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Communications should be addressed to
The Editor, Platinum Metals Review
Platinum Recovery in Ammonia Oxidation Plants

A NEW PROCESS USING GOLD-PALLADIUM CATCHMENT GAUZES

by Dr Hermann Holzmann
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This article describes a novel process for the recovery of platinum lost in ammonia oxidation plants for the manufacture of nitric acid. The process, based on the finding that the platinum lost is in vapour form, is particularly suitable for medium and high pressure plants in which the present methods of recovery are relatively inefficient.

The first manufacture of nitric acid by the oxidation of ammonia, using platinum as a catalyst, was carried out in 1908 using Wilhelm Ostwald’s process. From this small beginning a vitally important branch of the chemical industry has developed and with it the enormous artificial fertiliser and explosives industries.

For the ammonia oxidation reaction, the catalyst now takes the form of pads of gauzes, up to 4 m diameter, located horizontally in the ammonia burner. The ammonia oxidation reaction is highly exothermic and, once the gas stream has ignited and thermal equilibrium has been reached, the gauzes maintain themselves at their operating temperatures in the range 750 to 950°C.

The rhodium-platinum gauze wires roughen rapidly in service and there is considerable grain growth. In turn, rhodium and platinum are lost into the gas stream. In atmospheric plants this loss may range from 0.15 to 0.35 g/ton N and in plants operating between 3 and 9 atmospheres from 0.5 to 1.8 g/ton N. These losses have led to the use over many years of processes that recover part of the metal otherwise lost, such as glass-wool or other filters and Raschig rings. These techniques are, however, applied more generally to pressure plants and are limited in effectiveness.

Research carried out by Degussa in collaboration with several nitric acid producers and a plant construction company has now led to the development of a practical recovery process, suitable for medium and high pressure plants. A fuller account of the theory upon which this process is based, and of the experimental work leading to its successful development, has been given elsewhere by the present writer (1).

Theory of Platinum Loss from Gauzes

The author does not agree with existing explanations of these phenomena, particularly with that of Figurovskii (2) who concluded that particles detached themselves mechanically from the gauze. Instead he suggests that the loss can be explained by the intermediate formation of a volatile platinum oxide.

Direct volatilisation can be discounted: even at 1570°C the vapour pressure of platinum is only $6.76 \times 10^{-9}$ Torr corresponding with a loss on heating in vacuum of 10 g/cm²h. However, heating in air causes significant weight losses, even at temperatures under 1000°C, while in oxygen the losses are much higher. These phenomena are shown graphically in Figs. 1 & 2. However, in ammonia oxidation the loss of platinum is considerably higher than could be deduced from these data. The author’s theory is that the volatile PtO₂ is formed during the reaction.
The production of nitric acid by the oxidation of ammonia on rhodium-platinum gauzes constitutes one of the world's major chemical industries and well over twenty million tons of acid are made annually in plants such as this. Loss of platinum from these gauzes contributes significantly to the operating costs, and the development of a process for the recovery of a major proportion of the lost platinum is therefore of considerable potential value to the industry.

and that this accounts for the weight loss from the gauzes.

It was, therefore, on the assumption that platinum is principally carried into the gas stream as vapour, and not as discrete particles, that work on new recovery techniques was initiated. The basic principle was to "getter" the platinum atoms at the high temperatures in the burner, immediately below the catalyst gauzes.

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**Fig. 1 (left)** Loss of platinum when heated in air at various temperatures

**Fig. 2 (above)** Loss of platinum when heated in oxygen at various temperatures
To translate this principle into practice, it was necessary first to choose metals that did not form oxides at temperatures of about 950°C and which would not react with the gases in the stream (NO, O₂, H₂O, N₂). Moreover, the gauze form seemed ideal, so that ductility of the metal chosen was essential. On these considerations the choice lay finally between gold, palladium and platinum.

In fact platinum was rejected primarily on the grounds of price, so that the choice appeared to lie between gold and palladium. For the trials described below fine gold and fine palladium, together with a series of binary alloys of these two metals, were evaluated as wire 0.125 mm diameter, placed through a coarse mesh gauze of an austenitic stainless steel. This gauze was installed immediately below the rhodium-platinum gauzes in a 7 atmosphere plant and was, in turn, supported by a second similar, stainless steel gauze. Its location ensured an operating temperature of 940°C.

The purpose of these trials was to determine whether the wires could collect platinum and to establish whether or not they would survive. A similar assembly was also tested in a cooler zone of the burner at 800°C.

The results were significant: at 800°C the wires appeared unaffected and had collected little platinum. At 940°C they had the furred appearance associated with used catalyst gauzes but they had collected worth-while amounts of platinum, as shown in Fig. 3.

![A Rhodium-Platinum Catalyst Gauze Being Installed in an Ammonia Oxidation Plant](image)

*Fig. 3 Recovery of platinum in relation to the proportion of gold and palladium in the recovery wire*
It will be seen that pure palladium is the most effective, but this could not be used as the palladium wire was mechanically damaged. The 20 per cent gold-palladium alloy wire seemed to provide the best compromise between optimum recovery and mechanical properties, and subsequently this alloy formed the basis of all tests. Other alloying constituents were also tried, but while they improved mechanical properties they were less effective in terms of recovery.

**Confirmation of the Theory**

In the author's opinion the presence of platinum vapour was confirmed by the fact that the platinum had collected uniformly on the wires, not solely on the face opposite the gas stream. Microsection showed apparent pitting, with crystal formation on the surface identified as solid solutions from the diffusion between the gauze alloy and the "captured" platinum at prolonged high temperature. It was, however, impossible to identify phases.

Two explanations are offered for the poorer results at 800°C: the "getter" effect is reduced with decreasing temperature and, in the cooler zone, less platinum is present in the vapour phase.

At 940°C the platinum recovery was partly offset by losses of catchment material. The gold loss was minimal but the palladium losses were more significant. The author cannot precisely explain the phenomenon, particularly the relationship between palladium lost and platinum recovered. The vapour pressure of palladium in vacuum, even at 1200°C, is so low that it cannot provide the explanation. In practice the 20 per cent gold-palladium gauze loses roughly one-third of a gramme of palladium for every gramme of platinum recovered. (If account is taken of the relative intrinsic values and densities, this appears less significant.)

**Production Trials**

As already mentioned, the 20 per cent gold-palladium alloy appeared to be the best proposition, and for production trials wire of this alloy 0.09 mm diameter was woven into 1024 mesh/cm² gauzes. These gauzes were tested in a 7 atmosphere plant comprising two ammonia burners connected in parallel, each with a throughput of 23 ton of nitrogen per day. The loss of platinum from the catalyst gauzes was approximately 1 g/ton N. The 20 per cent gold-palladium "catchment" gauzes were mounted in the burners below the catalyst gauzes, and coarse mesh gauzes of stainless steel were used to separate the recovery gauzes from each other and from the pad of rhodium-platinum gauzes.

The following conclusions were drawn from these trials:

(1) Under these operating conditions the first recovery gauze collected about 23 per cent of the platinum otherwise lost.

(2) The next gauze, lying under the first, collected 17.5 per cent, i.e. 23 per cent of the 77 per cent remaining from the first gauze. In fact, each gauze collected 23 per cent of the platinum presented to it. The following equation expresses total recovery percentage:

\[
S = [1-(1-a/100)] \times 100 \quad \text{(Equation I)}
\]

Where \( S \) is the total recovery percentage of all gauzes
\( a \) is the percentage recovery of the first gauze
\( n \) is the total number of recovery gauzes used.

Although \( a \) varies according to plant conditions, this exponential equation applies broadly to all plants.

(3) As a result of examination after 35 and 68 days, it was established that the rate of recovery after 68 days was almost the same as after 35 days, thus the limit of recovery was not reached within that trial period.

(4) The 68-day period was the better economic proposition. Nearly twice as much platinum was recovered, but many of the fixed costs (e.g. catchment gauze manufacturing and refining) were spread over nearly twice as much recovered platinum.
The gold-palladium catchment gauze is fitted in the converter immediately behind the rhodium-platinum gauzes in order to recover the rhodium and platinum carried away in the gas stream. Left, a gold-palladium gauze as installed. Centre, the same gauze after 90 days in operation, and, right, after 190 days, showing the effect of the collected platinum.

Tests were subsequently conducted on other plants with operating conditions ranging from 9 atmospheres to atmospheric. These tests revealed unexpected variations from plant to plant in the percentage of platinum recovered. In high pressure plants with a specific load of nearly 30 ton N/m²/day each single catchment gauze recovered about 22 per cent of the platinum presented to it: in medium pressure plants (3 atmosphere) this figure rose to about 45 per cent and in atmospheric plants to about 60 per cent. It was, therefore, apparent that more gauzes would be necessary in high pressure plants than would be required in low pressure and atmospheric plants.

These figures relate to the percentage of platinum recovered from the gas stream (a in Equation I). However, in considering the overall economies of the use of catchment gauzes it is also necessary to relate the weight of metal recovered to the weight of the catchment gauzes when new. This can be treated as a percentage and known as $K_r$ (recovery constant), where:

$$K_r = \frac{\text{Weight of Platinum Recovered}}{\text{Weight of Catchment Gauzes when New}} \times 100$$

To assess the viability of the process, account must also be taken of the time in which an acceptable amount of platinum is recovered. A value for $K_r$ of 80 per cent

<table>
<thead>
<tr>
<th>Platinum Offer and Operational Period</th>
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<tbody>
<tr>
<td>(Wire 0.09 mm diameter)</td>
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<tr>
<td></td>
</tr>
<tr>
<td>Operating pressure (atmospheres)</td>
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<td></td>
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<tr>
<td></td>
</tr>
<tr>
<td>9</td>
</tr>
<tr>
<td>7</td>
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<td>3</td>
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*Platinum Metals Rev.*, 1969, 13, (1)
provides a good basis for comparison but does not represent the limit of the process.

Whereas the atmospheric plants have the advantage of requiring fewer catchment gaizes than the high pressure plants because each gauze collects a higher percentage of the platinum presented, it must be remembered that the rate of presentation of platinum is very much lower. Consequently, with gauze woven from 0.09 mm diameter wire they may take an uneconomically long time (because of interest charges) to attain this notional 80 per cent recovery (see above). The table compares the averaged level of platinum offered per day in typical plants of different operating pressures and shows the time required to achieve this figure of 80 per cent.

In fact this table illustrates the fact that the time taken to attain the notional 80 per cent recovery figure with gauzes woven from wire 0.09 mm diameter is uneconomically long in the lower pressure plants. This is best overcome by using smaller diameter wire for the catchment gaizes. Subsequent tests showed that by using 0.06 mm diameter wire in gaizes of the same mesh (1024 mesh/cm²) the percentage of platinum recovered from the gas stream (a in Equation I) was not greatly affected—despite the reduction in surface area—but the recovery times were reduced to about 43 per cent. These reduced recovery times make the process viable for the lower pressure plants.

**Limits of Recovery**

Although it is established that 20 per cent gold-palladium gaizes woven from either 0.09 mm or 0.06 mm diameter wire can capture 80 per cent of their original weight of platinum (i.e. $K_a = 80$), the limit of recovery has not yet been established. Nevertheless, the rate of recovery has remained more or less constant in all tests so far conducted.

An important factor in assessing this rate of recovery is the increase in surface area of the gauze as platinum atoms diffuse into the wire and so cause "roughening"—with consequent increase in surface area. The importance of this "roughening" was confirmed in an experiment with a gauze manufactured from wire in which 10 per cent of platinum had already been alloyed. This captured far less platinum than a normal 20 per cent gold-palladium gauze which had in service already collected 10 per cent of platinum.

**Experience So Far**

Degussa have gained experience with atmospheric and medium pressure plants that are representative in operating conditions of nearly all such current plants in use. With high pressure plants they have, as yet, no experience with daily loadings in excess of 30 tons of nitrogen per square metre of burner, nor with plants operating at pressures greater than 7.5 atmospheres—but preparations are in hand for these tests.

Certainly the installation of the catchment gaizes is simple in that they are easily mounted—together with their stainless steel support gaizes—in the same flange as the catalyst gaizes. Adequate mechanical support is essential throughout their operating life.

**Economics of the Process**

At a time when interest rates and metal prices are subject to fluctuation, it is impossible to cite examples of the overall savings achieved by this process. Nevertheless, it is worthwhile to consider which factors contribute to overall viability.

Second only in cost to the ammonia used in the production of nitric acid is the cost of the metal lost from the catalyst gaizes. Discussion so far has concerned platinum losses but in practice rhodium is also lost. Some rhodium is recovered by this process: typically 1.5 to 3.5 per cent of rhodium (as a percentage of the platinum recovered) is recovered from gaizes containing 10 per cent of rhodium.

The catchment process described in this article has, in fact, shown itself to be viable in several plants operating in various parts of the world, in that it recovers so much more platinum from the gas stream than the
methods hitherto employed that its cost is well justified. Obviously account must be taken of the manufacturing costs of the catchment gauzes, the interest that must be paid on their intrinsic values and the costs of their subsequent refining, but overall experience so far points to the promise of universal adoption of the process in nitric acid plants in the years to come.

The benefits of the process are simply assessed. A catchment gauze pack can be installed in a burner and after a short period of service removed for analysis and refining.

The analysis provides an immediate indication of the recovery rate and this can be related to the additional costs involved.

The process described above is internationally patented. (British Patent No. 1082105 applies in the U.K.) Johnson Matthey & Company Limited and their overseas subsidiaries are appointed licence agents for the process in the United Kingdom and all other countries in the world except those of North America, the European Common Market and Spain.

References
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2 N. A. Figurovskii, Zh. prikladnoi Khim., 1936 9, 37; 1938, 11, 1440

Economics of Platinum Catalysts in Fuel Cells

The advantages of employing platinum metal electrocatalysts in fuel cells continue to be debated, but a paper by K. R. Williams, of “Shell” Research, presented at the Sixth International Power Source Symposium at Brighton, gives a useful guide to the economics of their use in certain types of systems.

Starting from the basis of using methanol or hydrocarbons in a low temperature system in the range 1 to 5 kW, the author compared the costs and performance of cells fuelled by pure hydrogen, impure hydrogen and methanol. Pure hydrogen may be obtained by steam-reforming methanol in a fluidised bed reactor and extracting the hydrogen by means of a silver-palladium diffusion cell. This system produces a very pure hydrogen fuel. Methanol can also be reformed to yield impure hydrogen; the cost of a diffusion cell and associated equipment would be saved, but the system weight would scarcely be reduced since more reforming catalyst is required to achieve an adequately low carbon monoxide concentration. Obtaining hydrogen by hydrocarbon reforming necessitates the use of a two-stage system – a reforming stage in the temperature range 500 to 700°C, followed by a shift reaction at lower temperatures to increase the hydrogen content of the gas.

Ruthenium-platinum electrocatalysts applied to electrodes comprising microporous plastics coated with a conductive metallic layer have been demonstrated to show a number of advantages in this type of system. In 6N KOH systems at platinum loadings of 1 mg/cm² power outputs of 100 mW/cm² can be achieved with hydrogen fuel, compared with only 40 mW/cm² with less expensive nickel catalysts. The ruthenium-platinum catalysts, moreover, can deal effectively with impure hydrogen, as well as with methanol directly, at a small cost of slightly increased electrode polarisation. When total system costs are compared for fuel cells operating with ruthenium-platinum and nickel catalysts, a 1 kW battery would cost around £60 in the former case (with two-thirds of this sum being attributed to the platinum) and about £50 in the latter instance. There is thus only a slight saving when non-platinum catalysts are used, due to the increased construction costs that almost completely offset the savings in electrocatalyst. The weight of such a system, moreover, is increased significantly.

In acid electrolytes the catalyst loading has a very marked effect on cell performance. Ruthenium-platinum electrocatalysts operate best around 70°C when impure hydrogen is used as fuel, but—in general—construction costs are much higher when acid electrolytes are employed due to corrosion problems.

