate link between H_2S and the N atom of D.P.P.H. This will be possible if the free radical electron on the N atom of the surface molecules moves off into the interior of the solid, leaving an unoccupied surface orbital to receive the electron pair of the S atom. Since this movement may require thermal activation energy to the extent of 0.2 eV. it is perhaps understandable, why the observed effect does not occur instantaneously, and suggests a new concept of activated adsorption which

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might be applicable to oxides. The effect of such a displacement of electrons into the interior may well be to increase the crystal conductivity. However since we know that the D.C. conductance of a loosely packed powder of D.P.P.H. crystals is determined mainly by the conductance of intercrystalline barriers, the effect of the chemisorbed H_2S will presumably be to lower these barriers. We should expect a donor link from H_2S to the crystal surface to have this effect, by giving rise to a double layer around the crystal with its positive side outwards, and thus assisting the removal of electrons from the crystal. Further work on this system is clearly desirable using the A.C. method.

The effect of a deposited D.P.P.H. film on the resistance of a palladium layer is comparable in sign and magnitude with that reported for several gases on metal films of similar character by Suhrmann[15][16]). The aluminium films possessed the semi-conducting characteristic first noted for molybdenum films by De Boer and Kraak[31]). Such films possess an intrinsic interest, but the 20% increase due to D.P.P.H. 'adsorption' may in part arise from increased intercrystalline resistances. In the case of the palladium film the increase in resistance may be attributed to electron transfer from the conduction band of the metal to D.P.P.H. Presumably a covalency is formed between the metal surface and the N atom of the D.P.P.H. There is an analogy with the effect of D.P.P.H. in admixture, promoting the catalytic activity of ZnO[11]). To explain this effect Harrison and McDowell[13]) postulated a complete transfer of an electron from an interstitial Zn atom to D.P.P H, giving a negative picryl hydrazyl ion, but no evidence is available at present to distinguish the degree of electron sharing. The formation of an adsorbed ion is always more likely on the oxide surface, where it may be stabilised by Coulombic interaction with Zn^{++} and O^{--} ions on lattice sites, than on metal surfaces where only the image forces are available for this role.

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