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Communications should be addressed to
The Editor, Platinum Metals Review
The development of electrochemical routes in the industrial production of organic compounds is beginning to attract considerable interest. Already two large-scale processes are in operation, one producing adiponitrile from acrylonitrile, an intermediate step in the manufacture of Nylon 66, and the other producing lead tetra-ethyl anti-knock compounds. This article reviews the basic electrochemistry involved in this type of synthesis and outlines the great possibilities being opened up by advances in technique, in reactor design and in the development of new types of electrode structures in which platinum and its associated metals will play an important part.

In recent years research in the field of organic electrosynthesis has received considerable stimulation from the forecast that, with the advent of nuclear power, electricity will become cheaper compared to chemical oxidants and reductants. Furthermore, the reasons for the failure of earlier workers to achieve selective reactions have become apparent and by controlling the electrode potential, the solution conditions (solvent, pH, concentration of species, etc.) and by choice of suitable electrode materials, some measure of selectivity is now possible. It therefore seems likely that electrochemical techniques will have an increasing role in preparative organic chemistry, both in industry and in the laboratory as a standard method for oxidations and reductions as well as other reactions such as substitutions and cyclisations.

In order to explain the interest in electrochemistry it is convenient to contrast electrochemical reactions with homogeneous or heterogeneous reductions and oxidations using hydrogen and air or oxygen. The free energy change, \( \Delta G^\circ \), of these processes is equivalent to a cell potential, \( E^\circ \), given by \( \Delta G = -nFE^\circ \).

By referring to a scale of free energies or electrode potentials, Figure 1, it is evident that such spontaneous reactions are only possible within the potential range limited by the reduction of oxygen or the oxidation of hydrogen. This driving force only amounts to approximately 0.5 eV or 10 kcals/mole. By contrast, it is possible to carry out electrochemical reactions at potentials between +3.5 V and -2.5 V even in aqueous solution, if suitable electrolytes and electrodes are chosen. Thus, the driving force for an electrode process is of the order of 3eV or 60 kcals/mole. Electrochemical reactions therefore enable one to introduce considerable energy into molecules at low temperature and the order of magnitude of this energy is, in fact, that required to break chemical bonds. Figure 2 compares the energy ranges in which different methods of activating molecules will be effective.

Clearly, in view of the energy which may be introduced, it is not surprising that many "high energy" chemicals that are used as oxidants and reductants in synthesis are prepared electrochemically (e.g. sodium, manganese dioxide, chlorine) and there are obvious advantages in avoiding such intermediates.
The intermediates formed in electrode processes are indicated in Figure 1 and are entirely consistent with the large driving force of such reactions. While the figure is not drawn to scale, it nevertheless shows the approximate points at which radical ions, radicals, carbanions and carbonium ions would be expected to form. Thus it can be seen that by controlling the electrode potential a measure of selectivity may be achieved. The classical example of this idea is the reduction of nitrobenzene where phenylhydroxylamine may be produced at low negative potentials and aniline at more negative potentials (1).

A further example is the oxidation of 9, 10-...
diphenylanthracene at platinum electrodes in aprotic solvents. At low potentials this leads to the radical cation and at high potentials to the dication (2).

\[
\text{\begin{align*}
\text{\text{C}_{2}H_{8}} & \rightarrow \text{\text{C}_{2}H_{6}} \\
\text{\text{C}_{2}H_{8}} & \rightarrow \text{\text{C}_{2}H_{6}}
\end{align*}}
\]

It is also possible to exert a measure of control over electrode reactions by maintaining the electrode at a series of potentials for controlled durations. In this way it is possible, for example, to switch successively from oxidation to reduction and thus to change the products of the reaction (3).

\[
\text{\begin{align*}
\text{R} & \text{---} \text{R}^{+} \text{I}^{2+} \text{e}^{-} \\
\text{RCOO} & \text{---} \text{R}^{+} \text{CO}_{2} + 2e^{-} \\
\text{RH} & \text{---} \text{R}^{+} \text{H}^{+} + 2e^{-}
\end{align*}}
\]

Carbanions and dianions are generated in the reduction of alkyl halides, aromatic hydrocarbons (9), quinones (10), nitrocompounds (11), and activated olefins (12), e.g.

\[
\text{\begin{align*}
\text{R} & \text{---} \text{R}^{+} \text{I}^{2+} \text{e}^{-} \\
\text{OH} & \text{---} \text{OH}^{+} \text{e}^{-} \\
\text{CH}_{2} & \text{---} \text{CH}^{-} \text{CN} + 2e^{-} \\
\end{align*}}
\]

A further important application of pulse electrolysis is likely to be the control of electrode activity by control of the electrode history. For example, in the use of platinum metal electrodes for the oxidation of hydrocarbons in non-aqueous solutions the electrode activity rapidly falls with time. In view of the wide range in potential over which the inert metals may be used the polarisation can be reversed for short controlled periods of time and the electrode reactivated cathodically. In this way controlled successful oxidation of hydrocarbons may be achieved.

Intermediates of the kind shown in Figure 1 will be formed in many electrode reactions. For example, carbonium ions will be generated at platinum electrodes during the oxidations of alkyl halides (4), carboxylic acids (5), hydrocarbons (6), and amines (7).

\[
\begin{align*}
\text{RI} & \rightarrow \text{R}^{+} \text{I}^{2+} + 2e^{-} \\
\text{RCOO} & \rightarrow \text{R}^{+} \text{CO}_{2} + 2e^{-} \\
\text{RH} & \rightarrow \text{R}^{+} \text{H}^{+} + 2e^{-}
\end{align*}
\]

Radicals are also frequently produced as in the oxidation of carboxylic acids (13) and of carbanions (14, 15), and the reduction of some alkyl halides (8), ketones (13), quinones (17) and tetra-alkylammonium salts (18), e.g.

\[
\begin{align*}
\text{RCOO} & \rightarrow \text{R}^{+} \text{CO}_{2} + e^{-} \\
\text{CH} & \text{(COOEt)}_{2} \rightarrow \text{CH} & \text{(COOEt)}_{2} + e^{-} \\
\text{Al(CH}_{2} & \text{)}_{3} & \rightarrow \text{Al(CH}_{2} & \text{)}_{3} + \text{CH}_{2} + e^{-}
\end{align*}
\]

\[
\begin{align*}
\text{\begin{align*}
\text{O} & \text{+ H}^{+} + e^{-} \rightarrow \text{OH} \\
\text{O} & \text{+ H}^{+} + e^{-} \rightarrow \text{OH} \\
\text{RI} + e^{-} & \rightarrow \text{R}^{+} + \text{I}^{-}
\end{align*}}
\]

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In order to study these highly reactive intermediates, it is clearly necessary to use unreactive solvents and electrode materials. Indeed, it is the advent of aprotic polar solvents in which the intermediates have an appreciable half life that has allowed the characterisation of many intermediates by electrochemical and spectroscopic methods (in particular ESR). In many other cases the nature of the intermediates has been inferred from the products of the reaction and by analogy to known reaction mechanisms.

**Reactions at Platinum Electrodes**

The generation of the reactive species naturally also demands inert electrode substrates and platinum metals have been widely used in aprotic solvents over the range +3.0 to −3.0 V. On the other hand, in water or other protic solvents the use of platinum metals has been confined to anodic reactions because the decomposition of solvent to form hydrogen is strongly favoured. However, at the present time a considerable research effort is being devoted to investigations of the oxidation and substitution of organic compounds and for these processes the use of inert platinum electrodes is of key importance. Indeed, most of the oxidative reactions listed in this article have been carried out on platinum metal electrodes.

The formation of the intermediates has been written as if the electrode surface is not directly involved in the reaction step. In many cases, however, the reactive species will be adsorbed on the surface and the catalytic role of the electrode will be of key importance. For example, the reductive hydrogenation of olefines is dependent on the use of platinum blacks (19) as is the dissociative adsorption of saturated hydrocarbons or methanol as an essential step in the overall reactions on fuel cell electrodes (20). Again the coupling of radicals produced from carboxylic acids in the Kolbe or Brown-Walker reaction is dependent on the electrode surface, being favoured by platinum in aqueous solutions (13).

The intermediates which are formed react in similar ways to those observed when they are generated in homogeneous processes, although their reactions will often be modified by the adsorption on the electrode. In typical reactions, radicals will dimerise (21),

$$2 \text{EtOOC (CH}_2)_4 \text{COO}^- \rightarrow 2\text{CO}_2 + 2 \text{EtOOC (CH}_2)_4 \text{COOEt}$$

attack double bonds (22),

$$\text{EtOOCCOO}^- \rightarrow \text{CO}_2 + \text{COOEt} \quad \text{butadiene} \rightarrow$$

$$\text{EtOOC} \cdot \text{CH}_2 \cdot \text{CH} = \text{CH} \cdot \text{CH}_2 \rightarrow \text{dimer}$$

or react with certain electrode metals (23),

$$\text{R Mg I} \rightarrow \text{MgI}^+ + \text{R}^+ \rightarrow \text{PbR}_4$$

Carbanions or dianions formed from aromatic hydrocarbons will protonate to form dihydroaromatic compounds (9) or undergo other typical coupling reactions such as that with carbon dioxide (17).