From an analysis of costs and performances of the systems reviewed, the author concludes that although the least expensive system at the 5 kW level is that using a methanol reforming system giving pure hydrogen and non-platinum catalysts in an alkaline electrolyte, the additional cost of using platinum catalysts is minimal and bestows significant advantages in increased performance/weight parameters. The system using impure hydrogen is about 2 1/2 times as expensive; most expensive is that using methanol directly in an acid medium.

H. C.
Nitrogen Complexes of the Platinum Metals

POINTERS TO A MECHANISM OF FIXATION

By Professor Joseph Chatt, F.R.S.
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The discovery three years ago of the first well-defined complex compound containing the nitrogen molecule—a complex of ruthenium—aroused great interest in such compounds and in their relation to nitrogen fixation. Since then a number of other nitrogen complexes have been obtained, but as yet, despite reports to the contrary, attempts to reduce their nitrogen to ammonia have been unsuccessful. In this article the author, who is Director of the Agricultural Research Council’s Unit of Nitrogen Fixation, puts into perspective the considerable amount of work now being done in this field, which may eventually point the way to a mechanism by which atmospheric nitrogen may be fixed and then reduced to yield ammonia and, for example, amines for the plastics industry.

Since the 1930s chemists have thought that co-ordination compounds containing the nitrogen molecule as a ligand might exist. They were stimulated into this line of thought by the discovery, in 1930, that nitrogen-fixing bacteria metabolised nitrogen gas only in the presence of traces of molybdenum. Nevertheless, the bacteria would grow without molybdenum if they were provided with a source of fixed nitrogen such as urea or ammonia. Molybdenum is evidently involved in the nitrogen fixing process, and it was thought that the nitrogen molecule was activated directly by a molybdenum ion in nitrogenase, the nitrogen fixing enzyme. This led to attempts, using nitrogen under pressure, to obtain complexes of molybdenum containing the nitrogen molecule, but of no avail, and the work went largely unpublished.

The formal analogy between the triple bond in acetylene and nitrogen molecules also led chemists to attempt the preparation of nitrogen complexes of the platinum metals, analogous to the acetylene and olefin complexes. It was again of no avail. We now know that the electronic energy levels in the nitrogen and acetylene molecules are completely different. Thus the highest filled electronic level in nitrogen is a σ-molecular orbital at −15.6 electron volts, whereas in acetylene it is a much more accessible degenerate pair of π-molecular orbitals at −11.4 electron volts.

Chemists were beginning to accept the view that nitrogen did not form stable complex compounds, when by chance, just three years ago, Allen and Senoff in Toronto obtained indirectly the first nitrogen complex, [Ru(NH۳)5(N۳)]2+ (3). Its discovery revived world-wide interest in nitrogen complexes generally and in their relation to nitrogen fixation by bacteria. Since then experiments in widely separated laboratories in various parts of the world have thrown up some dozen nitrogen complexes. These vary in stability from the thermally stable and chemically inert osmium complex [Os(NH۳)5(N۳)]2+ to the highly reactive and thermally labile uncharged complexes of iron, cobalt and nickel.
Despite reports to the contrary, the nitrogen ligand has not been reduced to ammonia in any complex (4).

So far only the Group VIII metals are known to form nitrogen complexes, and those of cobalt, ruthenium and iridium have received most study. This article is not concerned with nitrogen complexes of the first transition series. They are difficult to obtain pure, owing to their extreme lability and sensitivity to oxidation, but the cobalt compound formulated, perhaps incorrectly, as [Co(N₂)(PPh₃)₃] is important. It was the first nitrogen complex reported to be obtained rapidly in high yield from gaseous nitrogen at atmospheric pressure (5). The hydride [CoH(N₂)(PPh₃)₃] is equally important because it was the first nitrogen complex to be obtained in a protic solvent. It is obtained by passing nitrogen gas through a solution of a cobalt hydride complex in ethanol according to the following reversible reaction (6).

\[ \text{[CoH(N₂)(PPh₃)₃]} + \text{N₂} \rightleftharpoons \text{[CoH(N₂)(PPh₃)₃]} + \text{H₂} \]

There is some doubt as to whether the two cobalt nitrogen complexes are different, but our experience suggests that both exist, although the non-hydridic complex is usually contaminated with not less than 15 per cent of the hydride.

The best-defined complexes of the platinum metals are listed in Table I. The most important are the ammine complexes of ruthenium, obtained in good yields by the following reactions in aqueous solution. In reaction 3 the co-ordinated azide ion decomposes to leave nitrogen on the metal.

\[ \text{RuCl₃ + N₂H₄} \rightarrow \text{[Ru(NH₃)₄(N₂)Cl]₂} \quad 2 \ (3) \]
\[ \text{[Ru(NH₃)₅N³]} \Delta \rightarrow \text{[Ru(NH₃)₄(N₂)]³⁺} \quad 3 \ (3) \]
\[ 2\text{[Ru(NH₃)₄(H₂O)]³⁺ + N₂} \rightarrow \text{[Ru(NH₃)₃(N₂)]⁴⁺ + H₂O} \quad 4 \ (7) \]
\[ \text{[Ru(NH₃)₅N³]} + \text{NH₃} \rightarrow \text{[Ru(NH₃)₄(N₂)]⁴⁺ + [Ru(NH₃)₅N³]} \quad 5 \ (7) \]

Ruthenium trichloride also picks up nitrogen to give a material of analysis, \( \text{RuCl₃(N₂)(H₂O)(THF)} \), when its tetrahydrofuran (THF) solution is reduced by zinc amalgam under nitrogen. It has \( \nu(\text{N=N}) \) at 2153 cm\(^{-1} \) and is converted to \( \text{[Ru(NH₃)₅(N₂)]²⁺} \) by ammonia (8, 9).

The product of reaction 2 is grossly contaminated with a hydrazine complex, perhaps \( \text{[Ru(NH₃)₅(N₂H₂)]²⁺} \), which cannot be removed by re-crystallisation, but it can be destroyed by mercuric chloride oxidation leaving the relatively inert nitrogen complex untouched. This impurity was not suspected until recently and many of the chemical properties recorded as belonging to the ruthenium nitrogen complex are those of a hydrazine complex. The most important of these reactions was the supposed reduction of the nitrogen ligand to ammonia by sodium borohydride. However, tracer studies using \( \text{[Ru(NH₃)₅(¹⁵N₂)]²⁺} \) show that no \( ¹⁵NH₃ \) is obtained by sodium borohydride, or any other tried reductant (4, 9). The ammonia previously reported as coming from the nitrogen ligand in this complex must have had its origin in the hydrazine.

The formation of the nitrogen complex by Harrison and Taube's method (Reactions 4 and 5) is important because it shows that nitrogen gas can compete successfully with

<p>| Table 1 |
| Nitrogen Complexes of Platinum Metals |</p>
<table>
<thead>
<tr>
<th>Ref.</th>
<th>( \nu(\text{N=N}) )</th>
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<tr>
<td>Ru</td>
<td>( \nu(\text{N=N}) )</td>
</tr>
<tr>
<td>2105</td>
<td>3</td>
</tr>
<tr>
<td>2175, 2120</td>
<td>12</td>
</tr>
<tr>
<td>Os</td>
<td>( \nu(\text{N=N}) )</td>
</tr>
<tr>
<td>2175</td>
<td>19</td>
</tr>
<tr>
<td>Rh</td>
<td>( \nu(\text{N=N}) )</td>
</tr>
<tr>
<td>2152</td>
<td>14</td>
</tr>
<tr>
<td>Ir</td>
<td>( \nu(\text{N=N}) )</td>
</tr>
<tr>
<td>2095</td>
<td>13</td>
</tr>
</tbody>
</table>

A few other poorly defined complexes have been claimed, e.g. see ref. 20. No complex of Pd or Pt is known.

† of chloride, solid state spectra.

† [BPh₄]⁻ salt.
water for a suitable metal site in aqueous solution. Reaction 4 even occurs when air is bubbled through the aqua-ruthenium complex solution, but oxidation of the ruthenium complex also occurs (10). It is the only known reaction of nitrogen at ordinary temperature and pressure in aqueous solution, and might well provide a model for the uptake of nitrogen, possibly by iron, in the enzyme nitrogenase. However, it does not lead to an easily reducible species, and if it provides a true model the reduction step still has to be worked out.

The osmium complexes are remarkably stable. The analogue of the ruthenium complex, \([\text{Os}(\text{NH}_3)_2(N_2)]^{2+}\) is obtained by reaction of hydrazine on aqueous ammonium chloro-osmate(IV) (11). The nitrogen is so strongly bound that it is not lost even in boiling hydrochloric acid but it yields to a mixture of hydroiodic acid and iodine to form \([\text{Os}(\text{NH}_3)_3\text{I}]^{2+}\). By diazotisation with nitrous acid the mononitrogen complex yields the only known stable di-nitrogen complex (12):

\[
[\text{Os}(\text{NH}_3)_3(N_2)]^{2+} + \text{HNO}_2 \rightarrow \text{cis-[Os}(\text{NH}_3)_4(N_2)_2])^{2+} + 2\text{H}_2\text{O}
\]

The planar iridium complex trans-[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_4] was the second nitrogen complex to be discovered. It is obtained very easily by the reaction of Vaska's compound, trans-[\text{IrCl}(\text{CO})(\text{PPh}_3)_4], with acid azides (13):

\[
\text{trans-[IrCl(CO)(PPh_3)_4]} + \text{PhCON}_2\text{O} \rightarrow \text{trans-[IrCl(N_2)(PPh_3)_4]} + \text{PhCONCO}
\]

The complex reacts with \(\pi\)-bonding ligands, particularly acetylenes, to lose nitrogen. The corresponding rhodium complex is formed by an analogous reaction and is very unstable (14).

In addition to the reasonably-defined nitrogen complexes listed in the table and discussed above, a number of other nitrogen complexes too unstable to be identified have been reported but none containing platinum or palladium.

In the above mono-nuclear complexes the nitrogen is always bonded end-on to the metal as is carbon monoxide in the carbonyl complexes. The mode of bonding in nitrogen complexes is also very similar to that in carbonyl complexes with back donation of non-bonding d-electrons from the metal into the anti-bonding orbitals of the nitrogen molecule as shown in the diagram. The feedback of electrons into anti-bonding orbitals of the nitrogen molecule weakens the N-N bond and so lowers the stretching frequency, \(\nu(N=N)\). In nitrogen gas \(\nu(N≡N)\) is observed at 2331 cm\(^{-1}\) in the Raman spectrum. In the complexes it is observed as a very strong sharp band in the infrared spectrum at 180–320 cm\(^{-1}\) lower than in nitrogen gas. The frequencies have been listed, together with the complexes in Table I. Because the band in the infrared spectrum is intense, the electrical asymmetry of the complexed nitrogen molecule is probably high. However, neither the electrical
asymmetry nor the reduction in bond order is sufficient to increase materially the reactivity of the nitrogen molecule in the complex and there is no evidence that it can be either hydrolysed or reduced in aqueous solution. Just as nitrogen reacts with the complex \([\text{Ru(NH}_3)_6\text{H}_2\text{O}]^{2+}\) to form the bridged compound, so the free end of the nitrogen molecule in \([\text{Ru(NH}_3)_3(N_2)]^{4+}\) reacts with the aqua-complex to form the bridged complex \((7)\) (Reaction 8).

\[
[\text{Ru(NH}_3)_6\text{H}_2\text{O}]^{2+} + [\text{Ru(NH}_3)_3(N_2)]^{2+} \rightarrow \{[\text{Ru(NH}_3)_3(N_2)]^{4+} + \}
\]

In this reaction the nitrogen complex has no greater affinity for the ruthenium of the aqua complex than has gaseous nitrogen itself \((15)\). The nitrogen molecule is evidently symmetrically bonded in the dinuclear ruthenium complex because the intense N–N stretching band is missing from the infrared spectrum.

All of the nitrogen complexes lose their nitrogen as gas on oxidation by such reagents as ceric sulphate. Even hydrochloric acid liberates the nitrogen and oxidises the metal to a higher oxidation state, in most cases evolving hydrogen as well as nitrogen, but no ammonia \((4)\). Only the mononitrogen complex of osmium has failed to give up its nitrogen on treatment with hydrochloric acid.

Since the nitrogen complexes of ruthenium, osmium, rhodium and iridium are known to contain ammonia or tertiary phosphines as ligands it might be thought that analogues of these complexes could be prepared and also homologues containing amines or other tertiary phosphines. However, this is true to only a very limited extent indeed. Even the minutest change in the ligands of the complex is usually sufficient to render it completely unstable. Thus the iridium complex \([\text{IrCl(N}_2)(\text{PPh}_3)_2]\) is very easily prepared, but the corresponding bromide is less easy and the iodide is too unstable to be obtained pure \((16)\), as is the thiocyanate, although the azide has been obtained. Similarly, if one attempts to use other tertiary phosphines in place of triphenylphosphine the nitrogen complex is obtained, if at all, only as a very unstable and impure material. Its presence can be established, from the N$_2$ stretching band in the infrared spectrum of the crude product, but it decomposes on attempted isolation. This applies even when one attempts to make such close derivatives as the ethyldiphenylphosphine analogue. It is evident that some critical and perhaps rather extreme arrangement of energy levels is necessary in the metal atom before nitrogen can be held strongly, and the minutest change in the ligands often causes sufficient re-adjustment of the levels to render the nitrogen complex unstable. In our own work we have found evidence of other unstable nitrogen complexes of the platinum metals and rhenium, but these have been too unstable to isolate in a pure condition, although when the correct ligands are found one or two stable complexes should be isolable.

The structures of two nitrogen complexes have been determined by X-rays but neither is entirely satisfactory because of the difficulty in getting good crystals. The structure of \([\text{Ru(NH}_3)_6(N_2)]\text{Cl}_2\) is disordered and so exact bond distances could not be obtained, but it was shown that the complex is an octahedral one in which the Ru–N–N bond system is linear \((17)\). The other structure is that of the cobalt complex \([\text{CoH(N}_2)(\text{PPh}_3)_3]\) \((18)\). In this the molecule is essentially a trigonal bi-pyramid with the phosphine ligands in the three equivalent equatorial positions, the hydrogen on one apex and the nitrogen molecule on the other. The cobalt is out of the plane of the three phosphorus atoms, being displaced slightly towards the nitrogen molecule which is bonded end-on to the cobalt; the Co–N–N bond system is bent from linearity by 5°. In these complexes the N–N distances are slightly longer than in the nitrogen molecule and comparable with that in the aliphatic diazo-compounds. Indeed the nitrogen complexes may be regarded as inorganic diazo-compounds, and similarly their main reactions result in the liberation of nitrogen, rather than the incorporation of
Table II

Bond Distances in some Diazo-compounds
(Angstrom Units)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond Lengths</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrous oxide</td>
<td>O-N: 1.187 N-N: 1.129</td>
</tr>
<tr>
<td>Hydrazoic acid</td>
<td>H-N: 1.240 N-N: 1.134</td>
</tr>
<tr>
<td>Diazomethane</td>
<td>H-C: 1.32 N-N: 1.12</td>
</tr>
<tr>
<td>[Ru(NH3)6(N2)]Cl2</td>
<td>Ru-N: 2.11 N-N: 1.12</td>
</tr>
<tr>
<td>[CoH(N2)(PPh3)3]HCo</td>
<td>Co-N: 1.80 N-N: 1.16</td>
</tr>
</tbody>
</table>

Nitrogen N-N: 1.098  
† Subject to rather high possible error (see text).

nitrogen into other molecules. Table II shows a comparison of bond lengths in a series of diazo-compounds and nitrogen complexes.

The structure of the dinuclear ruthenium-nitrogen complex has not yet been established. It may be written \([\text{NH}_3\text{RuN}_2\text{Ru(NH}_3\text{)_3}]^+\) which at first sight appears analogous to aromatic azo-compounds, for example azobenzene, Ph-N=N-Ph, but the ruthenium complex cannot be reduced to ammonia by sodium borohydride, sodium dithionite or other such reagents. It is evident, therefore, that the nitrogen, even in this complex, still retains the inactivity which is characteristic of gaseous nitrogen. It seems, therefore, that the complex should be represented as containing two ruthenium(III) atoms bridged by a neutral nitrogen molecule rather than two ruthenium(II) atoms bridged by the \([\text{N}_2\text{N}]^+\) ion, as would be required for formal analogy with azobenzene. The ruthenium(II) type structure would require a linear Ru-N≡N-Ru bond system whereas the ruthenium(III) would require a bent Ru-N≡N-Ru bond system capable of giving cis and trans isomers, analogous to cis and trans-azobenzene.

