

tions during the previous few years have dealt with such phenomena²⁻⁵. It was thought, at the time that my first note was published, that the oscillating effect might be a good starting-point for further development. Unfortunately, these effects have presented so complex a picture that I have not yet derived a conclusion worthy of publication, except for an additional short note⁶ on the influence of membrane/solution boundary conditions on such oscillations.

Nevertheless, I should like to use this occasion to present a number of generalizations which have been based on observations made during the past few years. (1) The described anharmonic oscillations need not necessarily occur with all types of membranes under all conditions. (2) Generally, such oscillations increase more than linearly with current density. (3) They generally increase in amplitude with time of direct current transfer through the membrane, or may appear after some time of current passage. No case has been observed where the oscillations disappear during current transfer.

I hope that with the continuation of the work, results will be obtained which will provide a wider understanding of the problem, in which event they will, of course, be submitted for publication.

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- ¹ Forgacs, C., *Nature*, **190**, 339 (1961).
² Stein, G., and Forgacs, C., *Science*, **142**, 953 (1963).
³ Forgacs, C., and Stein, G., *Israel J. Chem.*, **2**, 209 (1964).
⁴ Forgacs, C., *Israel J. Chem.*, **2**, 209 (1964).
⁵ Forgacs, C., and Stein, G., *J. Phys. Chem.*, **69**, 4221 (1965).
⁶ Forgacs, C., *Bull. Res. Council Israel*, **11A**, 192 (1962).

Electronic Structure of the Pt₆Cl₁₂ Molecule

It has recently been found that in addition to the crystal form which consists of ribbons of PtCl₂ units, each chlorine being shared by two platinum atoms¹, PtCl₂ crystallizes in a form² containing Pt₆Cl₁₂ molecules which are isostructural with the Ta₆Cl₁₂²⁺ cation³. However, these isostructural species are not isoelectronic, the cation effectively having forty valence electrons⁴ and the platinum compound seventy-two. In both cases each chloride anion is assumed to contribute two 'σ' electrons only; the four 'π' electrons may, in general, be neglected and assumed non-bonding⁵. The bonding within the Ta₆Cl₁₂²⁺ cation has recently been described in terms of a topological-equivalent-orbital approach⁴ and it is the purpose of this communication to extend the treatment to the isostructural platinum compound.

When three precisely equivalent orbitals interact they do so to form a single and a degenerate pair of molecular orbitals. In the present example there are eight sets of three orbitals of this type, one set for each of the faces of the octahedron⁴. These orbitals are a₁b₂e hybrids located on each platinum atom (here we classify the hybrid orbitals by the symmetry species which they span in the C_{4v} local symmetry at each platinum atom; in this way we give more flexibility to the mixing coefficients). When the symmetric combination of a set of these orbitals is the only one occupied, then a three-centred 'face' bond is formed which contributes to the molecular stability. Such bonds are found in the Ta₆Cl₁₂²⁺ cation. If more electrons are fed into each set of three orbitals, then a diamagnetic molecule will only result if four electrons are added. Further, occupation of these three orbitals by six electrons is essentially equivalent to having three non-bonding lone pairs of electrons. This is the situation which exists in Pt₆Cl₁₂, the thirty-two electrons added to the forty in the Ta₆Cl₁₂²⁺ structure occupying anti-bonding orbitals to give a molecule held together by the chlorine bridges alone. This conclusion finds support in the Pt-Pt distance of about 3.4 Å (compare Ta-Ta in Ta₆Cl₁₂²⁺ which is about 2.9 Å).

Clearly, there is little to choose between the two crystal forms of (PtCl₂)_n from the point of view of energy. In both, each platinum is surrounded by four chlorine atoms at the corners of a square and is bonded to neighbouring platinum atoms by them, all other platinum electrons being effectively non-bonding.

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- ¹ Falqui, M. T., and Rollier, M. A., *Ann. Chim. (Italy)*, **48**, 1154 (1958).
² Brodersen, K., Thiele, G., and Schnering, H. G., *Zeit. Anorg. Allg. Chemie*, **337**, 120 (1965).
³ Vaughan, P. A., Sturtevant, J. H., and Pauling, L., *J. Amer. Chem. Soc.*, **72**, 5477 (1950).
⁴ Kettle, S. F. A., *Theoretica Chim. Acta*, **3**, 211 (1965).
⁵ Kettle, S. F. A. (unpublished results).

Tritium Enrichment by Gas Chromatography

GAS-SOLID chromatography has proved to be a promising method for enrichment of tritium in hydrogen gas samples¹. Previous work has shown that tritium can be enriched with a concentration factor of about 20 in hydrogen samples of up to 300 ml. and with a tritium loss of up to 5 per cent in a relatively small system. Many problems involving low-level tritium determination, however, require much larger samples of hydrogen (or its equivalent as water) to obtain sufficient tritium for detection and it was, therefore, of interest to see how far the gas chromatographic system could be extended in this direction.

An important primary consideration is the size of the 'low background' counter ultimately intended for the determination of tritium. Two types have been considered here, one of low volume (approximately 40 ml.)², which implies the necessity of high concentration factors, and the other of relatively large volume (1.5-2.0 l.)³ where a lower factor can be tolerated.

In the former case, an apparatus with a three-column system was used¹. The first column was made of copper tubing with an inner diameter of 10 mm wound in a spiral and with an active length of 2 or 4 m. The second, also of copper, had an inner diameter of 5 mm and an active length of 160 cm, while the third or 'retention' column was a glass capillary of 1.2 mm inner diameter with an active length of 35 or 70 cm. In all cases, activated Linde molecular sieve 5A was used with a grain size of 0.5-0.8 mm for the first column and 0.3-0.5 mm for the other two. As before¹, the elution-displacement technique was used with helium as the eluting gas and the columns cooled in liquid nitrogen. The results of experiments using various combinations of column lengths are shown in Table 1.

Table 1. TRITIUM RECOVERY FOR VARIOUS THREE-COLUMN SYSTEMS

Experiment	First column (m)	Second column (cm)	Third column (cm)	Sample volume (ml.)	Hydrogen fraction activity (per cent)	Tritium fraction Volume (ml.)	Activity (per cent)	Enrichment factor
1	2	160	35	1,290	1.2	12	98.8	106
2	2	160	70	1,530	0.3	25	99.7	61
				2,000	2.8		97.2	78
3	4	160	35	1,810	1.2	12	98.8	149
				2,120	3.7		96.3	170
4	4	160	70	3,060	3.8	25	96.2	118

It can be seen that 3 l. of hydrogen can be handled with an acceptable tritium loss. The final volume of tritium-hydrogen fraction is defined by the capacity of the third column and was 12 and 25 ml. for the 35 cm and 70 cm columns respectively. Some increase in the size of this third column would probably make it possible to deal with samples of more than 3 l. Any further increase in the size of the first column introduces the technical difficulty of satisfactorily winding copper spiral from large-diameter tubing.

Large volume counters (1.5-2.0 l. capacity) with an acceptable low background have been described and are produced commercially. In this case, a two-column system has proved to be satisfactory. The first column (of glass)