$$\text{H}^+ + \text{CO}_2 \rightarrow \text{HCOO}^-$$

Similarly, the dianions formed from activated olefines will react with unsaturated compounds as in

$$\text{CH}_2 = \text{CH} \cdot \text{CN} + \text{CH}_2 = \text{CHCN} + 2 \text{H}^+ \rightarrow \text{NC} = (\text{CH}_2)_4 \cdot \text{CN}$$

and intramolecular reactions leading to cyclisation are also possible (24),

$$\text{CH}_2 = \text{CH} \cdot \text{CO} \cdot \text{Et} + 2 \text{e} + 2 \text{H}^+ \rightarrow \text{CH}_2 \cdot \text{COOEt}$$

$$\text{CH}_2 \cdot \text{COOEt}$$

Carbonium ions are naturally highly reactive and usually attack the solvent or deprotonate to form olefines. For example, in acetonitrile amides are formed (4)

$$\text{R}^+ + \text{CH}_3 \cdot \text{CN} \rightarrow \text{CH}_3 \cdot \text{C}^- \cdot \text{N}^- \cdot \text{R} + \text{H}_2\text{O} \rightarrow \text{CH}_3 \cdot \text{CO} \cdot \text{NHR}$$

and in methanol ethers are the products (25)
as shown by the reaction

\[
\text{MeO} \quad \text{OMe} \quad \text{OMe} \quad \text{OMe} \quad \text{OMe} \quad \text{OMe} \quad \text{OMe} \quad \text{OMe} \quad \text{OMe} \quad \text{OMe} \quad \text{OMe} \quad \text{OMe} \quad \text{OMe} \quad \text{OMe} \quad \text{OMe} \quad \text{OMe} \quad \text{OMe} \quad \text{OMe} \quad \text{OMe} \quad \text{OMe} \quad \text{OMe} \quad \text{OMe} \quad \text{OMe}
\]

In other cases carbonium ions show their typical rearrangements as in the oxidation of neopentyl iodide (4), ring formation (26), e.g.

\[
\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-COO}^- + 2e^- \rightarrow \text{CO}_2 + \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2^+ + \text{H}^+ \text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-H}\]

ring expansion (27), or ring contraction (28), e.g.

\[
\text{CH}_3\text{COO}^- \rightarrow \text{OH}^- \quad \text{OH}^- \quad \text{CH}_3\text{OH} \quad \text{CH}_3\text{OH}^+ \quad \text{OH}^-
\]

The substitution, for example cyanation or acetoxylation, of aromatic compounds also takes place via cationic intermediates since the reaction will only take place at potentials at which the hydrocarbons are oxidised even if the substituting anion is oxidised at lower potentials (29).

**Industrial Processes in Operation**

It will be seen that many of these reactions lead to industrially useful products, for example, diterminal substituted compounds. Indeed, the formation of lead tetra-alkyl and of adiponitrile have been made the basis of new commercial synthetic processes by Nalco and Monsanto respectively.

Figure 1 also indicates the potential regions in which a number of inorganic intermediates are generated. For example, Co^{III} may be generated in situ at an electrode and allowed to react with an organic substrate with re-

 generation of Co^{II}. In this way reaction occurs within a zone adjacent to the electrode and the actual electrode process

\[
\text{Co}^{II} \rightarrow \text{Co}^{III} + e
\]

serves to “drive” the homogeneous catalytic reaction (30). Other examples of such reactions are the oxidation of propylene by Hg^{II}

\[
\text{CH}_3\text{-CH} \rightarrow \text{CH}_2 + 4\text{Hg}^{2+} + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{-CH} \text{CHO} + 4\text{H}^+ + 2\text{Hg}^{2+}
\]

where the mercuric ion is regenerated electrochemically (31). These indirect reactions which involve highly oxidising conditions can again only be achieved by the use of inert platinum metal electrodes. The oxidation of propylene to propylene oxide by electrochemically generated hypochlorite (32) and the reaction of olefines with carbon monoxide and methanol in the presence of platinum carbonyls to give methyl esters of \(\alpha - \beta\) unsaturated acids (33)

\[
\text{C}_6\text{H}_5\text{CR} \rightarrow \text{CH}_2 + \text{CO} \rightarrow \text{OMe} \rightarrow \text{C}_6\text{H}_5\text{CR} \rightarrow \text{CHCOOMe}
\]

are further interesting examples of indirect processes.

Some of the most extreme oxidations carried out at present are the perfluorinations of aliphatic hydrocarbons in anhydrous hydrogen fluoride. It is not clear, however, whether these proceed via the generation of oxidised aliphatic species or of fluorine (34, 35).

Figure 1 also shows that highly reducing species may be generated and the ultimate...
limit is, in fact, the formation of solvated electrons in suitable solvents such as ammonia, amines, or hexamethyl phosphoramidie (36, 37). The electrons will react with aromatic hydrocarbons and give di- or tetrahydro derivatives.

$$\text{HH} + 2e^{-}_{\text{solv}} + 2H^{+} \rightarrow \text{HH}$$

It may be noted that benzene cannot be directly reduced at electrodes.

**Importance for Large-scale Synthesis**

It will be apparent that many of the intermediates which have been described are of considerable importance for large-scale synthesis. A major aim of these synthetic procedures in the coming years will undoubtedly be the build-up of complex molecules from relatively simple starting materials as might be achieved by the reaction of radicals with olefines.

Linked to this aim will be the activation of unreactive substrates such as carbon dioxide and saturated hydrocarbons by utilising the high driving force of electrochemical processes. Of equal importance to the development of new synthetic routes will be the use of electrochemical procedures to increase the selectivity of existing reactions and to reduce the number of steps in a synthesis as well as simplifying the work-up by avoiding the introduction of reagents which must subsequently be removed.

**Development of Reactors and Electrodes**

A further major development is likely to be the construction of new electrochemical reactors which will permit an easier scale-up. In recent years the bulk of the effort has been devoted to the development of highly active catalytic electrodes for fuel cells, the aim being the complete oxidation of hydrocarbons to carbon dioxide. It is likely that further research will lead to structures capable of giving, for example, controlled partial oxidations but utilising many of the advantages inherent in the design of the porous fuel cell electrodes.

The development of these and other new types of electrode structures such as fluidised beds and packed beds and the development of membranes suitable for separating electrode compartments will undoubtedly lead to the construction of low cost reactors having a high throughput. The operation of many of these electrodes will be dependent on the use of finely divided platinum metals imbedded in the structure to give a high surface area for the surface reactions at low cost. There is every prospect, therefore, that the chemical engineering technology to make use of the chemical advantages of electrosynthetic procedures on the industrial scale will be available.

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Measurement of Electrodeposit Thickness

The use of the beta back-scatter technique for the non-destructive measurement of the thickness of electrodeposited coatings and the basic design of a commercial instrument, the Beta 750, were described some two years ago (Platinum Metals Rev., 1967, 11, 13). The success of this equipment has now led to the introduction of an extended range of instruments to meet specialised needs and to satisfy the increasingly stringent demands for consistency and accuracy, particularly where electrodeposits such as rhodium, palladium and gold are involved.

The Beta 751 provides a four-figure digital read out of the beta count over a pre-selected time, this figure being related to deposit thickness by reference to a calibration graph. Variations of this equipment provide the facility to pre-set a minimum thickness or a range of thicknesses, pass or fail lights being activated by the count figure obtained.

A direct reading instrument, the Beta 752, incorporates a meter reading of deposit thickness in micro-inches, based upon calibrated scales for specific combinations of deposit and basis metal. This instrument is particularly suitable where large numbers of tests must be carried out and maximum accuracy is not a vital consideration.

The units are produced by Panax Equipment Limited and marketed by Johnson Matthey.

The Beta 752 unit is fitted with a calibrated scale for the direct reading of electrodeposit thickness. Zero and full-scale deflection points are set by adjusting the two potentiometers.
Electron Concentration as a Guide to Alloying Behaviour

ENGEL-BREWER AND THE PLATINUM METALS

By A. S. Darling, Ph.D., M.I.Mech.E.
Research Laboratories, Johnson Matthey & Co Limited

Some unexpected reactions in platinum metal alloys have been successfully predicted by the Engel-Brewer relationships. Although the basic principles involved are still uncertain, interesting possibilities emerge and several possible applications for the reactions suggested by this theory are proposed.

The practical metallurgist is rarely able to make use of theoretical predictions and much of the interest aroused by the Engel-Brewer correlation stemmed from its claims of direct utility in the design of transition metal alloys. Although Hume-Rothery (1) has demonstrated the unsound foundations of some parts of the theory most of the failures he discussed were associated with the metallurgy of copper, silver and gold. In the transition element field considerable successes have been achieved and one is encouraged to consider the practical implications of these ideas and how these might lead to the development of new commercially viable materials.

Pure Metals

In his early attempts (2) to correlate the stable crystal structure of metals with the electron configuration of free atoms Engel predicted that bond strength was determined almost completely by the number of d electrons participating. This conclusion has since been qualified by Brewer (3, 4) who now suggests that over the main range of the transition elements the bonding energy of the s and p electrons is greater than that of the d electrons. The type of crystal structure adopted is still, however, regarded as being determined by the s and p electrons alone, the b.c.c., c.p.h., and f.c.c. structures correlating to 1, 2 and 3 (s+p) electrons per atom.

Over the three transition series the bonding effectiveness of a d electron falls to a minimum when the number of unpaired d electrons arrives at a maximum of 5 per atom. The magnitude of the d bond strength increases with progress from the first to the third long period.

The stability of the crystal structures as predicted from Brewer’s calculations is determined by the difference between the total bonding energy and the original promotional energy assumed. Tungsten offers a good illustration of the methods of calculation adopted. The ground state of tungsten is \(d^4\) \(s^2\), and the two s electrons would appear to indicate a close-packed hexagonal crystal structure. The promotional energy associated with the change from the \(d^5\) \(s^2\) configuration is only 8 kcal/mole, however. Since this slight expenditure of energy releases six electrons for bonding the most stable structure, associated with the single s electron is of course b.c.c.

Such arguments are used to explain the change from b.c.c. to c.p.h. structure on passing from tungsten and molybdenum to elements of higher atomic number. If the additional electrons entered the d orbital, pairing would occur, the number of electrons...
available for bonding would decrease, and the stability of the structure would fall catastrophically. Such a fall is avoided by a change in electron configuration. Thus, if the configuration \( d^6 s \) is changed to \( d^5 sp \), all five \( d \)-orbitals are made available for bonding and the close-packed hexagonal structure is thereby stabilised. In the neighbourhood of tungsten the promotional energies associated with such changes in configuration are claimed to be negligible compared to the improved bonding energies obtained. Movements to the right of osmium and ruthenium involve a change from the \( d^{6.5} sp \) configuration to that of \( d^6 s p^3 \), which by placing three electrons outside the \( d \) shell makes more electrons available for bonding and stabilises the f.c.c. structure.