The nitrogen complexes of the transition metals are only just in process of being discovered. Their reactions have not been very thoroughly investigated. Undoubtedly more nitrogen complexes will be found, but many long series of analogues and homologues are never likely to be obtained. To the present no complexes have been obtained containing nitrogen which can be easily reduced to ammonia, but perhaps these may also be found. Also, to the present, there is no evidence of complexes containing nitrogen bonded sideways to the metal as dialkylnitrenes are in their complexes. Such nitrogen complexes may be just possible, but they seem unlikely because the electrons in the \(\pi\)-bonding molecular orbital are so low in energy that the orbital can have little donor capacity. Such complexes, however, would be rather difficult to detect because the more symmetrical N≡N bond, which they would contain, would not give a strong band in the infrared spectrum. If they do exist they are not likely to be found until the taking of Raman spectra becomes as much a routine as taking infrared spectra is at present.

What is the significance of nitrogen complexes? Their preparation from gaseous nitrogen has shown that nitrogen can react readily at atmospheric temperature and pressure with reagents so mild that they attack neither water nor other protic solvents. They may eventually serve to point the way to the design of catalysts for reactions involving nitrogen under ambient physical conditions, and leading to useful products such as ammonia, and amines for the plastics industry.

References
1 See W. D. P. Stewart, "Nitrogen Fixation in Plants", The Athlone Press, 1966, 89-90
Maintaining Accurate Temperature Control

THE CARE OF PLATINUM THERMOCouples

The use of carefully prepared thermocouples, the exercise of care and attention to details of installation, and the maintenance of calibration by frequent checking, all demand infinite patience, but are essential to the assurance of accurate and consistent furnace temperature control. That this is of primary importance in the semiconductor industry is emphasised in a paper by Ivan O. Nielson of Fairchild Semiconductor (Solid State Technology, 1968, 11, (10), 29). A typical example of the diffusion process for introducing controlled impurities into silicon or germanium wafers requires a furnace operating at 1020°C ± 2°. Wider temperature variation produces variance in the beta characteristics of the devices.

The thermocouples used for control are platinum: 13 per cent rhodium-platinum in the form of wire 0.014 inch diameter to give quick response. The junction, formed by a butt weld, is little larger than the wire diameter. Before use each thermocouple is electrically annealed at about 1350°C for one hour to remove work hardness and volatile surface impurities. The thermocouple is insulated with double-bore refractory tubing and protected in the furnace with a quartz sheath. Leads are terminated with a crimp spade lug to ensure good mechanical connections.

Working-standard thermocouples are calibrated at known points of reference, and are used to calibrate the furnace thermocouples by comparison, using a heat-sink block in the calibration furnace and connecting the couples so as to give a difference reading. Working-standards are calibrated every four weeks and are used only for one week at a time.

Owing to the quicker deterioration of thermocouple e.m.f. at higher temperatures, the frequency of calibration varies according to the temperature being measured, ranging from every two weeks to every six months. Each diffusion furnace has a thermocouple that is used only in that furnace.

The temperature profile of each furnace is carefully checked before use. A period of 10 to 15 minutes is allowed to equalise the temperature at each point and for the system to become thermally stable. The furnaces are wound in three zones and thermocouple controls are so arranged that variations in the centre zone control the end zones. A diffusion furnace is only as good as the instrumentation system which controls it.

Advancements in technology, not only in the semiconductor field, demand higher productivity, and the accurate control of temperature is a means to this end. Particular care must, therefore, be given to frequent calibration of working thermocouples and measuring instruments, to constant checking of all connections in the system, and to allowing sufficient time for thermal sensing devices to reach stability.

H. E. B.
Platinum Mining at Rustenburg

GROWTH OF THE WORLD'S LARGEST PRODUCER

The scale of operations at Rustenburg Platinum Mines has been extended many times over the last thirty years to meet increasing demand, the most recent expansion programme providing for an output of one million ounces of platinum a year. This article describes the mineral resources available and the mining methods and extraction processes in use to provide the world's largest source of the platinum metals.

Demand for platinum has increased substantially over the past ten years or so, and indications for the next few years are that no slackening in the pace is to be expected. Of the three principal sources, Rustenburg Platinum Mines in South Africa, International Nickel in Canada, and the Russians, only one, Rustenburg, has been able to respond significantly to increased demand because the South African mines are worked primarily for the platinum metals and yield copper and nickel as by-products, whereas elsewhere the converse is the case. Rustenburg is in fact the world's largest single source of platinum and the only major mine whose main business is the production of the platinum metals.

The pattern of expansion at Rustenburg is familiar to readers of this journal. Output has...
been increased from some 200,000 ounces of platinum in 1963 to 850,000 ounces a year at present, with a further expansion programme in hand to yield 1,000,000 ounces a year by 1971. Corresponding increases have, of course, taken place in the output of the other members of the platinum group of metals – palladium, rhodium, ruthenium, iridium and osmium.

This has been achieved by very substantial capital expenditures on the sinking of new shafts, the installation of additional grinding, milling and flotation equipment, and the building of an additional modern smelting plant, together, of course, with a consequent expansion in all the facilities and services, including the housing of some 20,000 employees. The expenditure involved in the expansion programme over the seven years 1967 to 1973 will probably exceed £37 million.

Today Rustenburg constitutes the largest underground mining operation in the Republic of South Africa, its two mines together extending more than eighteen miles from one end to the other, and providing about 60 per cent of the Western world’s needs of platinum.

**Relating Supply to Demand**

One of the problems faced by Rustenburg – and by Johnson Matthey as its refiner and distributor – is the forecasting of demand in the face of the hard fact that a decision to expand output does not result in an increase in the supply of refined metal for a full three years. Decisions to expand, involving many millions of pounds and taken on the best available data, can therefore be vulnerable to changing conditions, and this lengthy period between conception and realisation has inevitably led to criticism by some users whose
predictions of future needs were too cautious or too tentative. Forecasting demand necessarily depends upon reliable projections from users and potential users, who in turn have their own uncertainties to consider. Fortunately, when predictions of demand turn out to need revision, Rustenburg is capable – given the necessary time – of expanding its operations very considerably. At any presently conceivable rate of production the ore reserves known to be available will ensure continuity of operations well into the next century.

Because platinum is capable of being recovered from many of its important fields of application and used again, a continuing demand for increased supplies of new metal depends upon a steady growth in technologically advanced industries. During the last five years the consumption of newly-mined platinum has been accounted for as to approximately 30 per cent in the chemical industry, about 25 per cent in petroleum reforming, 20 per cent in electrical and allied uses, and 10 per cent in the glass industry, with some 15 per cent covering dental, medical, jewellery and miscellaneous applications. Thus the use of platinum is not associated with one or two industries, and many of its applications are in areas of industrial growth.

Mineral Resources

The deposit worked by Rustenburg Platinum Mines forms part of the Merensky Reef of the Bushveld Igneous Complex. This reef, named after the geologist Hans Merensky who was responsible for the prospecting programme that led to its discovery in the 1920s, is shown in red on the map on page 20. It has been traced on outcrop a distance of some 75 to 80 miles along both the eastern and western limbs of the Complex. The eighteen miles of outcrop which are mined at

From the working face the platinum ore is loaded into small panel cars, tipped into a central gulley and then scraped into a stope box. Here it is being transferred from the stope box into haulage cars for conveyance to the surface.
the two operations, the Rustenburg section a few miles to the East of the town, and the Union section about sixty miles to the North, are considered to contain the highest grades of the entire igneous complex – most of the remainder containing lower grades which will no doubt be profitably turned to account some time in the future.

The reef at Rustenburg dips at approximately 10° to the north-north-east, but the dip steepens to about 22° at the Union section. Platinum values at these two sections show a very even tenor, the platinum being partly in the form of native metal, invariably alloyed with iron as ferro-platinum, and partly as the sulphide, arsenide and sulph-arsenides, these always occurring in intimate association with the sulphides of iron, copper and nickel. Associated with platinum, the predominant metal, are smaller proportions of palladium, ruthenium, rhodium, iridium and osmium, in descending order.

The platinum bearing reef averages only some twenty inches in thickness, but its regularity makes for relatively straightforward mining. The dip and strike of the ore bodies on each property are consistent, and although an occasional dyke is met with there is generally an absence of faulting. Although the Merensky reef persists to depths beyond the limits of practical mining, the reserves down to a depth of 3,000 feet are immense.

**Mining Methods**

The length of strike and the comparative shallowness of the deposit have made possible the rapid development of large areas of ground whenever a greater demand for platinum has arisen – one reason why Rustenburg has been able to follow world demand so closely. In both sections mining technique is virtually the same. In the shallower portions of the deposit inclined haulages are sited about 2,500 feet apart and are connected by drives on reef. The deeper
areas have been opened up by means of four vertical shafts ranging in depth from 500 to 2,000 feet, while two further shafts are currently being sunk to exploit the ore body to a depth of 3,000 feet.

From the shaft systems a network of cross-cuts and haulages extends to intersect the ore body, and shallow gullies divide the working face into panels. Ore broken on the face is washed down, loaded into small panel cars and tipped into a central gully, from which it is removed by a scraper winch into a stope box and loaded into trains of 4-ton hopper trucks hauled by electric locomotives conveying the ore to the shaft for hoisting to the surface.

A great deal of thought and investigation has gone into the laying down of standard working methods to ensure the delivery to the mill of a product of the highest value at the lowest cost.

**Reduction Practice**

Treatment of the ore, comprising crushing, ball milling, gravity concentration and flotation, is carried out in two reduction plants, an older unit and a more modern mill erected in the last few years, while a third mill is now in course of construction to handle the increased output.

The ore is first crushed in a series of jaw crushers and fed to the primary and then the secondary ball mills which are in closed circuit with hydrocyclone classifiers. This is followed by gravity concentration on corduroy tables to separate the coarse particles of platinum-bearing minerals and the free metallic particles. The corduroy concentrate is dressed on an elaborate system of shaking tables up to a final high grade concentrate which is sent directly to the Johnson Matthey refineries in England.

The tailings from the tables are returned to the mill circuit, the final pulp from here being treated in a series of thickeners before going to the flotation plant. Here banks of cells are arranged in a normal rougher-cleaner circuit which recovers most of the remaining platinum-bearing minerals. The flotation concentrates, consisting mainly of nickel,
The location of the platinum-bearing Merensky reef is shown in red, together with the two mines operated by Rustenburg Platinum Mines.
copper and iron sulphides with the balance of the platinum metals, are thickened, filtered, dried and pelletised, ready for the smelter while the tailings are dumped.

**Smelting and Refining**

The initial stage in the recovery of the platinum metals is to smelt to a copper-nickel-iron matte in a series of blast furnaces. This matte is then tapped periodically into ladles, transferred to a group of converters, and blown to a high-grade matte which is cast into moulds and then broken up in a jaw crusher. Part of this converter matte is shipped to the Johnson Matthey smelter in England, the balance being treated by Matte Smelters, a joint subsidiary of Johnson Matthey and Rustenburg, in a plant adjacent to the mine. In both plants the matte is treated by smelting to separate the copper and nickel sulphides. The copper sulphide is blown in converters to give blister copper which is cast into anodes, while the nickel sulphide is roasted, reduced to metal in reverberatory furnaces and also cast into anodes. Both the copper and the nickel anodes are electrolytically refined to pure metals, the platinum group metals being recovered in the form of adherent anode residues.

At the two matte treatment plants in South Africa and in England new and improved processes have been introduced in which the nickel and copper are separated more efficiently and the platinum metals are further enriched.

Final concentration and separation of the platinum metals is carried out in the Johnson Matthey refinery in England, but an additional refinery is now under construction in South Africa to supplement supplies by treating some part of the output of Matte Smelters.

After roasting and leaching to remove the last of the copper, nickel and iron, the enriched anode residues join the platinum-bearing gravity concentrates shipped from South Africa and together enter the wet process refinery, where the platinum metals are brought into solution for their separation and individual refining. The complete cycle of treatment is very complicated but basically
it involves their precipitation as complex salts followed by successive stages of recrystallisation and then by calcination under carefully controlled conditions in electrically heated muffle furnaces, to produce the metals in the form of sponges or powders suitable for melting.

From this refinery, which has of course been enlarged in line with the Rustenburg expansions, the six platinum metals are supplied in pure form to independent fabricators and catalyst manufacturers and to the Johnson Matthey group of companies throughout the world.

Throughout all the stages of extraction and refining new and improved methods are under constant development, and the numerous extensions to plant both at Rustenburg and in the Johnson Matthey refineries have been designed to take full advantage of more sophisticated metallurgical techniques.

**Osmium Complexes Containing Four Metal Atoms**

The preparation of interesting new complexes containing four metal atoms has been reported by C. W. Bradford, of the Johnson Matthey Research Laboratories, working under the guidance of Professor Sir Ronald Nyholm (Chem. Comm., 1968, 867). These are obtained by reacting osmium carbonyl, \( \text{Os}_{2}^{\varphi}(\text{CO})_{12}^{\varphi} \), with triphenylphosphine gold halides. It appears that only one of the three Os-Os bonds in the original triangular cluster is broken and this gives rise to what is possibly the first case of a linear arrangement of four covalent bonded metal atoms:

\[
\text{Ph}_{2}\text{PAuX} + \text{Os}_{2}^{\varphi}(\text{CO})_{12}^{\varphi} \rightarrow
\]

\[
\begin{align*}
\text{Cl} & \quad \text{Os} \quad \text{Os} \quad \text{Os} \quad \text{AuPPh}_{3} \\
(\text{CO})_{4} & \quad (\text{CO})_{4} \quad (\text{CO})_{4}
\end{align*}
\]

This new compound is red in colour, monomeric and a non-conductor in solution, and has an infra-red spectrum in the C-O stretching region which is consistent with a linear arrangement of the Au-Os-Os-Os moiety.

The corresponding bromo-compound:

\[
\begin{align*}
\text{Br} & \quad \text{Os} \quad \text{Os} \quad \text{Os} \quad \text{AuPPh}_{3} \\
(\text{CO})_{4} & \quad (\text{CO})_{4} \quad (\text{CO})_{4}
\end{align*}
\]

has also been isolated and has properties similar to those of the chloride.

If X-ray crystallographic studies at present being made show that a linear arrangement is indeed present, then it is interesting to speculate on the possibility of synthesising from these compounds other compounds containing even longer chains of metal atoms.
Platinum Metal Complexes in Homogeneous Catalysis

PAPERS AT THE FARADAY SOCIETY GENERAL DISCUSSION

By G. C. Bond, D.Sc., F.R.I.C.

Research Laboratories, Johnson Matthey and Co Limited

A General Discussion of the Faraday Society was held at the University of Liverpool last September on the subject of "Homogeneous Catalysis with Special Reference to Hydrogenation and Oxidation". Of the eighteen papers presented for discussion, six related particularly to platinum metal salts and complexes, five being concerned with hydrogenation or hydrogen transfer and one with oxidation. These papers are reviewed here.

The General Discussions of the Faraday Society are internationally noted as occasions for leisurely and penetrating consideration of limited fields of research at the borderline between chemistry and physics. They are usually held at a time when the selected field is ripe for such consideration, that is, when sufficient work has been done to show that much more work is needed; and for this reason they frequently act as important milestones along the scientific way, to be looked back on in future years with affectionate regard.

