experiments is that branching in a high-polymer molecule is unlikely to be easily detected even though an authentic linear polymer of the same number average molecular weight were available for comparison. In a similar way, the variation of viscosity with concentration of the branched-chain molecules as compared with linear molecules is in qualitative agreement with the theories already put forward, but the results are not nearly so clear cut as the theories would predict.

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Catalytic Poisons and Magnetic Susceptibility

THE alkyl sulphides are powerful catalytic poisons for palladium, and the nature of the adsorption link is therefore of great interest. On chemical grounds, Maxted¹ has suggested a co-ordinate link from the sulphur atom to the metal. Here we record some preliminary measurements on the change in magnetic susceptibility of palladium due to adsorption of dimethyl sulphide. We conclude that electrons from the sulphur atom enter the *d* band of the metal (in an analogous way to the electrons from dissolved hydrogen atoms²).

A finely divided sample of palladium powder (prepared by reduction of palladium chloride in glycerine by hydrogen gas at 150° C.) was evacuated in an ampoule at 150° C., sealed off, and its susceptibility measured by the Sucksmith method³. The ampoule was then reattached to the vacuum apparatus and the palladium saturated with dimethyl sulphide gas at 20° C. The amount adsorbed was measured, the ampoule resealed and measured in the magnetic balance.

Column 2 of the accompanying table shows the change in susceptibility of the palladium powder expressed as a percentage change on the original value χ . Column 3 gives the percentage change in χ due to the effect of adsorption on the palladium alone; that is, it is the value in column 2 *minus* the calculated diamagnetic susceptibility of the adsorbed dimethyl sulphide.

$\frac{100 a^*}{b}$	$100 \frac{\Delta\chi}{\chi}$	$100 \left(\frac{\Delta\chi}{\chi} \right)_{\text{Pd}}$	$100 \left(\frac{\Delta\chi}{\chi} \right)_{\text{calc.}}$
27 23	10.1 7.9	8.0 6.0	13.5 11.5

* *a* moles dimethyl sulphide adsorbed on *b* gm. atoms palladium powder.

The effect of the dimethyl sulphide is outside the experimental error of 2 per cent on χ , and is of the right order to be expected if one electron from the dimethyl sulphide enters the *d*-band of the metal. Since dimethyl sulphide is an easily condensable gas, the adsorption will correspond to *at least* two monolayers; that is, a van der Waals layer on top of a chemisorbed layer. Only the chemisorbed layer will affect the susceptibility, and this will contain *up to* half the adsorbed quantity in column 1. At this stage we can do no more than assume that a chemisorbed molecule transfers an electron to a vacant surface *d* orbital, and thus the susceptibility of the

surface palladium atoms is reduced to zero (there is 0.55 mole in the *d*-band per palladium atom²). This would then yield the calculated decrease in susceptibility shown in the last column.

It is not worth discussing the discrepancy between observed and calculated figures until experiments with clean surfaces have been made. The main point of contrast is that if the electrons entered the *s*-band of the metal, the susceptibility change would have been immeasurably small.

It is hoped to develop this experiment along more quantitative lines, since it offers an approach to an important aspect of adsorbed layers. These preliminary measurements were made in the Physics Department of the University of Bristol, and we are grateful to Drs. H. Heitler and L. C. Jackson for their help and advice.

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¹ Maxted, *J. Soc. Chem. Ind.* (in the press).

² Mott and Jones, "Theory of Metals and Alloys" (Oxford University Press, 1936).

³ Sucksmith, *Phil. Mag.*, **8**, 158 (1929).

Synthetic Pentapeptides Related to Gramicidin-S

THE polypeptide nature of several antibiotics is of considerable interest. As recent work in this field overlaps to some extent with our own, we wish to give a preliminary account of our studies on synthetic peptides related to gramicidin-S.

Synge¹ extended the limited data published by Russian workers²⁻⁴, and suggested that gramicidin-S was the hydrochloride of a basic peptide with a stoichiometric minimum unit containing equimolecular proportions of the five amino-acids, *L*-ornithine, *L*-proline, *L*-valine, *L*-leucine and the unnatural *D*-phenylalanine. Each stoichiometric unit contained one free amino group but no free carboxyl groups. The free amino group was later identified⁵ as the δ -amino group of ornithine, and gramicidin-S was formulated as a cyclic peptide of five amino-acids linked through their α -amino and carboxyl groups. Degradative studies involving the technique of partition chromatography furnished strong evidence for the structure $[\alpha\text{-(valyl-ornithyl-leucyl-phenylalanyl-prolyl)}]_n$ ⁶. On the basis of the physical information so far available, gramicidin-S is best formulated as a cyclopentapeptide, or as a cyclodecapeptide where the above unit occurs twice in a closed peptide chain.

In the hope that some light might be thrown on the origin of the striking antibiotic action of this peptide, we decided to carry out parallel syntheses so as to obtain two pentapeptides with phenylalanine present in both its optically active forms. Numerous alternative routes to such a pentapeptide might be envisaged. After several different combinations had been tried, it was decided that for ease of handling, which was a dominant consideration, synthesis of a tripeptide from leucine, phenylalanine and proline, and the coupling of this tripeptide with a dipeptide from valine and ornithine, would have a reasonable chance of success. For all syntheses carbobenzoxy derivatives were employed according to Bergmann's