Increasing refinement in Brewer's treatment has shown that such integral configurations can only be approximate, and the optimum configurations required for the most stable structures are non-integral. Thus the optimum configuration for ruthenium is \( d^{6.3} s^{0.7} \) rather than the \( d^6 s p \) configuration originally proposed.

The promotional energies involved in such configuration changes increase as the right-hand side of the three transition series are approached and this increase is used to explain the decrease in melting-point and increase in vapour pressure with increasing atomic weight. The assumption that melting-points and vapour pressures provide a true index of crystalline stability is, of course, very dubious, and the errors involved in an attempt to predict the melting-point of gallium from its vapour pressure would be considerable.

Osmium and iridium have the highest elastic moduli of any of the metals. They also have the lowest compressibilities and it does not seem likely therefore that bonding processes deteriorate rapidly as soon as tungsten is left behind.

The main weakness of the configurational adjustments referred to above has been well exposed by Hume-Rothery (1). Thus the simple electronic concentrations are translated into configurations which satisfy the Engel correlation. Conclusions based on these translated values could in most instances have been reached on the basis of simple electronic concentrations alone. Such correlations were considered by Robins (5) who in 1959 suggested that a tendency exists for the number of bonding electrons per atom to equal half the co-ordination number. This tendency explains why tungsten and molybdenum, each presumed to have six valency electrons and an effective co-ordination number of 12 have the highest melting-points in their respective series. The change in crystal structure on passing from tungsten to rhenium helps to maintain this two-to-one ratio and thus stabilises the hexagonal structure.

Alloys

In the prediction of alloy-phase equilibrium Brewer (4) made considerable deviations from the integral electron concentration values used for pure metals. In the copper, silver and gold alloys the treatment was largely unsuccessful and it has not been explained, for example, why the composition ranges of \( \alpha \) and \( \beta \) brass overlap.

The treatment of transition metal alloys has been rather more successful. The \((s+p)\) electron concentration ranges associated with the b.c.c., c.p.h., f.c.c. phases are respectively 1.0–1.5, 1.7–2.12 and 2.5–3. Taking the basic electron configuration of molybdenum and tungsten as \( (4d^5) (5s) \) Hume-Rothery (1) has used these concentration ranges to calculate the solubility limits shown in the table in these two metals.

Reasonable agreement has been obtained particularly when the solvent and solute are close together in the Periodic Table. The effect of temperature upon solubility does not clearly emerge from the various publications involved. This is obviously of great importance, and Selman (6) has recently shown that the solubility of platinum in molybdenum increases from approximately 2 atomic per
Molybdenum cent at 1400°C to more than 10 atomic per cent at 1700°C. Although Brewer states that “the Engel correlations make thermodynamic predictions and must therefore be valid for the entire temperature range” (7), it would be interesting to see a practical application of this philosophy to the calculation of a temperature solubility curve.

Stable Platinum Metal Compounds

An important feature of the Engel-Brewer theory is the prediction that metals from opposite ends of the second and third transition series should react strongly with each other to form compounds of high stability. This subject has been briefly referred to in a previous article (8).

By reacting platinum with stable carbides Brewer (8) formed an estimate of the free energies of formation of these compounds. Thus, platinum reacted with zirconium carbide to produce the hexagonal compound ZrPt₃. Since zirconium carbide has a free energy of formation of −47 kcal/mole, the free energy of formation of ZrPt₃ was presumed to be higher. It is difficult, however, to pursue such arguments to their logical conclusion. It is known that all the carbides can be dissociated by heating in contact with the platinum metals and in no instance does the formation of a compound appear to be necessary. If an excess of platinum is employed the end product is a dilute solution of the transition element in platinum, and the main function of the platinum is to keep the activity of the carbide-forming element at a low level. Molybdenum and tungsten carbide are readily dissociated in this way although there should, according to the Brewer-Engel correlation be no driving force for this reaction. Molybdenum carbide is by no means as stable as zirconium carbide. Both these compounds are, however, far less stable than alumina, which has been shown (9) to be readily dissociated under unoxidising conditions in the presence of platinum, which takes the aluminium into solid solution at temperatures above 1400°C.

Accurate thermodynamic measurements on zirconium-platinum alloys are obviously required. The electron negativities of the two metals are very different and a fairly high heat of reaction would be suggested by this fact alone (1). The transference of charge in such a reaction would, however, be in the opposite direction to that proposed by Brewer.

Some Practical Applications

Whatever the mechanism of the reactions involved it seems that practical attention might well be devoted to the varied lines of thought suggested by the theory. Exothermic

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solute</th>
<th>Solubility Limits in Atomic Per Cent</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Predicted by Brewer</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Tc</td>
<td>50</td>
</tr>
<tr>
<td></td>
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fuses are one possibility. Here the hafnium wire would be sheathed with an appropriate thickness of palladium. Such a fuse wire would withstand corrosive conditions for long periods without failure, but would, if overheated disrupt explosively and provide instantaneous protection for the circuit.

Applications might also exist in the field of age-hardening and dispersion-strengthened alloys. Thus small quantities of yttrium and palladium, dissolved stoichiometrically in an inert metal matrix should react upon suitable heat treatment to produce a finely divided compound of considerable strengthening power (10).

Interesting possibilities can be discerned in the sintered carbide field. Cobalt, the normal cement used for the liquid-phase bonding of carbides is unfortunately not very resistant to oxidation at high temperatures and this restricts the high temperature applications of such materials. Palladium or a palladium-based alloy would be more resistant to oxidation and would also react chemically with the carbide in the way described by Brewer. By suitably proportioning the amount of palladium added to the carbide mixture improved oxidation resistance might be achieved with stronger chemical bonding between the cement and the carbide. Appreciable improvements might result even if the palladium replaced only a small proportion of the cobalt binder (11).

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A Rhodium-Platinum Probe for Flame Velocity Measurement

A probe for velocity vector measurements in flames consists of a spherical tip with one pressure point on the axis and four others spaced equally around it at 40° to the central point. Pressure differences between opposite pairs of these holes, when referred to the pressure at the central point, give gas flow direction and velocity. Stainless steel probes are suitable for cooled airflows or, when water-cooled, for large industrial furnaces, but in the relatively much smaller dimensions of gas turbine combustion systems the application of this technique depends on devising a method permitting the construction of compact probes in a manner suitable for use at kerosene-air flame temperatures.

A technique of construction has recently been developed at the National Gas Turbine Establishment in which both the spherical probe head and the five lengths of hypodermic tubing are fabricated in 20 per cent rhodium-platinum, the whole then being brazed to a stainless steel water-cooled probe body. The stainless steel hypodermic extension tubes and water jacket then pass through a cylindrical brass block, carrying a 360° scale to indicate angle of rotation, to a cluster of unions. This assembly can be used in flame temperatures up to 1800°C.

A complete water-cooled probe unit in which the rhodium-platinum head is nickel-brazed to the stainless steel probe body.
Ruthenium-Platinum Oxide Catalysts for Hydrogenation Reactions

A CRITICAL COMPARISON OF PUBLISHED RESULTS

By G. C. Bond, D.Sc., F.R.I.C., and Dennis E. Webster, Ph.D.

Research Laboratories, Johnson Matthey & Co Limited

Since the publication of earlier papers from the Johnson Matthey Research Laboratories on the catalytic properties of mixed platinum group metal catalysts, two other groups have published their findings. These are in certain respects in disagreement with each other and with the original work and results relating to the ruthenium-platinum system are critically discussed in this paper.

A technique for the preparation of intimate homogeneous binary mixtures of oxides of the platinum group metals by a modification of the Adams method has been described in a previous publication (1). These mixed oxides are in the main easily reduced by hydrogen under ambient conditions to yield what we believe to be finely divided alloys of the two metals, and many of the catalysts produced in this way are much more active in a variety of hydrogenations than either component oxide alone. Our previous publications describe results obtained with ruthenium-platinum catalysts (1) and a number of other mixed metals (2).

Two other groups of workers have since reported their own work on these systems. The results published (3) by D. V. Sokol'skii and his associates at Alma Ata for the ruthenium-platinum system are in broad agreement with ours in the composition range which we originally covered, but they reported a further substantial activity maximum (at about 90 per cent ruthenium) which we had not observed. The work of P. N. Rylander and his colleagues (4) of Engelhard Industries on this system is in complete and utter disagreement with both ours and Sokol'skii's, but because the conditions have not been identical (and in particular the other groups have used other solvents) we decided to check their observations. The purpose of this paper is to give a brief summary of our further work on the ruthenium-platinum system and to compare it critically with the other published results.

Surface Areas

It is unlikely that the reported differences in catalytic properties are significantly due to differences in the surface areas of the starting oxides. Values of surface areas given by the Engelhard workers (4) (their method is not described) are in approximate agreement with ours obtained using low temperature nitrogen adsorption with a Perkin-Elmer-Shell Sorptometer (e.g. about 100 m² g⁻¹ for PtO₂); Sokol'skii's values (3), obtained by low temperature adsorption of air, are lower by a factor of about 2.5, but all groups agree there is a tendency for the area of the oxide to fall with increasing ruthenium content. In our hands the surface area for a given composition is not closely reproducible from one preparation to another, the variation being much greater than is the case with catalytic activity. We therefore consider it inappropriate to quote specific activities using areas of the oxides.

Incidentally neither Rylander nor Sokol'skii appear to have assayed their mixed oxides.
We find a substantial loss of ruthenium during the preparation, presumably as the volatile tetroxide. The figures given in the table are representative of our findings.