Although the catalytic action of base metal ions (especially cobalt ions) in oxidation has been known for many years, and still features prominently in current research, the ability of palladium salts to catalyse the partial oxidation of olefins has been recognised for only a little more than a decade. Our knowledge of the catalytic properties of salts and complexes of the platinum metals in general for hydrogenation and hydrogen transfer (as in olefin isomerisation) results from work published only during the last five years; and so rapid has been the progress in this period, and so many the unsolved problems which have arisen, that a discussion of the field in depth was most timely.

Hydrogenation and Hydrogen Transfer

The homogeneous hydrogenation of olefins catalysed by complexes of the platinum metals has attracted enormous attention in recent years, but many aspects of the mechanism remain unresolved. It is well established that there are three basic processes whereby a metal atom in a complex can activate molecular hydrogen: these may be represented as:

\[ M + H_2 \rightarrow MH \] \hspace{1cm} (1)
\[ M + H_2 \rightarrow MH^- + H^+ \] \hspace{1cm} (2)
\[ 2M + H_2 \rightarrow 2MH \] \hspace{1cm} (3)

where M is the complexed metal atom. The first certainly operates in the case of d8 complexes such as \((\text{Ph}_3\text{P})_2\text{RhCl}\) and Vaska's complex \((\text{Ph}_3\text{P})_2\text{Ir}^1(\text{CO})\text{Cl}\). The heterolytic process (2) operates with uncomplexed ions such as \(\text{Cu}^{++}\) and \(\text{Ag}^+\) and probably also with \(d^6\) compounds (e.g. \(\text{Ru}^{11}\text{Cl}_2\)). The third process has not been observed with platinum metal complexes although it holds where M is the pentacyanocobaltate ion \([\text{Co(CN)}_5]^{3-}\). It is also well known that metal hydrides may be formed by the complex abstracting a hydrogen atom from the solvent, e.g. when this is an alcohol:

\[ M + \text{H-X} \rightarrow MH + X \] \hspace{1cm} (4)

Olefins are well-known to co-ordinate to
metal atoms, especially those having a $d^6$ or $d^8$ configuration:

\[ M + Y \rightarrow M-Y \quad \ldots \quad (5) \]

where $Y$ represents an olefin.

It is now possible to set down a number of formal mechanisms to account for hydrogenation and hydrogen transfer catalysed by metal complexes. For olefin isomerisation it is now generally agreed that a metal-alkyl must be formed: then by loss of a hydrogen atom from a carbon atom other than that to which the first hydrogen atom added, an isomerised olefin is formed and may appear as a product after disORIZATION, e.g.:

\[ R-\text{CH}=\text{CH}_2 \rightarrow R-\text{CH}CH-\text{CH}_3 \]

This represents the metal-alkyl $M-R$ as having been formed from co-ordinated olefin and metal hydride, viz.

\[ MH+Y \rightarrow MH-Y \rightarrow M-R \quad \ldots \quad (6) \]

However this requires a vacant co-ordination site for the olefin, and an alternative formulation involves 'olefin insertion' in the MH bond, as:

\[ MH+Y \rightarrow M-R \quad \ldots \quad (7) \]

The paper by D. E. Webster and P. B. Wells and their associates (University of Hull) reported an extensive study of the formation of hydride species by process (4), using the complex $(\text{Ph}_3\text{P})_2\text{RhCl}_3$ as the starting material. It appears that at least one of the chlorine atoms is replaced by hydrogen in forming the active species, and that the vacant site required for olefin co-ordination is provided by solvolysis of one of the phosphines. In confirmation of this hypothesis they showed that more rapid catalysis of olefin isomerisation results if a hydrogen atom is present in the original complex (e.g. as in $(\text{Ph}_3\text{P})_2\text{RhCl}_3$). They also demonstrated that a vacant co-ordination site (as in $(\text{Ph}_3\text{P})_2\text{RuCl}_3$) is not alone sufficient to give efficient catalysis, but that much faster rates result when both a vacant site and a hydrogen atom are present (as in $(\text{Ph}_3\text{P})_2\text{RuHCl}_3$).

P. Abley and F. J. McQuillen (University of Newcastle upon Tyne) reported that $d^8$ complexes such as $(\text{Ph}_3\text{P})_2\text{RhCl}_3$, and Baska's complex and its rhodium analogue, catalyse olefin isomerisation in the absence of hydrogen at 60 to 80°C, but how the hydride intermediates were formed was not investigated.

Turning now to hydrogenation mechanisms, a number of formal possibilities need to be considered: these are represented as:

\[ \text{MH} + Y \rightarrow M + YH \quad \ldots \quad \ldots \quad (8) \]

\[ \text{MH} + Y \rightarrow \text{MH}_2Y \rightarrow M + YH \quad \ldots \quad \ldots \quad (9) \]

\[ \text{MY} + H \rightarrow \text{MH}_2Y \rightarrow M + YH \quad \ldots \quad \ldots \quad (10) \]

\[ \text{MY} + H \rightarrow \text{MYHY} \rightarrow H \rightarrow M + YH \quad \ldots \quad \ldots \quad (11) \]

All of these mechanisms have been proposed at some time or other, (8) and latterly (9) by Wilkinson and his colleagues, who rejected (10) from consideration on various grounds. J. P. Candlin and A. R. Oldham (I.C.I. Petrochemical and Polymer Laboratory) stated that both $(\text{Ph}_3\text{P})_2\text{RhCl}$ and the ethylene complex $(\text{Ph}_3\text{P})_2\text{RhCl}_2$ are active catalysts for the reduction of alkynes and olefins, and they queried whether the so-called "unsaturate route" (10) should be dismissed from consideration. B. R. James and G. L. Rempel (University of British Columbia) reported a careful kinetic study of the hydrogenation of maleic acid catalysed by RhCl$_3$ in dimethylformamide, and also decided in favour of mechanism (10); mechanism (11) was originally suggested by Halpern for hydrogenation catalysis by RuHCl$_3$.

A subsidiary question of general interest is the extent to which alkyl intermediates are formed from the hydrido-olefin complexes MH$_2$Y and MYH$^-$ before the saturated hydrocarbon YH$_2$ is formed. The paper by G. C. Bond and R. A. Hillyard (Johnson Matthey) reported the formation of considerable quantities of isomerised olefins during hydrogenation of 1-pentene catalysed by $(\text{Ph}_3\text{P})_2\text{RhCl}_3$: similar but less detailed observations were reported by Abley and McQuillen (although not by the I.C.I. group), suggesting that alkyl complexes are indeed formed. The mechanism proposed by James...
and Rempel for maleic acid hydrogenation also involved an alkyl intermediate. At the moment it cannot be firmly stated that isomerisation is associated with hydrogenation, and it may proceed quite independently; but several observations suggest that it requires (or at least is facilitated by) molecular hydrogen.

**Oxidation**

The partial oxidation of olefins catalysed by Pd\(^{II}\) salts received surprisingly little attention at this meeting, only the paper by D. Clark, P. Hayden and R. D. Smith (I.C.I. Heavy Organic Chemicals Division) treating this area. It is now well appreciated that oxidation of olefins in the presence of acetic acid and Pd\(^{II}\) gives rise to a variety of products whose concentration can be varied over a wide range by altering reaction conditions. The authors reported for example that, when oxidising ethylene with Pd(OAc)\(_2\) as catalyst in the presence of acetic acid, increasing the chloride ion concentration from zero to 2M decreased the yield of vinyl acetate from 85 to 1 per cent, and increased the yield of diacet-oxyethane from zero to 80 per cent (based on total products). Much further work is required before we can hope to understand this extremely complex system.

**Conclusion**

Both the areas of hydrogenation and oxidation continue to receive the keen attention of academic and industrial scientists alike. Much new and fascinating chemistry is appearing, although the day of its industrial exploitation may not be yet at hand.

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**Electrochemistry and Heterogeneous Catalysis**

A symposium on “Electrocatalysis” was held at the Technological University, Eindhoven, on November 21st and 22nd, and was attended by some 120 people, mainly from continental Europe. The purpose of the meeting was to bring together workers from the fields of electrochemistry and of heterogeneous catalysis for, although both are intimately concerned with the behaviour of surfaces and of adsorbed intermediates, there are all too few opportunities for the exchange of ideas and information in this area. Work performed in recent years on surface morphology at the atomic scale using techniques such as field-emission microscopy and low-energy electron diffraction has greatly influenced thinking about catalysis but seems not to have much influenced electrochemists. Conversely recent work on the mechanism of electrode processes and the influence of electrode structure on efficiency has not yet been received into the canon of heterogeneous catalysis.

Each author designed his paper to instruct persons not of his discipline concerning some aspect of his subject: some were inevitably more comprehensible and helpful than others. The one theme which ran through many of the papers and much of the discussion was that of the relation between bulk properties and surface reactivity. Professor W. M. H. Sachtler (Leiden) argued on the basis of his own work on the behaviour of Group VIII\(_2\)–IB alloys that each atom in the surface acts independently and that therefore the collective electron model is not the right one to use. Dr J. N. Butler (Tyco Laboratories, Waltham, Mass.) produced results which showed some of the limits of the “chemical” approach to alloy properties. He with his associates had studied the hydrogen evolution reaction on dilute amalgams of palladium and platinum, and had found they behaved just as mercury. A platinum amalgam containing 0.03 per cent platinum should have increased the exchange current density by more than 10\(^6\) fold, and Dr Butler concluded that the absence of surface structure might have been responsible for the lack of effect. Reporting on an extensive study of platinum black as a fuel cell catalyst, Dr Butler said their results indicated particle size to be the most important factor, and that stored energy had no effect on electrocatalytic efficiency.

The symposium served a useful purpose, but more frequent meetings of this kind are essential if the trend towards the compartmentalisation of science is to be arrested.

G. C. B.
A Fully Integrated Hydrogen Diffusion System

FIRST COMPLETE MATTHEY BISHOP UNIT IN OPERATION

G. L. Matlack, Ch.E.

The principle of hydrogen diffusion through a silver-palladium alloy membrane, developed by Matthey Bishop Inc. over the past few years, is now being applied to complete systems for processing steam-reformed hydrocarbons and hydrogen-rich gas mixtures as well as commercial purity hydrogen.

The initial work on this alloy, which has remarkable stability as well as a hydrogen transfer rate more than twice that of pure palladium, was described in this journal by J. B. Hunter (1). The Company has since progressed from building a range of silver-palladium diffusion cells to the design and construction of commercial scale units (2) and then to supplying the diffusion system for plant used in the production of high-purity hydrogen from dissociated ammonia (3). Now, through a newly formed Apparatus and Systems Division, and based on some ten years of experience in the field, Matthey Bishop is providing fully integrated installations.

The first such installation, employing dissociated ammonia, has recently been put into service at Kreisler Industries Corporation, East Paterson, New Jersey. This unit is rated at 1500 standard cubic feet per hour of ultra-pure hydrogen, and provides the atmosphere required for a critical brazing operation in the manufacture of complex tubing assemblies for jet engines. A better and cleaner braze has resulted from the use of ultra-pure hydrogen, while hydrogen consumption has been reduced. This has made the task of stringent quality control easier while reducing cost.

The unit consists of an ammonia dissociator, a dissociated ammonia compressor and the diffusion system with controls, with an anhydrous ammonia bulk storage system provided by the ammonia supplier. The ammonia dissociator, rated at 2,500 standard cubic feet per hour, is designed to operate at a pressure of 250 pounds per square inch and a temperature of 917° Fahrenheit.
cubic feet per hour, dissociates anhydrous ammonia over an iron catalyst at 955°C. The resulting gas, 75 per cent hydrogen and 25 per cent nitrogen (with traces of residual ammonia and water vapour) is raised from 10 to 250 psig by a heavy-duty reciprocating compressor, the pressure providing the driving force for diffusion. Eight Matthey Bishop Model B-71 diffusion cells are employed, each cell comprising a bundle of thin-walled small diameter silver-palladium alloy tubes manifolded together into a header and assembled into an outer envelope. This construction provides a thin membrane for diffusion, with high surface area in small volume and with high mechanical strength.

Within the cells the impure hydrogen at the moderate temperature of 370°C and at the increased pressure of 250 psig passes over the surface of the silver-palladium alloy. Only hydrogen can diffuse through the alloy, and a minimum of 90 per cent of the hydrogen present in the dissociated ammonia is recovered in the ultra-pure form. The remaining 10 per cent plus the impurities—nitrogen, water vapour and ammonia—are withdrawn continuously as a waste or bleed gas stream and vented to the atmosphere. In some cases this waste gas stream may be processed further and used.

References
1 Platinum Metals Rev., 1960, 4, (4), 130
2 Ibid., 1962, 6, (2), 47
3 Ibid., 1964, 8, (3), 91

Photochemistry of Platinum Metal Compounds
The photoresponsive behaviour of co-ordination compounds and the nature of the excited states involved have given rise to a considerable volume of literature during the last few years. Much of this has been concerned with compounds of cobalt, chromium and other transition metals, but among these interesting results have been reported on certain complexes of platinum, palladium, iridium and rhodium. A comprehensive review by A. W. Adamson and his co-workers at the University of Southern California (Chem. Rev., 1968, 68, 541), provides a valuable collection of data in this field.
The Solid Oxides of Platinum and Rhodium

FORMATION IN HIGH PRESSURES OF OXYGEN

By J. C. Chaston, Ph.D., A.R.S.M.

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At everyday temperatures and in air at normal pressures the solid oxides of the platinum metals are notably of uncertain composition. According to the method of preparation, samples are frequently mixtures of one or more oxides with free platinum and are often partly hydrated. Such uncertainties stem inevitably from the feeble nature of the binding forces in these materials when so close to dissociation.

In view of the importance of these oxides as catalysts, it is surprising that so little has been done in the past to characterise them more strictly. A recent paper (1) by Olaf Muller and Rustum Roy, working in the Materials Research Laboratory of the Pennsylvania State University describes, for instance, the first work that appears ever to have been reported on the use of high pressures of oxygen to stabilise the compounds in reasonably well-crystallised forms for structural examination.

The original intention was to determine the phase equilibria in the system Pt-O at high oxygen pressures. It was soon obvious, however, that it is an almost impossible task to define the phase limits with any certainty owing to sluggishness of the reactions at the temperatures under study. Apparent shifts of up to 50°C were observed in the phase boundaries, depending upon the starting materials used and upon the direction to which the 'equilibrium' temperature was approached.

Platinum black and such compounds as Pt(NH₄)₂(NO₃)₂ were quite unreactive below about 700°C and at the best produced mixtures of platinum metal with small amounts of mixed oxide phases even after several days under pressure. The most consistent results were obtained by heating small quantities of PtI₄ enclosed in platinum (generally 10 mg or less but sometimes up to 0.5 gm), for 1 to 2 days to 400°C to 900°C at pressures up to 3500 atm of oxygen. At the end of a run, the "bomb" was cooled in water before releasing the pressure. The samples were examined by X-ray diffraction to determine the structures of the phases produced, but chemical examination was not as thoroughly performed as might have been desired. The authors obviously lacked experience in platinum metal analysis and appear to have been daunted by the insolubility of some of the oxides in aqua regia.

Three platinum oxides were found: α PtO₂ (hexagonal), a new phase, β PtO₂ (CaCl₂ structure) and Pt₁O₄ (Na₂Pt₁O₄ structure). Tetragonal PtO and body-centred cubic Pt₃O₄ which have previously been reported in the literature were not found.

The evidence is that hexagonal α PtO₂ is the oxide stable at all pressures below about 570°C, the temperature at which it decomposes at atmospheric pressure. It is not easily produced in well-crystallised form even at the highest oxygen pressure; and it is possible that many months of reaction time might be needed for the growth of perfect specimens. There is a suggestion that the presence of sodium nitrate as a flux may promote crystallisation.

At higher temperatures the new β PtO₂ is formed provided that the oxygen pressure is
sufficiently high—above about 600 atmospheres at 700°C and 1000 atmospheres at 800°C. It is black, relatively stable and completely insoluble in mineral acid mixtures and it would be of interest to know more of its properties—particularly in the field of its catalytic activity.

At intermediate pressures, Pt₃O₄ is the stable oxide. For its preparation in bulk it is suggested that commercial platinum black or fine mesh platinum powder should be heated to 850°C under 200 to 300 atmospheres of oxygen and any unreacted platinum removed by treatment with aqua regia. Its structure appears to be identical with that of Na₄Pt₃O₄, the implication being that removal of the sodium atoms leaves empty positions in the lattice.

The work on the Rh-O system described by the authors is less extensive but is remarkable as indicating Rho₂, a phase not previously described, as the most stable structure. It is easily prepared by heating Rh₂O₃, 5H₂O at 700 to 850°C at high pressures of oxygen. It is shown to be stable at all temperatures up to about 1000°C at oxygen pressures above about 20 atmospheres and it is, moreover, the stable phase at atmospheric temperatures below about 700°C. It is a black compound, highly insoluble even in hot aqua regia, and obviously deserves further study. The two other oxide phases, both forms of Rh₂O₃, have relatively narrow fields of existence at 650 to 900°C and above 950°C respectively.

The interests of the authors as shown by this paper lie in the interpretation of the X-ray data on their samples. The methods of preparation chosen may, however, be of value in a much wider field. High pressure techniques may well help to resolve many outstanding problems of platinum metal chemistry by stabilising transient reactions which otherwise elude study.

Reference

Mechanism of the Catalytic Oxidation of Ammonia

The oxidation of ammonia to nitric oxide catalysed by platinum and its alloys forms an essential step in the manufacture of nitric acid, but, because of the high temperature and high space velocity at which the process operates academic investigation of the reaction has only been rarely attempted, and our detailed knowledge of the elementary steps which constitute the total process is very slender. Doubt has often been expressed as to whether the reaction is or is not entirely heterogeneous, and free radical reactions in the gas phase have often been thought to take place, particularly in the formation of nitrogen.

A recent short paper by C. W. Nutt and S. Kapur of the Department of Chemical Engineering, University of Birmingham (Nature, 1968, 220, 697) throws considerable light on the reaction mechanism. These authors examined the reaction in a mass spectrometer by causing an ammonia/oxygen mixture to contact a heated platinum filament: the reaction products passed under collision-free conditions through molecular beam apertures and thence through an ion source. The ionised products were detected in the usual way.

This technique ensures that only those species actually formed on the catalyst surface are sensed; because of the low background pressure, secondary products which might result from gas-phase collisions do not obtrude.

The reaction was examined with filament temperatures between about 400 and 1600 K. The results are very clear: both nitric oxide and nitrogen are formed on the catalyst surface and cannot arise from secondary processes. The reaction starts at about 500 K, the nitrogen yield is maximum at 700 K and nitric oxide at about 850 K. It is suggested that the rate decreases above this temperature because the residence time of the adsorbed species becomes progressively shorter.

G. C. B.
Palladium-Silver Resistor Pastes

AN INVESTIGATION OF FIRING REACTIONS

Thick film circuits produced by screen printing and firing circuit component materials in paste form on refractory non-conducting substrates are widely used in the electronics industry. The electrical properties of the components should be reproducible to within narrow limits, and to achieve this the rheological properties of the pastes and the parameters of the printing process are controlled to standardise deposit thickness. In the case of resistor pastes of the palladium-silver type, comprising palladium, silver and glass frit powders dispersed in organic media, chemical changes occur when the pastes are fired which necessitate rigid control of firing conditions to achieve reproducible results.

Thermogravimetric studies to elucidate the mechanism of reactions occurring in several Du Pont palladium-silver pastes have been carried out by P. H. Krahl and A. F. Bogenschutz, of the Research Institute of Allgemienen Elektricitätsgesellschaft, AEG-Telefunken, Ulm (Metall, 1968, 22, (10), 988). The authors used powder material for the gravimetric work, obtained by evaporating the liquid constituents from resistor pastes, and printed films for the electrical measurements. The powders were heated in stages to 900°C, and test values obtained by removing samples, cooling and weighing. Resistivities under parallel conditions were determined on printed specimens on alumina substrates.

The results show that a progressive increase in weight and resistivity occurs up to 600°C due to oxidation of palladium, and a reduction in weight and resistivity at higher temperatures due to reduction of palladium oxide. However, neither reaction seems to proceed to completion, nor do weight and resistivity entirely synchronise at above 400°C. Resistivity increases occur, particularly on prolonged heating, with no corresponding increase in weight. Some explanation for these anomalies may be found in the authors' conclusion that protection of some of the palladium and palladium oxide particles by sintering frit retards or inhibits chemical change and reduces electrical continuity. There is little evidence, however, to support the suggestion that palladium oxide assumes a more stoichiometric composition at the higher firing temperatures, or that significant amounts of palladium or palladium oxide dissolve in the zinc borosilicate frit.

No weight changes occur in the silver and frit constituents of the pastes, but silver is shown to have some effect on the palladium reactions. The evidence supports the authors' contention that this is due to a catalytic effect resulting from the formation and immediate decomposition of silver oxide, and not to the formation of a surface palladium-silver alloy as postulated by other workers.

The particle size of the frit is stated to affect the reactions. It seems likely that the particle size of the palladium and silver powders could also have some effect, and in addition that carbon derived from decomposition of the organic paste constituents could be retained in the film at 300°C to 400°C long enough to retard the oxidation of palladium, but these possibilities do not seem to have been investigated.

This work has shed some light on the reactions that occur when palladium-silver resistor pastes are fired, although more experimental evidence would be desirable to support some of the conclusions that have been drawn. Because the reactions do not reach completion, it is evident that unless the time and temperature of the firing operation is rigidly controlled, variations will occur in the chemical composition and physical form, and hence the electrical properties, of the resistor elements.

F. E. K.
ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Some Properties of Platinum, Palladium and their Alloys during Heating

The expansions of 25% Pd-Pt, 7% Rh-Pt, and 5% Rh-15% Pd-Pt after thousands of thermal cycles around 1300°C are tabulated. Results of annealing tests for 5h at 900 and at 1300°C confirm the high stability of Rh-Pt alloys compared to Pt or Pd, where grain growth occurs with increasing significance with temperature.

Volutilisation of Platinum-Ruthenium Alloys
E. I. RYTVIN and V. V. MALASHKIN, Tsvetnye Metally, 1968, (s), 80-81

Measurements of the volatility of 2, 5 and 10% Ru-Pt alloys heated in a resistance furnace in air at 1200, 1300, 1400, and 1500°C for 100h showed that increasing the Ru content causes a rise in the rate of volatilisation and that the addition of 5 and 10 wt% Rh does not alter this effect substantially. Microhardness measurements indicated that the main volatilising component was Ru. This was confirmed by volatility measurements in molten silicate medium, where the formation of volatile Ru oxides was prevented.

The Nature of the Coercive Force of Cobalt-Platinum Alloys in Well-regulated Conditions

A high coercive force can be produced in well-regulated Co-Pt alloys with anisotropy constant $\approx 10^3$ erg/cm$^3$ and in the single-phase state, where the magnetic reversal occurs by mixing of domains inside crystals of the ordered phase. Mixing is difficult when the phase boundaries are not well-regulated.

Superconductivity and Lattice Parameters in Face-centred Cubic Pt-W and Pd-W Solid Solutions

F.c.c. solid solutions of Pd and Pt were retained up to 44 and 67 at. % W respectively by adapting the liquid quenching technique to an arc furnace. Minima in the lattice parameter-composition curves occurred at 10 at. % W-Pd and 18 at. % W-Pt. 26-44 at. % W-Pd and 28-67 at. % W-Pt were superconducting below temperatures which varied as a function of lattice parameter.

The Thermal Conductivity of 87% Platinum–13% Rhodium Alloy

Values for $k_{PR}$, the thermal conductivity of 13% Rh-Pt, obtained by experiment fit the equation $k_{PR} = 0.607 - 0.092 \times 10^7 (1/T)$, where $T$ is in °K.

Thermodynamic Properties of Solid Rhodium-Palladium Alloys

Large positive deviations from ideal behaviour in the activities and free energies of formation, and positive enthalpies and entropies of formation of Rh-Pd alloys at 1575 K suggested a strong tendency towards phase separation in the solid solutions. Data was obtained from vapour pressure measurements made by the torsion-effusion method.

The Variation of Magnetoresistance in Copper-Palladium Solid Solutions in the Unordered and Ordered Atomic States

Room temperature measurements on Cu-Pd specimens coldworked, quenched from 800°C, and annealed showed that magnetoresistance varies as the square of the transverse magnetic field is decreased by cold working, and is increased by atomic ordering in CuPd but decreased in CuPd. Calculated and measured values were compared.

Strain Dependence of Exchange Interactions in Dilute PdFe Alloys and in Pure Pd

Measurements of the magnetostriiction and pressure dependence of Curie temperature in ferromagnetic 0.3, 1 and 3 at.% Fe-Pd indicate a positive strain-dependence of the exchange interaction between the conduction electrons and the local moments, contrasting with the negative strain-dependence value between the conduction electrons in pure Pd.
The Solubility of Carbon in Palladium and Platinum


Equilibrium solubilities of C in Pt and Pd at 875-1250°C were measured by a vapour transport technique. Pd dissolved large amounts of C, e.g. 0.7 wt% at 1200°C. Relative partial enthalpy and entropy of the C atoms showed that both solid solutions obey Henry’s Law.

Magnetic Moments in Amorphous Palladium-Cobalt-Silicon Alloys

M. E. Weiner, J. Metals, 1968, 20, (8), 99A

Studies of Pd$_{x}$Co$_{x}$Si$_{x}$ alloys, where $x = 3, 5, 7, 9, 10$ and $11$, at 1.8-300°K in fields up to 8.35 kOe showed that, for $x \ll 9$, Curie’s Law holds with negligible permanent moments at room temperature. When $x = 10$ or $11$, alloys obeyed Curie’s Law only above ~200°K and had significant permanent moments at room temperature. In all cases the moments derived from Curie’s Law were too high than moments of individual Co atoms would suggest. A model is proposed based on superparamagnetic clustering.

Electrical Resistivity of the Palladium-Deuterium System


Electrical resistivity measurements on Pd-D with up to 90 at.% D at 293, 77 and 4.2°K shown that at 4.2°K the resistivity increases at $\Delta$/Pd°.68. These variations are less pronounced at the higher temperature. Possible models of this behaviour are discussed.

A Study of Some Palladium-Tin, Silver-Tin, and Palladium-Silver-Tin Alloys


Lattice spacings, magnetic susceptibilities and 115Sn Mössbauer isomer shifts for some Pd-Sn, Ag-Sn, and Pd$_{x}$Sn$_{10-x}$ alloys, where $x$ varies from 0 to 98 at.%, are consistent with a charge transfer model in which the Sn valence electrons are donated to vacant d-states in the Pd-rich alloys. In the Pd-Ag-Sn alloys there is a two-phase mixture of Pd$_{4}$Sn and solid solution, in the range 33-10% Pd, and this is reflected in an anomaly in the variation of the isomer shift with composition.

Investigation of Liquid Palladium-Tin Alloys


The heat of solution of Pd in liquid Sn was measured as a function of temperature and concentration in the dilute solution range at 700-800°K. The partial heat of solution, when compared to the heats of formation of PdSn, PdSn$_{14}$, shows similarities, indicating similar bonding in all cases with each Pd atom in the liquid surrounded by four Sn atoms. Density measurements on liquid 4% Pd-Sn show that a tetrahedral PdSn$_{4}$ molecule would have a Pd-Sn distance close to that of the intermetallic compounds.

On the Tungsten Compact by Low-temperature Sintering. III. Effects of Palladium Addition


The sintering characteristics and mechanical and electrical contact properties of ≤5% Pd-W alloys were studied. 0.5% Pd-W gave dense compacts after 1h at >1000°C. Vickers hardness of 1-5% Pd-W sintered compacts had a maximum of 550 at 1000°C. Their transverse rupture strength was greater than that of Ni-P-W. Wear of ≤1% Pd-W contacts was similar to W with no observed transfer phenomena.

Thermal Expansion of Rhodium


Measurements from 28 to 587°C on Rh enabled expressions to be derived for the lattice parameter and its variation with temperature, and by differentiation of this value the temperature dependence of coefficient of thermal expansion.

Magnetic Behaviour of Ni-Rh Alloys


Most results of measurements of magnetic susceptibility, of paramagnetic resonance of Gd, and of the speed of sound in Ni-Rh samples agree with a band model with exchange interaction. Ni$_{42}$Rh$_{58}$ doped with 0.8% Fe has a giant moment of ~12 Bohr magnetons. This drops to 2.5 $\mu_B$/Fe atom in pure Rh. Magnetostatic measurements around Ni$_{42}$Rh$_{58}$ composition presented anomalies which are discussed.

A Calorimetric Study of the Rhodium-Tin System


The solution of Rh in dilute Rh-Sn at 700, 725, 750, and 775°K was very exothermic, -29,950 to -28,260 cal/g atom at infinite dilution. A sharp decrease in the heat of solution just before the solubility limit enabled the liquidus boundary to be established accurately at each temperature and also the heat of formation of RhSn$_{4}$ to be calculated.

Crystalline Phases in the Rhodium-Beryllium System. I. Rhodium Monoberyllide


Metallographic and X-ray diffraction studies
together with microhardness and optical measurements on 0-14% Be-Rh identified the isotropic phase RhBe with CsCl-type lattice, a = 0.2379 nm, microhardness 13700 MN/m² and also the anisotropic phase RhBe₄ with density 6.8 g/cm³, microhardness 9300 MN/m².

Mechanical Relaxations in Polycrystalline Molybdenum, Tantalum, and Iridium at High Temperatures and Low Frequencies
Studies on polycrystalline specimens of Mo, Ta and Ir up to 2000°C using an inverted torsion pendulum with period \( \approx 1 \) Hz indicated an internal friction peak at \( \approx 150^\circ \)C in Ir, identified as a grain boundary peak. The activation energy associated with each relaxation was \( \approx \) activation energy for self-diffusion. The relaxation strength for Ir was large. Since the peaks were only present in polycrystalline specimens, the grain boundary type of relaxation is confirmed.

Resistivity of Some \( 5d \) Elements and Alloys Containing Iron
Resistivity-temperature studies on Fe-Ir, Fe-Os-Ir and Fe-Ir-Pt alloys showed that the resistivity due to Fe has a strong anomalous temperature dependence which is related linearly to Fe concentration and which changes gradually with alloy composition. No discontinuity in the resistivity behaviour of Ir-Fe was noticed. Anomalous scattering persists in Os-Ir alloys, where no magnetic moment resides on the Fe impurities.

F.I.M. Imaging of Solute Atoms in Dilute Binary Alloys
For \( \geq 2 \) at.\% W-, Pd-, Co-, Ni-, or Au-Pt, bright spots and vacant sites in field ion microscope images correspond to the lattice sites of solute atoms, while for \( \leq 2 \) at.\% vacant site concentration exceeded solute concentration by \( \sim 1 \) at.\%. The distribution of solute atoms is discussed.

CHEMICAL COMPOUNDS
Preparation and Semiconducting Properties of Platinum Antimonide
PtSb₂ single crystals of the highest purity were prepared by horizontal zone refining and by Czochralski methods. Extrinsic carrier concentrations \( \approx 10^{14}/\text{cm}^3 \) and hole and electron mobilities at 50-60°C of 7,500 and 6000 cm²/V sec were achieved. The semi-conducting properties of this compound are listed in full.

Crystal Chemistry and Electrical Transport Properties of Some Precious Metal Oxides
Two rutile-type dioxides, Rh₂O₃ and PtO₂, have been synthesised and crystals of RuO₂, OsO₂, IrO₂, and PdO have been grown. Single crystals of PdCoO₂ and Pt₁₋₄Co₂₋₄S Wy, O₄, where \( 0.6 \leq \alpha \leq 0.8 \), have been grown which are isostructural with CuFeO₂ and have twofold co-ordination of the precious metal by anions. Qualitative models of chemical bonding are related to occurrence, crystal chemistry and electrical behaviour of these materials.