<table>
<thead>
<tr>
<th>Nominal and Actual Ruthenium Contents (wt%) of Mixed Ruthenium-Platinum Oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nominal</strong></td>
</tr>
<tr>
<td>2.5</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>50</td>
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</table>

We find a substantial loss of ruthenium during the preparation, presumably as the volatile tetroxide. The figures given in the table are representative of our findings.

**Reduction of Aromatic Nitro-compounds**

In our earlier publications (1, 2), we demonstrated the existence of a very sharp activity maximum for the reduction of nitrobenzene in methanol at 25 atomic per cent ruthenium: a similar but less pronounced maximum was shown with o-nitroaniline. We have confirmed the generality of the maximum in this position by obtaining results for 2,4-dinitrotoluene in acetone/isopropanol (see Figure 1): the rate at the maximum is about three times less than for nitrobenzene. Sokol'skii and his associates (3) report results for the reduction of o-nitrophenol in 96 per cent ethanol. These are also shown in Figure 1, as are our own rates for the reduction of this compound in methanolic solution. It is clear that the reaction is enormously faster in methanol than in 96 per cent ethanol (by a factor of about 30): it is however known that water can be a powerful catalyst poison in the reduction of aromatic nitro-compounds. However, Sokol'skii observes a maximum at about 35 atomic per cent ruthenium, and, significantly, a second smaller maximum at about 80 atomic per cent ruthenium. As our catalysts are inactive when containing more than 85 atomic per cent ruthenium because they are not reduced under our experimental conditions, we infer that Sokol'skii's catalysts are pre-reduced in some manner, although his publications give no details.

Now the Russian authors also report that the second maximum in the reduction of o-nitrophenol is much more pronounced when the solvent is aqueous decinormal KOH, i.e., when the reactant is the o-nitrophenoxide ion. In order to check this and to obtain further information on the effect of pre-reduction of the catalyst, we have studied the reduction of o-nitrophenol in this solvent in the normal manner and also using catalyst pre-reduced by shaking in hydrogen under ambient conditions before adding the reactant. The results, together with Sokol'skii's, are shown in Figure 2. With catalysts not pre-

![Fig. 1 Hydrogenation of aromatic nitro-compounds in the presence of ruthenium-platinum catalysts.](image)
reduced we find a broad maximum between 10 and 50 atomic per cent ruthenium with a slight dip which may or may not be genuine. Pre-reduction lowers the activity slightly in this region but certainly causes ruthenium-rich catalysts to be active, although our second maximum is far less marked than is Sokol’skii’s. As the solvents are identical in this case, differences can only be caused by differences in catalyst preparation or experimental procedure.

We turn now to examine the results of the Engelhard workers. Their results for the reduction of nitrobenzene in glacial acetic acid are so much at variance with ours obtained using methanol as solvent, that we decided to repeat our work using their solvent. These results are shown in Figure 3. Unfortunately it is not possible to make a direct comparison of rates even for PtO₂ as the Engelhard papers (4), do not mention the weight of catalyst used: however it would appear from our results that theirs refer to 10 mg of catalyst and the line through their points is shown in Figure 3 based on this assumption. The disagreement, which is profound and inexplicable, is not commented on by Rylander. Glacial acetic acid is anyhow an unsatisfactory solvent, the maximum rate of nitrobenzene hydrogenation in it being some three times less than when methanol is the solvent (see also Figure 3).

It is abundantly clear that rates of hydrogenation with this catalyst are very much
dependent on the kind of solvent used, but other factors must be operating: their nature will only be revealed by further work.

**Other Reactions**

Sokol’skii and his associates report (3) for the hydrogenation of olefins (cyclohexene and 1-heptene) using ruthenium-platinum catalysts that maximum rates occur at 45 and 88 atomic per cent ruthenium. We originally showed the existence of a maximum rate for the hydrogenation of maleic acid in methanol at about 30 atomic per cent ruthenium and have since found a maximum at about the same concentration in glacial acetic acid.

One of the interesting features of our earlier work was that, with acetylenic substances such as methylbutynol, maximum rates occurred with very low concentrations of ruthenium: the Engelhard group report (4) a similar observation (almost the only point of agreement between us) but their maximum rate is only about 20 per cent greater than for PtO₂, whereas we found a maximum rate about 2.2 times greater.

**Other Catalysts**

Comparison of our results with those of the Engelhard group for rhodium-platinum catalysts again demonstrates the existence of a large solvent effect. With this system glacial acetic acid is a much better solvent than methanol for nitrobenzene hydrogenation: with methanol we find rates which vary somewhat erratically with catalyst composition, the maximum rate (at 39 atomic per cent rhodium) being only about 50 per cent greater than for PtO₂. However, with glacial acetic acid as solvent the maximum rate occurs at the same composition but is four times greater than for PtO₂. Rylander reports the factor to be about 2.5. Again we cannot compare absolute rates for the reasons given.

**Conclusions**

Substantial and inexplicable differences are shown between the results of the various groups which have worked on mixed platinum group metal catalysts. Solvent effects are partly responsible, but the precise method of preparing the mixed oxides and differences in experimental procedure are other possible factors which may account for the discrepancies.

Ruthenium-platinum oxide catalysts, their preparation and use, are covered by British Patent Nos 1,099,406 and 1,016,058 and U.S. Patent No. 3,305,402, and are the subject of pending patent applications in a number of other countries.

**References**

1 G. C. Bond and D. E. Webster, *Platinum Metals Rev.*, 1965, 9, 12
2 G. C. Bond and D. E. Webster, *Platinum Metals Rev.*, 1966, 16, 10

**Complexes of Substituted Olefins with Salts of the Platinum Metals**

One of the small but intriguing parts of organometallic chemistry concerns the complexes formed between salts of the transition metals—more particularly those of the platinum metals—and substituted olefins. The discovery of this class of compound has not only advanced our knowledge of chemistry and of chemical bonding, but has stimulated our understanding of catalytic processes both in solution and at solid surfaces. A recent review by Richard Jones of the ICI Petrochemical and Polymer Laboratory (*Chem. Rev.*, 1968, 68, 785) provides a thorough survey of this field. Among the type of substituents discussed are halogens, where perfluoro-olefins behave in some respects quite differently from simple olefins, and amine and cyanide groups, both of which may also chelate to the central metal atom. Complexes of this type provide an increased range of stabilities by comparison with their unsubstituted analogues, and may well find industrial uses in the tailor-making of catalysts of specific activity.
Making Corrosion-Resistant Brazed Joints in Stainless Steel

ADVANTAGES OF PALLADIUM-BEARING BRAZING ALLOYS

By M. H. Sloboda, Dipl. Ing.
Research Laboratories, Johnson Matthey & Co Limited

Stainless steel parts brazed with standard low-melting brazing alloys are susceptible to a specific kind of corrosion by water or humid atmosphere, generally known as interface or crevice corrosion. One of the advantages of brazing alloys of the silver-copper-palladium type is that they will produce joints in stainless steel resistant to this form of failure.

Joints made in stainless steel with certain low-melting brazing alloys (of the silver-copper-zinc-cadmium type) and exposed to the action of water or humid atmosphere are susceptible to corrosion of a rather unusual kind.

The attack in this case consists in the dissolution of a very thin steel layer along the joint interface, as a result of which the bond between the steel and the brazing alloy is completely destroyed. A failure of this kind is illustrated in Fig. 1, showing a laboratory stainless steel joint specimen in an advanced stage of corrosion.

Since the quantity of metal that has to be dissolved to produce this effect is extremely small, the rate of bond destruction is very fast. Cases are known of stainless steel parts brazed with unsuitable materials falling apart after a week’s exposure to the action of ordinary tap water.

Another distinguishing feature of the corrosive attack of this kind, which is usually referred to as interface or crevice corrosion, is that neither the brazing alloy nor the stainless steel show any obvious symptoms of corrosion damage. Although iron dissolved at the joint interface is precipitated as a loose red rust deposit outside the joint area, once this corrosion product has been removed (by design or by accident), there is nothing to indicate that the separation of the brazing alloy from the steel was caused by corrosion. In fact, the usual reaction of an observer

Fig. 1 A ferritic stainless steel (EN 60) specimen brazed with a 50Ag-15Cu-16Zn-19Cd alloy and held for eight days in running tap water. The specimen was bent to reveal the extent of interface corrosion resulting in the destruction of the bond between the brazing alloy and the steel.
Fig. 2 Showing a blister formed in an austenitic steel (EN 58c) specimen brazed with a 54Ag-25Pd-21Cu alloy in dissociated ammonia under a flux cover and held for 106 days in running tap water. (× 50)

Fig. 3 A magnified view of a region of the specimen of Fig. 2 showing the presence of a partially oxidised steel layer at a certain distance from the joint interface along a plane coinciding with the path of the crack whose formation led to blistering. (× 550)

faced with a failure of this kind is to conclude that the joint fell apart because no bond formation had actually taken place.

The mechanism of interface corrosion, which now appears to be a much more complex phenomenon than first thought, has not yet been elucidated. However, extensive researches in this field have made it possible to classify various standard and specially developed brazing alloys in the order of their usefulness for joining stainless steel when corrosion resistance of the joints produced is an important consideration.

It has been established for instance that, although there are several low-melting silver brazing alloys with which joints resistant to interface corrosion can be made, each of these materials has certain limitations. And so, most alloys that are convenient to use from the purely brazing point of view will produce corrosion-resistant joints but only when used on stainless steel of the nickel-bearing austenitic type. On the other hand, low temperature brazing alloys that are suitable (from the standpoint of interface corrosion resistance) for joining both austenitic and ferritic stainless steels are often distinguished by somewhat inferior flow characteristics. Finally, the corrosion resistance of stainless steel parts brazed with low-melting alloys of this kind
may often be substantially affected by certain changes in the composition of fluxes used during brazing.

The only known materials that combine the freedom from the above limitations with many of the desirable properties of various silver solders are certain gold-base and palladium-bearing alloys. The latter are exemplified by the 54Ag-25Pd-21Cu composition which is one of the Johnson Matthey noble metal brazing alloys known as Pallabraze 950; its special advantages as a filler material for joining stainless steel can be summarised as follows:

(i) Pallabraze 950 will produce interface-corrosion resistant joints in both ferritic and austenitic stainless steels.

(ii) The corrosion resistance of joints made with this alloy is not affected by changes in the composition of the brazing flux, especially by the presence of free boron which is sometimes added to brazing fluxes to improve their flow-promoting properties and stability at elevated temperatures.

(iii) Joints made with Pallabraze 950 combine the resistance to interface corrosion with a relatively high strength at temperatures of up to 400°C.

(iv) Stainless steel parts brazed with this alloy are not damaged by erosion due to excessive interalloying during brazing.

(v) Due to its palladium content, Pallabraze 950 may be safely used when intergranular penetration of steel by a molten brazing alloy might otherwise lead to brazing failures.

(vi) Pallabraze 950 has excellent wetting and free-flowing characteristics and can be used both for brazing in air under a flux cover and for fluxless brazing in a reducing atmosphere.

In this last connection a rather unusual effect is worth reporting.

It is sometimes found in industrial practice that the oxide-reducing potential of a brazing furnace atmosphere which is sufficiently pure (dry) to preserve the initial bright finish of stainless steel parts is too low to make the steel surface wettable by the brazing alloy.

The usual remedy in such cases is to use both a reducing atmosphere and a small quantity of a suitable brazing flux. However, it has been recently found that this practice may have unexpected and rather puzzling consequences.

If an alloy is intrinsically capable of producing corrosion-resistant joints, it makes no difference whether the brazing is done in a reducing atmosphere or under a flux cover. When, however, both a reducing atmosphere and a flux are used in brazing with such an alloy (e.g. Pallabraze 950), the resultant joints—while resistant to interface corrosion—may be subject to failure of a different kind.

When observed under laboratory conditions on specimens tested in running tap water, the failure consisted in the formation of

![Fig. 4 Showing the absence of any obvious differences in the structure of joints brazed in an austenitic stainless steel (EN 58c) with a 54Ag-25Pd-21Cu alloy: (top) in dissociated ammonia; (middle) under a flux cover in air, and (bottom) in the presence of both a reducing atmosphere and a brazing flux. (×200)](image)
a crack inside the joint. The crack was propagated in the steel itself along a plane parallel to, and at a distance of several microns from, the joint interface; it was often associated with the presence of a partially oxidised steel layer. The crack plane approximately marked the boundary of the zone into which palladium and copper had diffused into the steel during brazing. The only external evidence of the development of this failure was the formation of blisters in regions where the brazing alloy coating was sufficiently thin. Photomicrographs of a specimen that had failed in this way are reproduced in Figs. 2 and 3.

It should be added in conclusion that metallographic examination of specimens in the as-brazed condition revealed no differences between joints made with the same alloy under a flux cover, in a reducing atmosphere, and in the presence of both these fluxing media (Fig. 4).

Further studies will be necessary to establish the precise conditions leading to joint failure of the kind described above and to ascertain that the effects observed were not due to some extraneous, as yet unidentified factors. Nevertheless, the evidence available so far is sufficient to advise against using a brazing flux in combination with a reducing atmosphere in the joining of stainless steel parts that may be exposed to the influence of water or humid atmosphere in service.

**Thermocouples Under Neutron Bombardment**

**CHANGES IN VOLUME AND COMPOSITION**

Under severe neutron radiation thermocouples are known to be unstable although little data on the changes in composition which occur has hitherto been published. A recent report by C. B. T. Braunton, D. N. Hall and C. M. Ryall, of the Atomic Energy Research Establishment, Harwell, (U.K.A.E.A., A.E.R.E. - R5837, 1968), now provides information which will greatly simplify the selection of thermocouple materials for experiments carried out under radiation at high temperatures. Under such conditions lattice damage anneals out and changes of thermoelectric behaviour can be predicted from the compositional changes. These have been computed from differential equations which were developed to describe the exponential transmutation of isotopes, and curves defining the composition of the various alloys at successive stages of time and radiation are provided in this report.

Pure platinum when irradiated produces only gold and mercury, each reaching a maximum concentration of rather less than 1 per cent after a year's exposure to a flux of $10^{14} \text{n/cm}^2/\text{sec}$. Under similar conditions, however, the rhodium content of rhodium-platinum alloys is almost completely consumed, to form palladium, mercury, gold and iridium.

Ruthenium alloys are far more stable. The ruthenium remains unchanged, all transmutation effects being confined to the platinum. The palladium content of palladium-platinum alloys is not greatly affected although small quantities of mercury, gold, cadmium, silver, iridium and rhodium are formed by transmutation. Molybdenum-platinum alloys are considerably more stable than rhodium-platinum alloys when irradiated being comparable to ruthenium-platinum alloys in this respect.

Tungsten, rhenium and tantalum all suffer severely in a neutron flux. Some 40 per cent of the rhenium is lost after one year at a flux of $2 \times 10^{14} \text{n/cm}^2/\text{sec}$; tungsten is rapidly replaced by rhenium, rhenium by osmium, and tantalum by tungsten. The compositional changes in molybdenum are small.

Platinum alloys increase in volume under neutron irradiation by amounts ranging up to 2 per cent after one year at $10^{15} \text{n/cm}^2/\text{sec}$. Tungsten, tantalum and rhenium decrease in volume to a considerably greater extent.

A significant conclusion of this report is that tungsten-rhenium thermocouples will suffer more damage, and are likely to be less stable than platinum-based thermocouples under similar conditions of neutron bombardment. It will be interesting to see whether the results of the experimental programme now being carried out in mixed thermal and fast neutron fluxes, referred to in this report, confirm this prediction.

A. S. D.
The Platinum Metals in the Measurement of Temperature

THE NEW INTERNATIONAL TEMPERATURE SCALE OF 1968

By C. R. Barber, B.Sc., F.Inst.P.

Quantum Metrology Division, National Physical Laboratory, Teddington

A revised definition of the temperature scale entitled the International Practical Temperature Scale of 1968 (IPTS-68) was introduced by the Comité International des Poids et Mesures (CIPM) in October 1968 to replace the IPTS-48. The new Scale was put into operation at the National Physical Laboratory on January 1st, 1969, and temperature values quoted in documents issued by the Laboratory from that date will be changed by the appropriate amounts. It is necessary to make these changes throughout science and industry, but as will be seen below the changes for many purposes will not be very significant.

Platinum plays an important role in the new Scale for the construction of the platinum: 10 per cent rhodium-platinum thermocouple and the platinum resistance thermometer which are the chosen standard instruments for the realisation of the Scale below the freezing point of gold.

The difference in numerical values of temperature introduced by the IPTS-68 are shown in Table I. They result from the adjustments made to the IPTS-48 to give agreement with thermodynamic values of temperature obtained from gas-thermometer measurements. These adjustments consist of assigning the best available values of thermodynamic temperature to the defining fixed points and modifications to the interpolation procedures in the parts of the Scale where the platinum resistance thermometer is the specified interpolation instrument.

The IPTS-68 extends down to 13.81K, the triple point of equilibrium hydrogen, whereas the IPTS-48 stopped short at the boiling point of oxygen (T_{bo}(O_2)=90.188K); the extension is made in terms of the platinum resistance thermometer which is now the interpolation instrument of the Scale over the wide range from $-259.34 \degree C (13.81K)$ to 630.74\degree C. The platinum to be used in the thermometer is required to be very pure; the completed thermometer must have a value of the resistance ratio $\frac{R(100 \degree C)}{R(0 \degree C)}$ not less than 1.39250. This value corresponds to 1.3920 on the old scale.

To conform with common usage the Scale is expressed in Kelvin temperatures below 273.15K and in Celsius temperatures above. From 13.81K to 273.15K the resistance of the thermometer is measured at a number of fixed points and then the calibration is obtained by difference from the reference function

$$T_{48} = [A_0 + \sum_{i=1}^{20} A_i (\ln W)^i] K$$

where $W = R(T) / R(273.15)$. The coefficients $A_0, A_1, \ldots, A_{20}$ are specified in the text of the Scale. The function has been evaluated and is available in the form of a detailed table. The differences from the function, $\Delta W$, are expressed by a polynomial for each of the ranges 13.81K to 20.28K, 20.28K to 54.361K, 54.361K to 90.188K and 90.188K to 273.15K. The last mentioned range was formerly defined by the Callendar-Van Dusen equation but we now use the difference from the reference function given by the equation.

$$\Delta W = A + B \left( \frac{T_{48}}{100 \degree C} - 1 \right) \frac{T_{48}}{100 \degree C}$$

Where $T_{48} = T_{48} - 273.15K$ and the constants $A$ and $B$ are determined by measurements of
Table I
Approximate Differences between IPTS-68 and IPTS-48 in kelvins

<table>
<thead>
<tr>
<th>t°C</th>
<th>-100</th>
<th>-90</th>
<th>-80</th>
<th>-70</th>
<th>-60</th>
<th>-50</th>
<th>-40</th>
<th>-30</th>
<th>-20</th>
<th>-10</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.022</td>
<td>0.013</td>
<td>0.006</td>
<td>-0.013</td>
<td>-0.013</td>
<td>-0.006</td>
<td>0.003</td>
<td>0.006</td>
<td>0.013</td>
<td>0.022</td>
<td>0.022</td>
</tr>
</tbody>
</table>

W at 100°C and -182.962°C (90.188K). Thus the experimental procedure for calibration in this range of temperature is simpler than formerly, requiring calibration at three points only instead of four, since it is not dependent on measurements at the zinc point.