Formation and Stability of the Platinum and Rhodium Oxides at High Oxygen Pressures and the Structures of Pt₃O₄, \( \beta \)-PtO₂, and RhO₂
O. Muller and R. Roy, J. less-common Metals, 1968, 16, (2), 129-146
Studies of the Pt-O and Rh-O systems at po ≈ 3500 atm, 400-900°C revealed the phases \( \alpha \)-PtO₂, \( \beta \)-PtO₂, Pt₃O₄, Rh₂O₃, and RhO₂. Hexagonal \( \alpha \)-PtO₂ has been described previously. CaCl₂-type \( \beta \)-PtO₂ and Na₂PtO₄-type Pt₃O₄ are black, highly insoluble solids, which are easily synthesised in these conditions. The reported tetragonal PtO₂ and b.c.c. Pt₃O₄ were not encountered. RhO₂ has rutile structure and is a black, easily synthesised solid, highly insoluble even in hot aqua regia.

The cyanation of ruthenocene to C₅H₅Ru(C₅H₅)₂CN is reported. The second section includes: the syntheses of Hg[Ru(CO)₅C₅H₅]₃, hexametallic Ru carbonyl derivations, cyclotetraene Ru carbonyl derivatives, Ru and Os pentacarbonyls, and olen complexes of Ru and Os; reactions of Ru₃(CO)₁₂; carbylation of Ru halides and the 1,2-cycloaddition reactions of C₅H₅Ru(CO)₂. The third section includes: improved syntheses of Rh and Ir carbonyls, their stereochemistry and reactions; syntheses from carbonyl chlorides, of Rh and Ir complexes from fulvenes; Rh derivatives containing both triphenylphosphine and \( \pi \)-allyl ligands, and Rh and Ir complexes containing both \( \pi \)-cyclopentadienyl and organosulphur ligands. The fourth section includes:
Pd and Pt derivatives containing tertiary phosphine ligands; the preparation of Pt and Pd olefin complexes; square planar Pt(II) complexes; n-allylic Pd derivatives, and methyl derivatives of Pt.

The Structure of IrBr₃ and the Causes of Defect-order Phenomena in Noble Metal Halides Crystallised in Layer Structures
IrBr₃ has a strongly defect-ordered layer structure with a monoclinic crystal and lattice parameters a = 6.30, b = 10.98, c = 6.34 Å, β = 108.7°. The defect arrangement is caused by stacking modifications of the metal layers.

Part III. Mechanism of the Formation of an Iridium Complex of Molecular Nitrogen
A mechanism for the formation of a complex between Ir and N₂ is proposed.

Iridium Complexes of Molecular Nitrogen
A study of the preparation of N₂ complexes with ClCO(Ph,P)₂Ir and azides, including the reaction mechanism, the effect of using different azides, central metals and ancillary ligands, and the properties of the N₂ complex.

Part I. The Synthesis of Metal-Metal Bonds via Iridium and Rhodium Carbonyl Anions
Part II. The Synthesis and Properties of Acyl Isocyanate Complexes of Iridium and Rhodium
Previously unknown Ir and Rh carbonyl anions were synthesised and complexed to post-transition metal halides by metal-metal bonding. Complexes were characterised and their oxidising abilities were examined. The first known acylisocyanate metal complexes were synthesised from a novel Ir compound of N with acylisocyanate.

A New Type of Osmium—Post-transition Metal Complex Containing Four Metal Atoms
Complexes containing four metal atoms were prepared by oxidising Os₅(CO)₁₂ with co-ordinated AuCl or AuBr. The red products are monomeric CHCl₃ and have spectra consistent with a linear arrangement of Au-Os-Os-Os. They do not conduct electricity. See comment on page 22 and succeeding abstract.

The Preparation and Vibrational Spectra of Compounds of the Type M(CO)₄(HX)₂
Ru(CO)₄(HX)₂ (H = Cl or Br) and Os(CO)₄(HX)₂ (H = Cl, Br or I) were prepared and their i.r. and Raman spectra were recorded at 2200–1900 and 700–70 cm⁻¹. All the compounds are monomers with cis-octahedral structures. Their spectra are compared with those of Fe(CO)₄(HX)₂ and other M(CO)₄L₂ molecules.

Binuclear Nitrido-complexes of Ruthenium
Tests indicated that the reaction of [Ru(NO)X₃]⁻, where X is Cl or Br, in complexes with HCHO or stannous halides yields compounds whose K salts are K[Ru₂(NO)₃(N₂)(H₂O)₃] with a linear Ru-N-Ru bridge. These are the first reported nitrido-complexes of Ru and join the small group of transition metal µ-nitrito-complexes. Spectra and diamagnetism of the new compounds are discussed.

ELECTROCHEMISTRY
Fluctuations of Overpotential at Metal Cathodes and Changes in Surface Concentration of Hydrogen Atoms
Fluctuation of the total apparent H₂ overpotential at platinised Pt cathodes at low current density were correlated with irregular changes of the H₂ content of the electrode surface. The comparative lack of fluctuations at palladised Pd cathodes was attributed to H₂ absorbed in the Pd lattice.

H₂ adsorption on Pt in H₂SO₄ solution was studied from charging curves. Heats of adsorption were calculated for surface coverage ranging from 90 to 5%. Data agree with previously reported work on smooth and platinised Pt.

Electrochemical Behaviour of Titanium-Platinum Alloys in Processes of Anodic Oxidation. II. Relation of the Electrochemical Behaviour of Ti-Pt Alloys in H₂SO₄ Solutions to their Chemical Composition and Structure
Kinetics and selectivity of anodes for the forma-
tion of $O_3$, $H_2SO_4$ and $O_3$ were studied on \( t, 2, 5, 10, 25, 40, 60, \) and 80 wt, Pt-Ti alloys in $12.3 N H_2SO_4$ at $0 \to -30°C$. The rate of $H_2SO_4$ synthesis rises with Pt content and is greatest for 60–80 wt, Pt-Ti at $3.4 V$ and $-30°C$. Yield of $H_2SO_4$ is high on $<1-2\% Pt-Ti$ alloys with a-solid solutions but is less on metallides even where they incorporate 60–80 C,H,-I in relation to the amount of poison Pt-Ti alloys with a-solid solutions but is less on Measurements during the hydrogenation of $H_2$ showed that two types of centre exist for oxides at the surface of the anodes made from separate Pt oxides in the mixture of Ti and Pt. This is accounted for by the presence of adsorbed on the surface of Pt black saturated with Pt. This change is independent of the mode of preparation over a $10^2$ change in surface roughness. Apparent changes in specific activity were observed on depletion of acetate ion and increased acidity in the micropores.

HETEROGENEOUS CATALYSIS

Catalytic Activity of Platinum Black


Measurements during the hydrogenation of $C_6H_{13}I$ in relation to the amount of poison adsorbed on the surface of Pt black saturated with $H_2$ showed that two types of centre exist for hydrogenation with activities differing $\sim 5$ times.

Catalytic Oxidation of Hydrogen on Platinum Studied by the ESR Method


Condensed products of the $H_2-O_2$ reaction on Pt were studied by the ESR method for various temperatures and pressures of the reaction mixture. The shape of the Pt rod affected results, indicating the progress of the heterogeneous-homogeneous mechanism.

Catalytic Decomposition of Methanols over Platinum and Ruthenium


The decomposition of $CH_3OH$, $CH_3OD$ and $CD_3OH$ at $70–250°C$ over Pt yielded mainly CO and $H_2$, the rates showing a marked kinetic isotope effect, whereas Ru was much more active giving high yields of $CH_4$. Above $155°C$ addition of Ru to Pt increased its activity until at $30\%$ Ru an abrupt change to the methanation mechanism took place. Mechanisms and information on the composition of the catalyst surface are discussed.

Study of the Regularity of Crystallisation of Platinum on Supports. I. Relation of the Dispersion and Activity of Platinum, Supported on Aluminium Oxide, to the Surface Concentration and Properties of the Supports


Studies of the dispersion of $0.1–2.0$ wt, Pt on $Al_2O_3$ samples with various structures and specific surfaces in conditions similar to those of the preparation and use of reforming catalysts showed a linear relationship between the inverse size of dispersion, expressed as $H/Pt$, and the surface concentration of Pt. This relation has a coefficient of proportionality characterising the ability of Pt to form aggregates or to crystallise on the surface of the support. This general relation also applies to Ag/corundum. All studied catalysts had the same specific activity for cyclohexane dehydrogenation. Results explain the existence of optimum concentrations of Pt in Pt/$Al_2O_3$ reforming catalysts.
Hydrocracking and Diffusion of Pure Compounds on Mordenite Catalysts


Pd on Al-deficient H-mordenite is ~4 times more active than Pd/H-mordenite for cracking n-C$_{10}$H$_{22}$ and decalin at 450 psig, 450-610°F. Activation energies are 44 and 33 kcal/mole for n-C$_{10}$H$_{22}$ and 25 kcal/mole for decalin. Pure n-C$_{10}$H$_{22}$ is more reactive than pure decalin but in approximately even mixtures the latter is converted while n-C$_{10}$H$_{22}$ is not. The increased activity of Al-deficient H-mordenite is partly due to its lower diffusion resistance.

Dehydrogenation of Monocyclic Naphthenes over a Platinum on Alumina Catalyst without Added Hydrogen

A. W. Ritchie and A. C. Nixon, Ibid., 209-215

Pt/Al$_2$O$_3$ showed good selectivity and catalytic stability in the dehydrogenation of cyclohexane and of its methyl and ethyl derivatives at 10 atm, 840-1200°F. The alkyl substituents increased the reaction rate by an amount depending on their positions in the ring, the stereochemistry and the reaction temperature.

Catalytic Properties of the Platinum Group Metals and their Alloys Based on Palladium


Studies of Raney catalysts of Pt group metals and their Pd-based alloys during hydrogenation of dimethylthelyncarbinols showed the effects of catalyst and of solvent on the kinetics and direction of the reaction. Charging curves during anodic polarisation by organic substances showed the ability of catalysts to adsorb H$_2$. The inactivity of Ru, Ir, Os, and Re is due to their insignificant adsorption of H$_2$. X-ray studies allowed comparison of catalyst surfaces during H$_2$ and air adsorptions. Not all of a catalyst surface is accessible to H$_2$.

Preparation of Highly Dispersed Catalytic Metals. Platinum Supported on Silica Gel


The dispersion of Pt in catalysts prepared by ion exchange of Pt-ammine cations with SiO$_2$ gel support, followed by reduction, was much greater than that in similar catalysts prepared by impregnation with aqueous H$_3$PtCl$_6$. H$_2$ chemisorption, X-ray diffraction and electron metallography methods showed that the Pt is in the form of finely dispersed 15 Å crystallites.

On the Selectivity of Platinum Catalysts


Initial rates of reaction of neopentane were measured at 300°C, 1 atm, H$_2$: neopentane = 10 on Pt powder and on Pt/SiO$_2$, Pt/C, Pt/γ-Al$_2$O$_3$, and Pt/γ-Al$_2$O$_3$. The Pt dispersion, defined as % Pt atoms at the surface, varied from $3 \times 10^{-7}$ for the powder to $>70$ for the supported catalysts. Neopentane underwent concurrent isomerisation to isopentane and hydrogenolysis to isobutane and CH$_4$. Selectivity for isomerisation varied by a factor of 100 for the catalysts studied. Selectivity of supported catalysts increased with increasing catalyst pretreatment temperature from 425 to 900°C and a mechanism is suggested for this behaviour.

Study of Supported Catalysts by the Exoelectronic Emission Method. IX. Zinc Oxide with Additions of Platinum, Silver and Gold. Investigation of Secondary Electron Multiplication


The intensity of exoelectronic emission at the surface of Pt/ZnO, Ag/ZnO and Au/ZnO, which reaches a maximum at 140-150°C, was not reduced by previous treatment in vacuum at 400°C. Preliminary adsorption of O$_2$ and H$_2$ at 200-300°C raised the intensity of emission at room temperature. Exoelectrons were localised due to chemisorption of O$_2$ and hydroxyl on the surface.

Chemical Transformations of Diols and Cyclic Ethers. XXVI. Investigation of the Conversion of 2,4-Dialkyl-substituted Oxetanes in the Presence of Platinum Catalyst by the Microreactor Technique


Conversions of 2-methyl-4-ethyl-, 2-methyl-4-n-butyl- and 2-methyl-4-cyclohexyl-oxetanes over Pt/thermolite and Pt/C in H$_2$ and He at 200-350°C yielded mainly isomeric ketones by breaking of the two C-O bonds (60-70%) and olefins and corresponding aldehydes by thermal decomposition (30-40%), the relative amounts depending on catalyst activity, temperature and substituent effects. Pt/C was the most active.

Kinetics of the Dehydrogenation of Cyclohexene on Palladium at Pressures below $10^{-3}$ torr


A new method of studying the kinetics of dehydrogenation at initial pressures of $1.10^{-4}$ to $1.10^{-3}$ torr, including reduction of the catalytic activity of Pd during the reaction, confirmed the stepwise nature of the reduction of cyclohexene. Study of the $\sim$50°C stage below $1.10^{-3}$ torr established that the kinetics below $3.10^{-4}$ torr can be explained by the Langmuir-Hinshelwood equation. The surface of Pd is heterogeneous due to its lattice structure.
Investigation of the Conversions of Cyclohexadiene-1,3 and Cyclohexadiene-1,4 in the Presence of Rhodium Catalysts
During room temperature conversion of cycloolefins over Rh black and Rh/C, cyclohexadiene-1,3 reacts before cyclohexadiene-1,4 and cyclohexene is formed. The direction of conversion of cyclohexadiene isomers depends on the amount of H₂ at the catalyst surface. Hydrogenation and disproportionation of cyclohexadiene-1,3 occur together at ordinary pressures but only at reduced pressures with cyclohexadiene-1,4. Cyclohexadiene-1,3 is disproportionated and dehydrogenated in N₂. Cyclohexane is hydrogenated more easily and is dehydrogenated less easily than the cyclohexadienes and is probably not disproportionated. Disproportionation is not observed when the cycloolefins cannot be dehydrogenated.

Catalytic Activity of Rhodium and Ruthenium in the Hydrogenolysis of Ethane
3.14% Rh/SiO₂ and 3.14% Ru/SiO₂ catalysts with wide pores were studied during the hydrogenolysis of C₂H₆ and it was found that the texture did not affect the activation energy and the orders of the reaction with respect to C₂H₆ and H₂.

Study of the Catalytic Properties of Iridium Supported by Alumina. I. Textural Study by Adsorption of Gas and Electron Microscopy
The surface area of Ir/Al₂O₃ was measured using the physical adsorption of N₂ and A at 77°K, and the activity of the metal surface using chemisorption of H₂ at 473°K. Agreement between those results and electron microscopy was satisfactory and the variation of metallic area was studied as a function of Ir content.

HOMOGENEOUS CATALYSIS
Homogeneous Catalytic Hydrogenation and Isomerisation of Olefines with Dichlorobis(triphenylphosphine)platinum(II) – Tin(II) Chloride Catalyst
Terminal double bonds proved to be the most favoured for hydrogenation with PtCl₂(Ph₃P)₂ and SnCl₂ and dienes with two terminal double bonds yielded small quantities of saturated material. Isomerisation occurred with dienes but conjugation was inessential for hydrogenation. Formation of a metal hydride-olefin intermediate is proposed in which an unusually strong metal-olefin bond would inhibit hydrogenation.

Arylation, Methylation, and Carboxyalkylation of Olefins by Group VIII Metal Derivatives
The reaction of aryl, methyl and carboxyalkyl derivatives of Pd, Rh and Ru with olefins is insensitive to O₂ and H₂O and can be made catalytic by employing CuCl₂ as reoxidant. It offers a useful method for a wide range of organic syntheses. See the following group of abstracts.

The Arylation of Allylic Alcohols with Organopalladium Compounds. A New Synthesis of 3-Aryl Aldehydes and Ketones
Ibid., 5526–5531
 Aryl-Pd salts were prepared in situ from aryl-Hg salts and a Pd salt and reacted with primary or secondary allylic alcohols to produce 3-aryl aldehydes and ketones.