The Callendar equation is still used for the range from 0°C to 630.74°C but a correction term is added, so that the calibration procedure is to measure the resistance of the thermometer at the 0°C point (obtained by way of the triple point of water), the boiling point of water (100°C) and the freezing point of zinc (419.58°C). It will be observed that only the temperature assigned to the freezing point of zinc has been changed, being 419.50°C on the 1948 scale. The Callendar equation is then used to determine an intermediate value of \( t' \)

\[
t' = 1/2 \left( W - t \right) + 0.45 \left( \frac{t'}{100°C} - t \right) \left( \frac{t'}{419.58°C} - 1 \right) \left( \frac{t'}{630.74°C} - 1 \right) \]

It is clear that the coefficient \( a \) for a particular specimen of platinum will be unchanged on the new Scale but the \( \delta \) coefficient will be different because of the change in the value assigned to zinc point. For example a \( \delta \) coefficient of 1.492 on the old scale becomes about 1.497 on the new.

Over the range from 630.74°C to the gold point (1064.43°C) the platinum : 10 per cent rhodium-platinum thermocouple is used to define the Scale as in the IPTS-48, but now the values of the fixed points are modified. The emf temperature relation is

\[
E = -a - bt_x + ct_x^2
\]

where the constants \( a, b, c \) are determined from the measurements made at 630.74°C - 0.2°C, 961.93°C (F.P. of silver) and 1064.43°C (F.P. of gold).

Above the gold point the IPTS-68 is defined as before by the Planck law of radiation using the freezing point of gold as the reference temperature and a new value of \( c_x \),
the second radiation constant, of 0.014388 metre kelvin. The numerical values of temperature in this range show a net increase over the 1948 values, the higher value of the gold point causing an increase and the higher value of $c_2$ a decrease.

The values of the freezing points of the metals relevant to this discussion and given either as defining fixed points of the temperature scale or in the list of secondary fixed points are set out in Table II with the corresponding IPTS-48 values for comparison.

The freezing points of silver and gold are defining fixed points of the Scale and therefore the temperatures assigned are the best available values of thermodynamic temperature. The other values in Table II are obtained from the IPTS-48 values corrected according to the differences in Table I and then rounded to the nearest kelvin.

The IPTS-68 embodies the decision of the CIPM to discontinue the use of “degree kelvin, symbol ‘K’ in favour of the “kelvin” to describe the unit of thermodynamic temperature which is defined as “the fraction $1/273.16$ of the temperature of the triple point of water”. It is appropriate to refer to a temperature difference in kelvins even when the temperatures are expressed in degrees Celsius, and this practice has been followed in the text of the Scale.

The full text of the English version of the IPTS is obtainable from Her Majesty’s Stationery Office. The official French text is obtainable from the International Bureau of Weights & Measures, F92, Sévres, France.

### Palladium-Titanium Alloy in Chemical Plant

The natural resistance of titanium to corrosion in oxidising conditions has been extended to reducing conditions by the addition of small amounts of palladium, and the wider use of titanium in chemical plant which this permits has been the subject of comment in this journal, most recently on the work of Takamura in Japan (1).

Whereas Takamura used the 0.13 per cent palladium-titanium alloy in hot concentrated chloride solutions, W. R. Fischer, of Friedrich Krupp, Essen, has now shown that the Krupp standard alloy containing 0.2 per cent palladium is most generally useful in extended tests with a number of chloride solutions (2). Adequate protection against crevice corrosion and pitting was obtained. However, in exceptional cases an alloy with more than 0.2 per cent palladium may be necessary where particularly awkward angles occur in fabricated chemical plant.

Fischer measured weight losses and potentials of palladium-titanium alloys with 0, 0.1, 0.5, and 1.0 per cent palladium in hot sulphuric acid and hydrochloric acids and in concentrated chloride solutions. His results show that 0.1 per cent palladium is inadequate to give titanium protection in reducing conditions but that 0.5 and 1.0 per cent alloys both give sufficient protection.

He warns that pilot tests to determine the most suitable palladium content are necessary in extreme conditions, where 0.2 per cent is insufficient. However, short-term tests may be inadequate as time is needed for the formation of the palladium-rich protective film.

The weldability of the alloys is comparable to that of ordinary titanium but the usual precautions are necessary. Pure dry argon should be used to prevent access of oxygen and nitrogen to the weld and iron and other metallic impurities must be excluded.

Fischer adds that a special palladium-tantalum-titanium alloy has yet higher corrosion resistance, especially in non-oxidising acids, and is available for special purposes.

F. J. S.

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1. *Platinum Metals Rev.*, 1968, 12, (2), 53
Sir William Crookes

Investigations on Iridium Crucibles and the Volatility of the Platinum Metals

By J. C. Chaston, Ph.D., A.R.S.M.
Johnson Matthey & Co Limited

William Crookes was born on June 17th, 1832, and after attending courses in chemistry at the College of Science, remained for three years as an assistant under Professor Hoffman. He then taught for nearly a year as lecturer in chemistry at Chester Training College, and was known as "Professor" ever afterwards. He had some private means, and in 1858 came to London and set up as a consultant with a small private laboratory at his home at 20 Mornington Road, near Regent's Park.

In December 1859, he founded the weekly journal The Chemical News and remained as editor for the next sixty years. The Chemical News prospered from the first and was widely read. It provided excellent summaries of important technical and scientific publications throughout the world and, through its correspondence pages, a forum for many notable – and often amusing – discussions.

Only fifteen months later Crookes had a piece of good fortune when he was able to announce on March 30th, 1861, the discovery of a new element which he later christened Thallium. The discovery is often described as the result of a spectroscopic examination. In fact, Crookes very simply – though no less to his credit – observed an unexpected, and hitherto unreported, bright green flash in the course of a flame test when a small sample of the seleniferous residues from sulphuric acid manufacture at Tilkeroede, in the Hartig mountains, was supported on a
In this detail from a painting by Il. Jumyn Brooks at the Royal Institution the front row shows, left to right, Mr A. J. Balfour (then Prime Minister), Sir William Crookes, Crichton Browne, Lord Rayleigh, George Matthey, Ludwig Mond and Oliver Lodge. The occasion was the demonstration by Dewar in 1904 of the properties of liquid hydrogen.

platinum wire in a gas flame. The material was left over from earlier work on sulphoselenides in which he had engaged at the College of Science. Crookes was a good experimenter, and he followed up his initial observation by isolating the new element and investigating its properties. A sample was inevitably shown at the Great Exhibition of 1862 and recognition very quickly followed (too quickly, some declared) by his election as a fellow of the Royal Society in November 1863.

His determination of the atomic weight of thallium, reported in 1873, was a first-class piece of work and the figure he obtained, 203.642, equivalent to 204.03 when corrected to modern values, compares very favourably with the 1961 International value of 204.37.

His flair for careful observation continued to serve him well. He devised the radiometer — though his explanation of its action was soon discredited — he described the Crookes dark space in the cathode discharge tube — but was less than profound in his theoretical views on electrical discharges through gases — he separated Uranium X, he devised the spintharoscope, and he developed Crookes glass to protect the eye against the ultra-violet. In his later years, like Sir Oliver Lodge, he explored the mysteries of spiritualism. Lord Kelvin is said to have remarked of him that “Crookes started more absolutely new hares than any other man among his scientific contemporaries”.

All his work was done in his private laboratory in his house, first in Mornington Road and after 1880 at 7 Kensington Park Gardens (which he claimed to be the first in England to be lighted by electricity) and much of it was financed by grants from the Royal Society. In his later years he was involved in a variety of commercial enterprises.

He was prominent in every area of scientific activity in London for nearly sixty years and was widely honoured. He was elected President of the Institution of Electrical Engineers in 1890, of the British Association in 1898, and of the Royal Society in 1913. He was awarded the Order of Merit in 1910. No scientific meeting of note failed to welcome him, and in scores of paintings and photographs of scientific gatherings of the...
period his distinguished bearded figure is prominent in the foreground.

The early issues of *The Chemical News* devoted a remarkable amount of space to the platinum metals. The first three issues serialised a translation of a classic paper by Deville and Debray, “On platinum and its associated metals”, which includes a description of a long-forgotten use of the lime furnace for the fire-refining of platinum. The base metals are slagged off, gold and palladium vaporised and collected in an earthenware tube, and osmic acid finally trapped in a vessel full of ammonia. Part of the osmium is deposited on the tube walls in the metallic state. Later issues included a reprint of a paper by Woolcott Gibbs, describing the treatment of osmiridium residues from Californian gold and from Siberia, and a translation of Claus’ classic paper “On certain properties of the platinum metals, particularly ruthenium”.

It was not until 1908 that Crookes published any original observations on the platinum metals, but in a communication read in May of that year to the Royal Society he was the first to “draw the attention of chemists to the great advantages of using crucibles of pure iridium instead of platinum in laboratory work”.

The crucibles were supplied by “Messrs Johnson and Matthey” and one of these has been preserved to this day. Crookes noted that the iridium crucibles resisted fusion of many fluxes, including caustic soda, and were not attacked by molten lead, zinc, nickel, gold and iron. Temperatures are not recorded. One paragraph introduces without comment a quite unexpected characteristic. “Copper melted in the crucible for some time”, Crookes wrote, makes it “hot rotten, i.e. it is brittle when hot. But if the copper is well burnt off at a high heat the iridium reverts to its original condition”. No explanation is given as to how copper could be “burnt off”.

One other passage reveals a common misconception. “Heated for some hours over a Bunsen burner insufficiently supplied with air the iridium crucible is unaffected and the deposit of carbon easily burns away, leaving the surface of the metal uninjured. All chemists know how seriously a platinum crucible is attacked in these circumstances”. In fact, a clean platinum crucible is quite unattacked, though it may be disastrously embrittled if it contains certain compounds (particularly arsenates or phosphates) which are reduced in the yellow flame and alloy with the platinum to form brittle phases. Many chemists even today attribute the trouble to attack on platinum by carbon.

These details apart, in advocating the use
The first page of Crookes' paper on “The Volatility of Metals of the Platinum Group” read to the Royal Society in March 1912, showing the platinum-wound furnace in which his investigation was carried out.

Crookes' results for the losses in weight of the platinum metals when heated in air at 1300°C. It will be seen that the loss is expressed as a percentage of the weight, not of the unit area of surface, in spite of the differences in size and form of the specimens

The measurements reported by Crookes to the Royal Society in March 1912 of the loss of weight of the platinum metals when heated in air are better known. They stemmed from his observation of the “fine glistening dust” deposits of platinum on the porcelain tube of a furnace wound with platinum ribbon. The furnace had failed through localised thinning of the winding after operating at 1500°C, and under the microscope the deposits appeared as “beautifully formal hexagonal plates with a brilliant metallic lustre and perfect crystalline form”.

of iridium (and rhodium) crucibles for certain chemical operations, Sir William Crookes was far in advance of his times. It is only within the last decade that any serious application has been made of iridium crucibles, although they are now employed widely for growing laser crystals and also for melting special glasses.

The Volatility of Metals of the Platinum Group.
By Sir William Crookes, O.M., For. Sec. R.S.
(Received February 15.—Read March 7, 1912.)

For the last two years I have been using an electric furnace, and some facts which came under my notice on the occasion of a breakdown of the heating arrangement led me to suspect that platinum was not so entirely fixed at temperatures well below its melting-point as has been universally accepted by chemists and physicists.

The electric resistance furnace used (fig. 1) is on the Heraeus system. It consists of a highly refractory porcelain tube, around which is coiled a ribbon of platinum foil, 11 mm. wide, 28 metres long, and 001 mm. thick.
Crookes accordingly set out to determine the loss of weight of the various platinum metals, using as his specimens a platinum crucible weighing 150 grains, an iridium crucible "as hard as steel" of about the same weight, a polished plate of palladium weighing 58 grains, a rhodium specimen (presumably as sheet) weighing 32 grains, and a "highly polished plate" of ruthenium. The weight and dimensions of the ruthenium are not specified; and it is of interest to reflect that there must be few, even today, who have seen highly polished ruthenium sheet. The choice of grains instead of grammes as units of weight is explained in a footnote: "I have used my standard platinum grain weights for nearly fifty years, and they are too valuable to discard in favour of grammé weights, which would demand many months' work on them to bring them to the state of accuracy into which I have now got the grain weights".

In devising the arrangements for heating, Crookes was concerned to avoid the possibility as he said of "the action known as 'air washing' (particles from a white-hot semi-molten surface being mechanically carried away by a current of impinging air)". Today it is not clear why the surfaces should have been thought to be "semi-molten" at 1300°C, the highest temperature used. Accordingly, the heating was carried out in a vertical resistance-heated tube furnace, closed at the top and "nearly closed at the place where the crucible stood and almost completely obstructed at the lower end". In this way, "the platinum was in almost still air".

The experiments were made at 1300°C and 900°C, the samples being removed for weighing every 2 hours, the total time of heating being 30 hours. The results are shown in Figs. 9 and 10 of his paper, reproduced here, and have been widely quoted ever since. The relatively high losses of platinum at the higher temperature almost certainly surprised Crookes, but he rejected the possibility that these could be due to a volatile oxide on the evidence that the crystals deposited on the walls of a platinum-wound furnace were metallic platinum. The concept of oxygen acting as a carrier to transport platinum from a hotter source (where platinum oxide concentration is high) to a cooler surface (yet above the decomposition temperature of the oxide) was of course not available to him.

It was a little unfortunate, perhaps, that the upper temperature chosen was 1300°C. At this temperature it is true that the vapour pressure of PtO₂ in air is rather higher than that of RhO₂ so that rhodium surfaces lose weight less than platinum ones. This led to a belief that at high temperatures in general rhodium is the less volatile in air; actually above 1300°C the vapour pressure of RhO₂ increases very rapidly and soon greatly exceeds that of PtO₂.

With iridium, rhodium and ruthenium it was obvious visually that oxidation occurs and Crookes endeavoured to ascertain whether iridium would volatilise in a vacuum at 1300°C. Experimental difficulties, however, prevented him from reaching a definite conclusion.

Crookes was certainly among the first to study the behaviour of the platinum metals when heated in air to high temperatures, though in this as in other directions he was an experimenter rather than a philosopher.
ABSTRACTS of current literature on the platinum metals and their alloys

PROPERTIES

Fusion Curves for Graphite, Tungsten and Platinum up to 60 kbar
L. F. VERSHMAGIN and N. S. FATEEVA, Zh. eksper. teor. Fiz., 1968, 55, (4), 1145-1152
Optical measurements on Pt agree well with those obtained by thermal analysis. The temperature of fusion of Pt increases linearly with pressure.

Rheological Properties of Platinum at High Temperatures
Measurements of the shear modulus, internal friction and creep of annealed and unannealed samples of Pt were carried out between 1300 and 1980°K and results are depicted graphically.

Coherent and Incoherent Precipitation in the Gold-Platinum System
J. WEISE and V. GEROLD, Z. Metallkunde, 1968, 59, (12), 904-909
Resistivity studies of 15, 20, 60 and 65 wt% Au-Pt wires during isothermal ageing and during re-heating to the homogenisation temperature showed two rates which can be attributed to coherent and to incoherent precipitation. The metastable coherent miscibility gap in the phase diagram was \(\sim 100-200\) deg C below the stable incoherent gap. The temperature dependence of the rate of resistivity change at the start of annealing 65 wt% Au-Pt agreed with spinodal decomposition theory or a nucleation mechanism.

Effect of Deformation on the Physico-mechanical Properties of an Alloy of Platinum with Silver
Studies of the deformation of 0.1-3 mm Ag-Pt alloy wires after quenching from 1000°C showed that wires of different diameter had different tendencies towards work-hardening. 99% deformation was required to obtain high strength in a 0.1 mm wire but for wires 0.2 mm diameter even 99.8% deformation only produced a UTS of 170 kg/mm².

Anomalous Low Temperature Susceptibility of Dilute Pt-Co Alloys
J. C. GALLOP and I. A. CAMPBELL, Solid state Commun., 1968, 6, (11), 831-833
Nuclear orientation measurements of the hyperfine field at \(^{60}\)Co nuclei in Co-Pt as a function of applied field suggest the formation of a spin-compensated state at low temperatures.

Effect of Chemical Composition and Heat Treatment Conditions on the Magnetic Properties of High Coercivity Cobalt-Platinum Alloys
Tests on cast and homogenised samples of 24, 25, 26.16, and 29.5 wt% Co-Pt alloys showed that the highest magnetic properties are attained with cast samples, e.g. 24-25% Co-Pt has maximum magnetic energy 40 kJ/m³, \(B_r=7500\) gauss, \(H_c=3950\) Oe. \(H_c\) decreases for >25% Co-Pt, i.e. highest magnetic properties occur for 23-25% Co-Pt, where concentration disordering is less important. Controlled cooling rates lead to more homogeneous and more dispersed structures due to prolonged keeping of samples at 770-830°C, the temperature favourable to nucleation.

Platinum-based Permanent-magnet Alloys
Studies of changes of magnetic properties of PtCo and PtFe when part or all of the Pt is replaced by Pd, Rh, Ir, and Ru with various preparations and heat treatments show that the pseudobinary alloys possess no better magnetic properties. Careful heat treatment of sintered and worked or of vacuum-melted PtCo gives energy products of 9.5 and \(10.0 \times 10^6\) Gs-Oe, and coercive forces of 5.0 and \(4.5 \times 10^3\) Oe respectively.

L. FITOUSSI, C. r., Sér. C., 1968, 267, (26), 1742-1745
Activation energies measured during diffusion through 23% Ag-Pd were 4.9 kcal/g.atom (±10%) for normal \(H_2\) and 3.54 kcal/g.atom (±10%) for \(H_2\) enriched with parahydrogen.

Electrical Resistivity Measurements in Palladium-Hydrogen Alloys
Studies of Pd and Pd-H at 2-300°C show that at 10°K < T < 60°C the electrical resistivity \(\rho_1\)
Thin Films of Iron-Palladium Alloys with High Coercivity


Studies of FePd showed that the coercivity $H_c$ is greatest when the crystallites of the alloy are smallest. It follows that a film, consisting of the smallest grain size of all, possesses the highest $H_c$. Thermal ordering increases the grain size and thereby decreases $H_c$.

The Surface Tension and Density of the Liquid Alloys Pd-Fe, Pd-Cr, Pd-Si


Liquids Fe-Pd alloys are nearly ideal. Isotherms of surface tension for molten Cr-Pd are smooth. In molten Si-Pd, molecular groupings in the ratio of the PdSi compound are maintained during isotherms of surface tension.

Alloys with Extra Specific Electrical Resistance and Low Temperature Coefficient of Resistance in a Wide Range of Temperature


Alloying Ni with Mn-Pd does not alter the resistivity $\rho$ or the temperature coefficient $\alpha$ of resistance of the alloy but annealing Mn-Pd-Ni at $300^\circ C$ alters both $\rho$ and $\alpha$. $0.3$ mm diameter rods of $65\%$, Mn-15\%, Pd-15\% Ni-5\% Cu have: $\rho = 2\mu\mathrm{ohm}\cdot\mathrm{m}$, $\alpha = 3.10^{-4}$ per deg C at $-60$ to $+120^\circ C$, $\alpha = (7-8)10^{-5}$ per deg C at $120-300^\circ C$. $\mathrm{e.m.f.}$ versus Cu $E = 0.7$ mV/deg C, $\sigma = 62-68$ kg/mm$^2$, $\delta = 20-28\%$. Repeated heating and cooling between $-60$ and $+300^\circ C$ does not change their electrical properties. Protracted annealing at $300^\circ C$ does not alter their structure or properties but at $500-600^\circ C$ reduces $\rho$ and leads to brittleness and decomposition.