Allylation of Aromatic Compounds with Organopalladium Salts
Ibid., 5531–5534
Moderate yields of allylaromatic derivatives were obtained from allylic halides by the same method.

Ibid., 5535–5538
Other uses for this reagent are the preparation of arylacetalddehyde derivatives, arylocetalddehyde enol ester derivatives, aryl ethylenes and stilbenes from aldehyde enol esters, stilbenes from vinyl ethers and halides and 2-ary ketones from ketone enol esters. Yields are generally low, but the reaction is simple and convenient.

Aromatic Haloethylation with Palladium and Copper Halides
Ibid., 5538–5542
Aryl mercuric halide and Li₃PdCl₄ reacted with olefins in the presence of Cu halides to form 2-arylethyl halides, a convenient method for introducing 2-haloethyl groups into aromatic systems.

The Addition of Alkyl- and Arylpalladium Chlorides to Conjugated Dienes
Ibid., 5542–5546
1-Arylmethyl and 1-alkyl-π-allyl-PdCl₂ dimers were formed in low to moderate yields when conjugated dienes were reacted with aryl- and
alkyl-Pd chlorides prepared in situ from aryl and alkyl Hg or Sn salts and Li₂PdCl₄. A catalytic synthesis of aryldiaryl ketones from a conjugated diene, an arylmercuric salt and Pt tetraacetate with catalytic amounts of Pd acetate is also reported.

A Synthesis of Diaryl Ketones from Arylmercuric Salts

Ibid., 5546-5548

Arylmercuric chlorides react with CO and Pd or Rh halide catalysts to form diaryl ketones in fair yields.

Vinyl Acetate from Ethylene in the Liquid Phase with Palladium Salts as Catalysts


PdCl₂, CuCl₂ and O₂ were used in a pilot plant for the production of vinyl acetate. CH₂CHO formed as a by-product provided enough CH₃COOH for the vinyl acetate production. Capacity was 50 t/month.

Exchange of Molecular Nitrogen with Nitrogen of the Coordination Sphere of Nitrogenyl Ruthenium


IR spectra of RuN₄(H₂O)₂Cl[THF], referred to as Ru₄N₄, after thermal decomposition in C₂H₂O in an atmosphere of N₂, indicated exchange between N₂ of the co-ordination sphere of Ru with atmospheric N₂. This is explained by the reaction of Ru₄N₄ formed during decomposition of Ru₄N₂ with dissolved atmospheric N₂ to give again Ru₄N₂. This is confirmed by the decreased rate of decomposition of the complex when the pressure of dissolved N₂ increases.

Molecular Structure of the Hydrogenation Catalyst Hydridochlorotris(triphenylphosphine)-ruthenium (II)


The crystal and molecular dimensions of RuClH(PPh₃)₃, the most active homogeneous catalyst yet known, were calculated using 3-dimensional X-ray analysis.

Oxidation of Olefins by Ferricyanide Using Osmium Tetroxide Catalyst


Qualitative and selective production of glycols from olefins in aqueous alkaline solutions used OsO₄ as homogeneous catalyst and K₂Fe(CN)₆. During the reaction Os⁴⁺ was converted to Os⁶⁺ and Fe(CN)₆³⁻ to Fe(CN)₅²⁻. Os³⁺ and Fe(CN)₅²⁻ were regenerated electrochemically. The reaction mechanism was studied.

FUEL CELLS

The Performance of Direct Ammonia Fuel Cells


NH₃-O₂ and NH₃-air fuel cells were tested with Pt black and Pt/graphite electrodes at 140, 120, 80, 60, and 25°C. Continuous operation at increasing load showed that at 800 mA/cm² at room temperature operation is possible using Pt black electrodes with no external heat source for starting. Results of runs at 120°C using 54% KOH electrolyte and Pt/graphite are plotted.

Improved Electro catalysts for Ammonia Fuel Cell Anodes

D. W. MCKEE, A. J. SCARPELLINO and I. F. DANZIG, Ibid., abstr. 350

The performance of 21.3% Ir-Pt and 51% Ir-Pt electrodes in the form of Adams-type blacks bonded with Teflon and of Ir and Pt co-deposited on graphite and B₄C in 54% KOH solution up to 140°C were compared with a standard Pt black electrode. Plots of results indicate that Ir additions considerably improve electrode activity. The mechanism is discussed. Ir appears to be much more active than the other Pt metals for the dissociation of NH₃ at elevated temperatures.

ELECTRICAL AND ELECTRONIC ENGINEERING

Hermetic Seals by Thick-film Techniques


The best combination of materials appeared to be Pt-Au metallisation over a glass or glass-ceramic crossover. Pt-Pd on glass ceramic had higher adhesive strength and all the layers could be fired at once but had slightly less resistance to thermal cycling and was sensitive to processing conditions. Pt-Au and Pd-Ag made good seals but were not subjected to low temperature cycling. Polymer sealents may not be as reliable but are cheaper.

TEMPERATURE MEASUREMENT

Pressure Effect on the Platinum versus Platinum 10% Rhodium Thermocouple

P. M. BELL, J. L. ENGLAND and F. R. BOYD, Carnegie Inst., Wash., Yr Bk, 1968, 66, 545-547

Corrections to the values recorded by Pt: 10% Rh-Pt thermocouples were determined for pressures up to 9 kbar at 20, 185, 305, and 509°C and amount to >3°C at 509°C, 5 kbar.
The Effect of Reactor Exposure on Thermocouple Materials


Neutron irradiation causes slight changes in the thermo-e.m.f. of thermocouple materials due to the formation of radiation defects. Tests using up to $10^{19}$ neutron/cm$^2$ on 60% Au-Pd, Pt, 13% Rh-Pt, and base metal alloys showed that after annealing there is a slight increase in thermo-e.m.f. for 60% Au-Pd and a slight decrease for Pt and 13% Rh-Pt. Results are tabulated and displayed graphically. Annealing reduces the number of defects and hence errors in thermocouples exposed to radiation at high temperatures may be lower than those at lower temperatures.

NEW PATENTS

METALS AND ALLOYS

Alloy

INTERNATIONAL BUSINESS MACHINES CORP.

British Patent 1,125,690

Magnetic thin films for computer storage elements may be made from an alloy of 69.9-80 at. % Ni, 18-20.2 at. % Fe and 1-12 at. % Pd.

Finely Divided Noble Metal Alloys

E. I. DU PONT DE NEMOURS & CO.

U.S. Patent 3,390,981

Alloys of two noble metals selected from Ag, Au, Pt and Pd are produced by mixing solutions of salts of these metals and then reducing the mixture (e.g. of Pd and Ag nitrates) to give an alloy in finely divided form. $\text{H}_3\text{PO}_4$ is a suitable reducing agent.

A Niobium-Tungsten Alloy

BIRMINGHAM SMALL ARMS CO. LTD

British Patent 3,395,012

An alloy consists of at least 30% Nb, 10-25% W, up to 40% Ta, and 0.1-10% of at least one element selected from Ru, Os and Ir.

Laminated Metal Plates and Strip

JOHNSON, MATTHEY & CO. LTD

German Patent 1,271,494

The bonding of Pt or Pt alloy to Ti, Ta, Nb, V or Zr mechanically, especially to produce electrodes, is improved by using pressures of 80-800 kp/cm$^2$ at 800-950°C.

Fountain Pen Ruthenium Alloy

W. C. HERAEUS G.m.b.H.

German Patent 1,271,332

A ternary alloy for nib tips comprises 10-40% Re, 15-45% Ru and 15-50% W.

CHEMICAL COMPOUNDS

Trimeric Ruthenium Carbonyl

LONZA LTD

U.S. Patent 3,387,932

$[\text{Ru}(\text{CO})_3]_3$ is prepared by reacting a basic Ru salt and a carboxylic acid or Ru acetylacetonate with CO at elevated temperature and pressure in the presence of MEK or a lower alcohol.

ELECTROCHEMISTRY

Porous Electrodes for Electrochemical Cells

GULF GENERAL ATOMIC INC.

British Patent 1,124,362

Metal porous electrodes are produced by shaping a mixture of metal particles, e.g. Ni, with C particles using heat and pressure and then removing the C by electrolysis. The porous Ni matrix is impregnated using a thermally unstable organic salt of a Pt metal.

Anodes for Electrolytic Cells

TSURUMI SODA CO. LTD

British Patent 1,128,136

Anodes for the electrolysis of halide compounds (e.g. NaCl) are produced from an alloy of 3-80% Pd and 97-20% Rh or of 5-80% Pd and 95-20% Pt which is subjected to oxidative treatment at 180-1350°C in an oxidising atmosphere, or electrolytic oxidation in a fused salt bath.

Electrocatalytic Surfaces

GENERAL ELECTRIC CO. (NEW YORK)

U.S. Patent 3,396,091

High electrocatalytic activity is produced by plating a Pt metal-base metal alloy from a common bath and then removing the base metal by etching.

ELECTRODEPOSITION AND SURFACE COATINGS

Metallising Compositions

E. I. DU PONT DE NEMOURS & CO.

U.S. Patent 3,385,799

Electroconducting areas are produced on non-conducting surfaces, especially ceramics, using a mixture of 30-90% noble metal alloy powder, dispersed in 10-70% of an inert liquid organic vehicle; the powder has 90% of the particles not greater than 5 microns in size and is made from two noble metals selected from Ag, Au, Pt and Pd.
Platinum Metal Chemical Plating
INTERNATIONAL NICKEL CO.
U. S. Patent 3,387,987
The chemical plating of metals, especially Ni and its alloys, is achieved by immersion of the metals in a bath containing, per litre, 1–10g of Pd, Pt, Rh or Ru, 64–96g HCl, 0.1–2.5g Cu and 0–5g Fe.

JOINING
Refractory Metal-to-Ceramic Seal
A. E. MILCH et al.
U. S. Patent 3,386,160
Ceramic surfaces are provided with a layer of spongy Mo and/or W and a wetting alloy, selected from Ta-Rh, Rh-Mo and Ru-Mo alloys, is melted on the spongy layer so that brazing to Ta and Nb alloys can take place.

Noble-metal-coated Ceramic for Seals
INFRARED INDUSTRIES INC.
U. S. Patent 3,390,969
A ceramic substrate is coated with (a) a metal oxide, (b) Cu, Ni, Cr, Mn, Ti, stainless steel or Ni/Cr and then with (c) Au, Ag, Pt, Rh or Ir. The laminate material is used for making glass-glass seals, especially in electronic components.

HETEROGENEOUS CATALYSIS
Process for Isomerising Terminal Olefines
ETHYL CORP.
British Patent 1,122,056
Internal olefines are produced from terminal olefines when contacted with one or more Group VIII metals, optionally together with an alcohol or aldehyde promoter. The preferred catalysts contain Ru with one or two other Group VIII metals.

Production of Hydroxylamine Sulphate
INVENTA A.G.
British Patent 1,122,103
HNO₃ is reduced with H₂ in aqueous H₂SO₄ in the presence of a Pt catalyst, e.g. Pt/C, to give hydroxylamine sulphate.

Improvements in the Treatment of Oils
UNILEVER LTD.
British Patent 1,122,398
The linolenic acid of edible vegetable oils is hydrogenated selectively to linoleic acid at 150–250°C in the presence of a mixture of Cu and a more active metal, especially Pd or Pt.

Improvements in or Relating to the Production of Esters
DISTILLERS CO. LTD
British Patent 1,122,444
Better yields of vinyl acetate are obtained in the oxidation of C₆H₅O over a Pt group catalyst in the presence of 5–15 wt% H₂O, acetate ions, CH₃COOH and halide ions.

Production of a Mixture of Stereoisomers of 4,4’-Methylenedii-(cyclohexylamine)
E. I. DU PONT DE NEMOURS & CO.
British Patent 1,122,609
Essentially complete hydrogenation of p,p’-diphenylmethane to give this mixture of isomers is achieved at high pressure and temperature in the presence of NH₃, inert organic solvent and a special Ru catalyst. The catalyst consists of (a) Ru supported on CaCO₃ and/or a rare earth oxide or (b) Ru supported on Al₂O₃, BaSO₄ or kieselguhr and moderated with 0.1–15% of a basic alkali metal compound.

Production of Carboxylic Acids or Esters
BADISCHE ANILIN- & SODA-FABRIK A.G.
British Patent 1,123,367
An unsaturated compound is reacted with CO and H₂O, an alcohol or a phenol at elevated temperature in the presence of Pd metal or a Pd chalcogenide with an acid and an organic phosphine and/or nitrile. Pd/SiO₂ and PdO are examples of the catalyst.

Catalytic Hydrogenation of Unsaturated Aldehydes
JOHNSON, MATTHEY & CO. LTD
British Patent 1,123,837
The catalyst for the selective hydrogenation of an unsaturated aldehyde to an unsaturated alcohol comprises Pt promoted with an alkaline hydroxide in an alcoholic solvent, e.g. Pd/C promoted with alcoholic KOH.

Dehydrogenative Coupling of Organic Compounds
BRITISH PETROLEUM CO. LTD
British Patent 1,123,874
Diphenyl is obtained from C₆H₆ by dehydrogenative coupling over Pt or Pd metal supported on a non-acidic inorganic support, e.g. SiO₂, quartz wool or Al₂O₃.

Improvements in and Relating to Catalysts
JOHNSON, MATTHEY & CO. LTD
British Patent 1,124,504
Catalysts of enhanced activity and comprising intimate homogeneous mixtures of the oxides of two or more Pt group metals (but excluding mixtures containing OsO₄ and mixtures of Pt and Rh oxides and Pt and Ru oxides) are prepared by the Adams method.

Preparation of Cyclohexanone
INVENTA A.G.
British Patent 1,125,199
Cyclohexanone is prepared by the hydrogenation of liquid C₆H₅OH as it trickles over a Pt group metal catalyst at up to 250°C in the presence of
H₂. The only catalyst specified in the examples is Pd/Al₂O₃.

**Hydrogenation of C₄-Hydrocarbons containing Butadiene and n-But-1-ene**

**FARBENFABRIKEN BAYER A.G.**

British Patent 1,126,848

Hydrogenation of butadiene mainly to the n-butene-2 isomer takes place in a descending stream over a fixed catalyst, especially Pd/Al₂O₃ or zeolite chips.

**Preparation of cis-Cyclodecene**

**UNIVERSAL OIL PRODUCTS CO.**

British Patent 1,127,702

The selective hydrogenation of trans, cis-1,5-cyclodecadiene to this compound at 0.100°C and 13.6-68 atm is catalysed by Pt/Al₂O₃.

**Preparation of Urethanes**

**AMERICAN CYANAMID CO.**

British Patent 1,127,988

A route avoiding the use of isocyanates in the production of urethanes consists of reacting an organic N compound, an organic hydroxyl compound and CO in the presence of a Lewis acid – noble metal catalyst. “Noble metal” is defined as one of the six Pt metals and the catalyst can be in the form of the metal or a salt of it. A typical catalyst consists of Pd/C and FeCl₃.

**Production of Vinyl Acetate**

**B.P. CHEMICALS (U.K.) LTD**

British Patent 1,128,993

A new catalyst for C₄H₈ oxidation in the presence of CH₂COOH is a Pt group metal deposited on TiO₂, an alkali, alkaline earth, Zn, Co, Ni or Fe silicate and/or their mixtures. A typical catalyst is PdCl₂ on TiO₂.

**Manufacture of β-Pinene**

**FARBWERKE HOECHST A.G.**

British Patent 1,129,622

The isomerisation of α-pinene to β-pinene is catalysed by a Pd/C catalyst in the presence of H₂ at 140-200°C.

**Production of Organic Esters**

**FARBENFABRIKEN BAYER A.G.**

British Patent 1,129,668

Anolefine with 3 or more C atoms or an alkyl benzene is reacted with O₂ and an organic acid having a higher molecular weight than CH₂COOH in the presence of Pt metal catalyst at elevated temperature. In 1,129,669 the Pd Pt metal catalyst is accompanied by the alkali or alkaline earth metal salt of an organic acid.

**Preparation of Hydroformylation Products**

**DEUTSCHE GOLD-UND SILBER-SCHEIDEANSTALT**

British Patent 1,129,809

Tetrahydrophthalic acid anhydride or esters are hydroformylated with H₂/CO in the presence of a Rh, Ir or Ru catalyst or a compound of these metals forming a carbonyl in the reaction conditions. A typical catalyst is Rh₂O₃.

**Dehydrogenation Process**

**MONSANTO CO.**

British Patent 1,131,983

Saturated hydrocarbons are dehydrogenated to olefines over a catalyst. The catalyst is prepared by impregnating Al₂O₃ with 0.02-5 wt% of a noble metal compound and then reducing the compound to the metal. Pt is the preferred metal.

**Catalyst Compositions**

**MONSANTO CO.**

British Patent 1,131,984

A dehydrogenation catalyst is produced from an Al₂O₃ support having a macropore volume of at least 0.05 cc/g with an alkali or alkaline earth compounds and noble metal compound to deposit at least 0.01 wt% alkali or alkaline earth metal and 0.02-5 wt% noble metal (especially Pd or Pt).

**Hydrotreating**

**Mobil Oil Corp.**

U.S. Patent 3,384,572

A high aromatic feedstock is cracked over a catalyst consisting of a hydrogenation component having an activity of 5-35 on a crystalline aluminosilicate, e.g. Pt on a rare earth aluminosilicate.

**Hydrocracking Catalyst**

**ESSO RESEARCH & ENGINEERING CO.**

U.S. Patent 3,385,781

Selective hydrocracking, especially of a pre-cracked feed, is carried out over a Pt catalyst supported on an aluminosilicate zeolite having pore openings of 6-15Å and containing less than 10 wt% alkali metal oxide.

**Hydrocarbon Hydrocracking**

**CHEVRON RESEARCH CO.**

U.S. Patent 3,385,782

Light 1-4C hydrocarbon gases are produced from heavy hydrocarbons by hydrocracking over a Group VIII metal catalyst on a crystalline aluminosilicate zeolite. A typical Group VIII metal is Pd.

**Alkyl Mononitrile Production**

**COMMERCIAL SOLVENTS CORP.**

U.S. Patent 3,385,880

Mononitriles are produced by the vapour phase reduction of nitroalkanes over Pt catalysts, e.g. Pt/Al₂O₃.

**Two-stage Steam Reforming**

**CATALYSTS AND CHEMICALS INC.**

U.S. Patent 3,388,074

A steam-gas hydrocarbon reforming catalyst
promoted with Pt or Pd supplies heat to the system while giving combustion and reforming in the first stage.

**Combustion Catalyst**

**Universal Oil Products Co.**

**U.S. Patent 3,388,677**

A catalyst for oxidising noxious gases consists of an Al₂O₃ porous carrier containing a Ca, Sr or Ba oxide uniformly distributed throughout it; 1-20 wt% of Pt is present as an embedded layer below the surface of the carrier.

**Hydroisomerisation Process**

**Texaco Inc.**

**U.S. Patent 3,389,191**

The hydroisomerisation of n-C₅H₁₀ with a chloride-activated Pt/Al₂O₃ is improved when the catalyst is spent, by treating it with H₂ under “non-flowing” conditions at 450-700°F.

**Hydroxylamine Production**

**Stamicarbon N.V.**

**U.S. Patent 3,390,954**

Hydroxylamine is produced by the hydrogenation of an alkyl nitrite in an acidic medium over a noble metal catalyst, especially Pd/C.

**Preparation of Cyclic Olefins**

**Stamicarbon N.V.**

**U.S. Patent 3,391,206**

These compounds, especially cyclohexene, are produced from aromatic compounds by hydrogenation in the presence of a lower alkanol solvent in the presence of a Ru catalyst, e.g. Ru black.

**Catalytic Dehydrogenation of Paraffins**

**Universal Oil Products Co.**

**U.S. Patent 3,391,218**

A 3-20 C paraffin is dehydrogenated in the presence of hydrogen and an aromatic hydrocarbon over a Group VIII noble metal catalyst, especially an As-attenuated supported Pt catalyst.

**Hydroisomerisation of Paraffins**

**Universal Oil Products Co.**

**U.S. Patent 3,391,220**

A 4-5 C paraffin is isomerised in the presence of a Pt metal-halogen supported catalyst, a halide promoter and a small amount of C₆H₁₄.

**Noble Metal-Alumina Catalysts**

**E. I. du Pont de Nemours & Co.**

**U.S. Patent 3,397,154**

Catalysts for ICE combustion consist of (a) oxides and mixed oxides of Fe, Co, Ni, V, Cr, Mn, Cu, Zn, Mo, Ag, Sn, Ba, Ce, W, Pb, or Bi, (b) Ru, Pt, Pd, Rh, Os or Ir metal and (c) an Al₂O₃ support having a crystalline cellular structure with walls of 0.3-200 mils thickness.

**trans-1,4-Diene Production**

**B. F. Goodrich Co.**

**U.S. Patent 3,398,209**

These dienes may be obtained by the reaction of a 4-6 C 1,3-diene and C₆H₄ in the presence of reduced Pd obtained from a Pt compound and an alkyl Al halide.

**Platinum Catalyst**

**Ste Francais Des Produits Pour Catalyse**

**French Patent 1,517,713**

Products of high octane number are obtained by reforming over a Pt/Cl/Al₂O₃ catalyst obtained in a specified way. Al₂O₃ is treated with aqueous HCl representing 0.5-5%, Cl₂, based on the Al₂O₃ and dried at 540-600°C until its IR spectra shows the absence of OH absorption bands. Pt is then incorporated in the usual way.

**Crotonaldehyde Hydrogenation**

**Johnson, Matthey & Co. Ltd**

**French Patent 1,519,568**

Butyraldehyde is produced by the hydrogenation of crotonaldehyde in a trickle column over a supported Pd catalyst, e.g. Pd/Al₂O₃.

**Suspended Platinum Hydrogenation Catalyst**

**Deutsche Gold- Und Silber-Scheideanstalt**

**German Patent 1,272,292**

Suspended, unsupported Pt metal catalysts in a liquid organic medium are recovered from the liquid by means of a carbon filter with a maximum pore width of 15µ. The catalyst particles have a diameter of 0.01-1µ.

**Production of Epoxy Organic Hydrogen Polysiloxanes**

**Farbenfabriken Bayer A.G.**

**German Patent 1,272,550**

Sill-group addition to an olefinic epoxide is catalysed by finely divided Pt or Pd, optionally in the presence of an inert solvent.

**Tetrachlorophthalodinitrile Production**

**Badische Anilin- & Soda-Fabrik A.G.**

**German Patent 1,277,838**

The reaction of phthalodinitrile with Cl₂ is catalysed by SiO₂ carrying 0.5-5 wt% Pd and/or Pt as well as 0.5-10 wt% of an alkali and/or alkaline earth phosphate and/or borate.

**HOMOGENEOUS CATALYSIS**

**New Organic Rhodium Complexes**

**Imperial Chemical Industries Ltd**

**British Patent 1,121,642**

New Rh catalysts, especially for chemical reactions, are new complexes of formula Rh(X)(YRR’R”)₂, where Y is P, As or Sb, X is an anionic element or group, especially Cl or NCS, and R, R’ and R” are hydrocarbon groups.
Preparation of Oxygen-containing Organic Compounds
LUMMUS CO.
British Patent 1,122,040
Acetals, ketals, cyclic ethers, aldehydes, ketones, etc., are produced by reacting unsaturated compounds with alcohols in the presence of Group VIII noble metal catalysts, especially in 0.001-0.1 M proportions. Usually PdCl₂ is used with CuCl₂.

Hydrogenolysis Process
HALCON INTERNATIONAL INC.
British Patent 1,122,702
Hydrogenolysis of an alpha-aralkyl alcohol to remove the OH group is catalysed at 50-120°C in the liquid phase by a Pt group metal catalyst, e.g. PdCl₂.

Production of Unsaturated Lactones Having a Five-membered Ring
BADISCH ANILIN- & SODA-FABRIK A.G.
British Patent 1,123,018
Lactones with side chains are obtained from an olefin, CO and (a) a Pd catalyst in an amount of 0.01-20% of the olefin and 20-150% based on the Pd, of a hydrogen halide or (b) 0.01-20% of a Pd halide, based on the olefin. PdI₂ is a suitable catalyst.

Decomposition of Formic Acid
IMPERIAL CHEMICAL INDUSTRIES LTD.
British Patent 1,126,022
HCOOH in admixture with another carboxylic acid is destroyed by contacting the mixture with a Pt group metal in the presence of a base. Ir, e.g. as H₂PtCl₆, is a suitable catalyst.

Catalysts
DOW CORNING CORP.
British Patent 1,127,675
A new catalyst for the SiH addition reaction is a reaction product of H₂PtCl₆ and at least one siloxane. These catalysts are more compatible with the reactants and less Pt is used.

Chemical Process
AEROJET-GENERAL CORP.
British Patent 1,128,103
N₂F₄ is produced by the oxidation of N,N-difluorocarbamate in the presence of an alkali metal complex salt and a higher metal halide, including Pt (IV), Ru (VIII) and Ir (VI) halides. For example, RuCl₃ may be used with KMnO₄.

Manufacture of Urethanes
IMPERIAL CHEMICAL INDUSTRIES LTD
British Patent 1,129,551
The production of urethanes by reacting hydroxyl compounds, CO and N compounds, such as azoxy compounds, is catalysed by transition metal complexes, especially phosphine complexes of Ir, Rh, Pt and Pd.

Preparation of Glyoxal
IMPERIAL CHEMICAL INDUSTRIES LTD
British Patent 1,130,760
C₂H₂ is oxidised to glyoxal by HNO₃ in aqueous medium in the presence of a catalytic mixture of a Li salt and Pd metal or a Pd compound, e.g. PdCl₂ and Li₂CO₃.

Polymerisation Process
UNIRoyal INC.
British Patent 1,131,160
The polymerisation of cyclic olefins is catalysed by an Ir trihalide, especially a complex of the trihalide with an olefin, e.g. Ir monochloride cyclooctene.

Platinum Catalyst for SiH-Olefin Addition Reactions
GENERAL ELECTRIC CORP. (NEW YORK)
U.S. Patent 3,385,876
A catalyst soluble in organic solvents is produced by reacting H₂PtCl₆ with Ti alkoxy, e.g. Ti(OBu)₄.

Catalyst for Cyclooctadiene Isomerisation
PHILLIPS PETROLEUM CO.
U.S. Patent 3,387,045
An unconjugated cyclooctadiene is isomerised to a conjugated diene over a complex catalyst formed from a nitrile and a Pt or Pd chloride or bromide, e.g. bis(benzonitrile)palladium dichloride.

Oxalic Ester Production
UNION OIL CO. OF CALIFORNIA
U.S. Patent 3,393,136
Oxalates are obtained when CO is reacted with a substantially anhydrous alcoholic medium containing 0.001-2 wt% of a Pt metal (e.g. PdCl₂) and 0.05-5 wt% of a soluble cupric or ferric redox salt.

Allyl Complexes of Palladium
MONSANTO CO.
U.S. Patent 3,397,214
Pd catalysts and additives are obtained by reacting bis-aryl cyanide-Pd(II) dihalides with tetraalkyl-allenes to give tetraalkyl-allyl palladium dihalides.

Diene Production
R. I. DU PONT DE NEMOURS & CO.
U.S. Patent 3,397,252
Dienes are produced from monoethylenically unsaturated compounds having a terminal halogen atom by their reaction with a stannous salt in the presence of a Pt group metal, e.g. IrCl₃, Na₂IrCl₄, PdCl₂ or (Et₄N)₄Sn₃P₅Cl₂₀.
Unsaturated Gamma-Lactone Production

BADISCHER ANILIN- & SODA-FABRIK A.G.

German Patent 1,276,029

These lactones may be produced from olefines and CO at elevated temperatures and pressures in the presence of PdCl₂/PdBr₂/PdI₂ optionally in the presence of excess halogen acid or Pd.

Production of Isopropenyl Carboxylic Esters

CONSORTIUM FUR ELEKTROCHEMISCHE INDUSTRIE

German Patent 1,277,246

The transesterification of isopropenyl acetate or propionate with another carboxylic acid is catalysed with 0.001-0.1 mol/mol acid of a Pd salt, e.g. a salt of one of the acids concerned or a double chloride.

FUEL CELLS

Method of Preparing Fuel Cell Catalysts

AMERICAN CYANAMID CO.

British Patent 1,123,957

Catalytic electrodes of enhanced activity are produced by reducing a noble metal compound, in the presence of an electroconductive filler, using a di- or tri-substituted silane containing a SiH group, dissolved in alcohol, so that the deposited noble metal has a crystallite size of 20-35Å. In an example graphite is suspended in C₆H₅OH and a mixture of H₂PtCl₆ and RhCl₃ dissolved in the alcohol. Diphenyl silane is added to reduce the salts to Pt and Rh.

Electrochemical Combustion of Methanol

ROBERT BOSCH G.m.b.h.

British Patent 1,130,733

The fuel cell catalyst is a Raney alloy of Ru which one or more Group VIII Pt metals and/or Au, e.g. a 4:3:3 alloy of Ru, Ir and Au.

Hydrogen Diffusion Anode for a Fuel Cell

LEESONA CORP.

U.S. Patent 3,393,098

A sandwich anode of three layers is used which comprises (in contact with the electrolyte) a non-porous H₂ diffusion membrane, a Group VIII metal black layer and a catalyst layer (in contact with the fuel). One combination that is proposed is Pd-Ag alloy/Pd black/Zn-Cu-Cr.

Porous Electrode Production

ESSO RESEARCH & ENGINEERING CO.

U.S. Patent 3,395,049

A mixture is formed from a finely divided halogenated hydrocarbon polymer, an active catalyst (including Group VIII metals and alloys) and a decomposable particulate filler. The mixture is shaped, the shaped product is heated to decompose the filler and further catalytic metal is deposited in the pores of the product. A catalyst may be Pt-Ir or Pt-Re deposited on C.

ELECTRICAL AND ELECTRONIC ENGINEERING

Cermet Resistance Element

BECKMAN INSTRUMENTS INC.

U.S. Patent 3,386,165

Noble metal conductors are attached to cermet resistors by applying a mixture of glass frit and noble metal particles to both items and firing them in contact. “Noble metal” is especially Ag, Pd, Pt, Rh and their alloys.

Metallic Coatings on Printed Circuit Boards

MATSUSHITA ELECTRIC INDUSTRIAL CO. LTD

U.S. Patent 3,391,455

A board base is dipped in a synthetic resin adhesive and then coated, by scattering, with a metal powder containing Cu, Fe, Co, Al, Ni, Au, Ag, Be, Pt, Pd, Rh or their alloys. The board is stoved after the powder has been pressed into the surface of the adhesive. The projecting particles of powder form a base for subsequent chemical (electroless) plating.

Production of a Tantalum Electrolytic Capacitor

SIEMENS A.G.

German Patent 1,275,207

A cathode for this type of capacitor is produced by applying a surface layer of Pt by means of a paint, burning off the organic portion and then firing the Pt.

TEMPERATURE MEASUREMENT

Electrical Resistance Thermometers

ROSEMOUNT ENGINEERING CO. LTD

British Patent 1,127,946

A strip of metal is formed into a roll with the adjacent layers insulated from one another, it is sliced in parallel planes normal to the axis of the roll to give spiral elements and these are attached to a ceramic disc. Pt foil may especially be treated in this way.

Noble Metal Thermometer Wires

DEUTSCHE GOLD- UND SILBERSCHEIDEANSTALT

German Patent 1,274,344

Noble metal, especially Pd wires are produced by making very fine powders by reduction at temperatures below 500°C, preferably below 350°C, to give a particle smaller than 0.06 mm. The powders are boiled in acidified water, dried at low temperature, compressed, sintered at 1300-1500°F for 2-8 hours and cold shaped to wire without an intermediate anneal. The wire is stress-relieving annealed at 1300-1500°C for 5-20 minutes.