Properties of Alloys of Manganese-Palladium, Manganese-Germanium, and Manganese-Gallium Systems

*Ibid.*, 35–42

The search for a high-resistivity alloy showed that when quenching high Mn content alloys from the $\gamma$ region a f.c.c. tetragonal lattice appears which upon alloying becomes f.c.c. Resistivity of Mn-Pd quenched from the $\gamma$ region is higher than that of Mn-Cu or of Mn-Ni. Resistivity $\rho$ of 20–32.7\% Pd-Mn varies slightly with temperature at 0–350$^\circ C$. $\rho$ decreases abruptly above $350^\circ C$ for all Pd-Mn alloys and dilatometric curves indicate a phase transformation at $350^\circ C$.

A Palladium-Magnesium Alloy Phase of Co-Al$_2$ Type


X-ray studies of hexagonal PdMg$_{1-x}$ give dimensions $a = 8.646-8.660$ Å and $c = 8.175-8.169$ Å. The phase has a range of homogeneity.
Magnetic Susceptibility of Alloys of Plutonium with Palladium
N. T. CHEBOTAREV, YU. N. SOKURSKII, M. A. ANDRIANOV and A. A. IVANOV, Ibid., 431–433
Magnetic susceptibilities of Pu-Pd alloys are tabulated and shown in graphical form.

Thermomagnetic Measurements on Alloys of the Platinum Metals with Chromium
Alloys of Pt metals with Cr which have similar structures have similar magnetic properties. F.c.c. L12 phases of Cr with 25–30 at. % Pt, Pd or Ir have a distinct maximum of magnetisation with typical ferromagnetic behaviour. Saturation magnetisation at −193°C is ~0.39 Vs/m2 for Pt, ~0.15 Vs/m2 for Pd, ~0.06 Vs/m2 for Ir and the respective Curie points are 900, 400 and 170°C. Tetragonal PdCr with L12 structure is weakly ferromagnetic. Rh-Cr, Ru-Cr and Os-Cr possess no L12 structure and are very weakly ferromagnetic. F.c.c. solid solutions rich in Cr are anti-ferromagnetic with high Néel points.

CHEMICAL COMPOUNDS
Mass Spectrometric Determination of the Dissociation Energies of Gaseous RuC, IrC and PtB
RuC, IrC and PtB molecules have been detected with dissociation energies Do(RuC) = 151.0 ± 3.0, Do(IrC) = 148.4 ± 3.0, Do(PtB) = 113.3 ± 4.0 kcal/mole.

Preparation and Properties of Some Ternary Selenides and Tellurides of Rhodium
MrbX3, where M is Cr, Co, Ni and X is Se, Te, and RhbTe4 have the monoclinic CrSe3-type structure with space group I2/m, except for CoRhbTe4 and NiRhXbTe4, which are trigonal with space group P3 m1. The symmetry of these compounds with defect NiAs structure depends on whether metal ion vacancies are ordered or randomly arranged in alternate metal layers.

Reversible Activation of Covalent Molecules by Transition Metal Complexes. The Role of the Covalent Molecule
A review of recent work on the mechanism of reactions involving Ir and Rh complexes. Data discussed are from determinations of the role of the reacting gas by studies of a series of reactions of one metal complex ML4 with a variety of addenda, and by comparison of kinetic, equilibrium and thermochemical data from these reactions and the electronic and geometric properties of the corresponding adducts (XY) ML4.

Thermal Decomposition of Rhodium, Iridium, and Ruthenium Chlorides
Decomposition studies of RhCl3, IrCl3 and RuCl3 hydrates in air and in H2 were studied by thermogravimetric analysis and reduction studies were made for dispersions on low- and high-area substrates. Reduction to the respective metals was complete at 105, 190, and ~350°C. In air, dechlorinization and oxidation was complete at 890, 680 and ~440°C respectively. B,C, which has low area, has little effect on the reduction temperature of the Rh salt but Al2O3, which has high area, is associated with desorption of decomposition products.

The Metallic Nature of Osmium Dioxide
Single crystals of OsO2 were prepared and electrical conductivity and Hall effect measurements were made. The data can be rationalised on the basis of a wholly collective electron approach involving the concepts of narrow bands and high density of states which are often encountered in the transition metals and their compounds.

ELECTROCHEMISTRY
Hydrogen Adsorption Equilibrium on Platinum Electrodes
A review of experimental evidence and theory of H2 adsorption equilibrium on Pt electrodes shows that most probably the observed effects are due to the several states of H2 adsorption on Pt, all of which obey the Langmuir adsorption isotherm to a good approximation. There are probably 4–4 such states.

Diffusion Coefficient of Hydrogen in Palladium Alloy Electrodes
Diffusion coefficient of H2 in 23% Ag-Pd alloy and in this alloy with 0.5, 0.9, 2.0 and 3.0 at. % B additions was determined as a function of H2 concentration and temperature at 30–300°C and varies with H2 concentration as D(C) = 12B [RT + C(T − C)d/dC(DH(C))].
On the Behaviour of a Ruthenium Electrode-catalyst in Solutions of Sulphuric and Oxalic Acid at Various Temperatures


The rate of catalytic hydrogenation of CH\textsubscript{3}NO\textsubscript{2} on Ru was \( \sim \) twice that of electrochemical reduction but the difference decreased as the temperature rose.

Catalytic and Electrochemical Reduction of Nitromethane on Ruthenium Electrode-catalyst


Further studies of these reactions in 0.1 \(N\) \(H_2SO_4\).

LABORATORY APPARATUS AND TECHNIQUE

Correction for Temperature Loading and High Gas Pressure Effects for the Constant-temperature Hot-wire Anemometer


Tests on Pt and 30\% Ir-Pt wires enabled a calibration curve to be plotted for a constant-temperature hot-wire anemometer using the alloy at high temperature in a high-temperature and high-density gas flow. The temperature coefficient of resistance for 30\% Ir-Pt was determined and also its thermal conductivity.

Electrolytic Cell with a Rotating Double Ring Electrode for High Frequencies in the Measurement of Fast Reactions


The construction of a double ring Pt electrode system is described together with requirements for its use at high speeds of rotation.

BRAZING AND WELDING

Bits for Soldering Irons


The suitability of Ru for the bits of soldering irons is limited by its cost and so methods have been developed to localise it on bit surfaces and also to protect the non-functional shank surfaces. The most promising tipped bit has an Al shank to which is welded Ru facing.

HETEROGENEOUS CATALYSIS

UOP Catalyst Improves Yield of Aromatics


Reduced operating pressures are claimed at high severity conditions without loss of stability for U.O.P.'s new R-16 Platforming catalyst. Improved product distribution selectivity at lower pressures permits dehydrocyclisation of paraffins and dehydrogenation of naphthenes to create aromatics with a minimum of hydrocracking to light hydrocarbons, i.e. yield of motor fuel reformate of a given octane number is higher at lower operating pressures. The aromatics-creating reactions are favoured by lower pressures. Plants which have switched to this catalyst have not yet taken full advantage of R-16 because of their different operating pressures. See also Chem. W., 1969, 104, (2), 60-61.

Results of Testing of Platinum on Alumina Catalysts by Hydrogenating Benzene to Cyclohexane


\( C_6H_6 \) hydrogenation tests using a modified Pt/Al\(_2\)O\(_3\) catalyst showed that the latter is extremely active, selective and stable, and is suitable for industrial use.

Investigation of the Conversion of Cyclohexene on Pt-Zeolite Catalyst under Pressure of Hydrogen


Studies of cyclohexene and cyclohexene isomerisations on decationised zeolite, on CaY and on 0.5\% Pt/CaY show that on Pt/CaY the isomerisation of cyclohexene proceeds via formation of cyclohexene on Pt with subsequent isomerisation on the acid centres of the zeolite. The isomerisation of cyclohexene depends on temperature.

The Effect of Heat Treatment on the Catalytic Activity of Platinum Catalysts


Sintering studies on Pt black in vacuum at 300, 400, 500, 600 and 700°C indicate a second order relation between changes in the activity and surface area. Sintering produces a fixed activity and surface area for each temperature. The relation between activity and roasting temperature is exponential. Given the activity at two temperatures, an equation relating activity to temperature can be derived. Kinetics of decomposition of \(H_2O_2\) and of hydrogenation of cyclohexene on sintered black are similar. Specific activity is unrelated to the duration and temperature of sintering but change of surface area and size of crystals are.

Hydroisomerisation of Normal Pentane over a Zeolite Catalyst


A series of screening tests on zeolite hydro-
Hydrogenation and Hydrogenolysis, X. The Hydrogenation of Methoxy- and Ethoxyanilines with Rhodium Catalyst


Hydrogenation of alkoxyanilines with alkali-promoted Rh catalysts showed that Rh oxide prepared by fusion of RhCl₃ with LiNO₃ gives high yields of methoxy- and ethoxyhydroxyamines from methoxy- and ethoxyanilines respectively. <6% hydrogenolysis occurred and secondary amine formation was negligible. Studies with LiNO₃ replaced by NaNO₃, LiOH and NaOH are reported and less satisfactory yields were obtained. Best conditions appear to be 90°C, high Pₐno and use of LiNO₃ with RhCl₃ when ~2% catalyst: substrate is required.

The Hydrogenation of Olefins. Part 4. Reaction of n-Butenes with Hydrogen Catalysed by Alumina-supported Ruthenium and Osmium


Studies in a static system of product distributions, orders of reaction and activation energies for hydrogenation and isomerisation of but-1-ene, cis- and trans-but-2-ene at 0–70°C using 1 mol.% Ru/α-Al₂O₃ and at 60–140°C using 1 mol.% Os/α-Al₂O₃ show that Ru gives more isomerisation than Os. The suggested mechanism is isomerisation by loss of one H atom from adsorbed C₅H₁₀ to yield adsorbed C₅H₆ and H, and hydrogenation where the rate is determined by H addition to adsorbed C₅H₆ for each C₅H₆. Rate-determining steps for cis-trans isomerisation and double-bond migration are discussed.

The Hydrogenation of Alkadienes. Part II. The Hydrogenation of Buta-1,3-diene Catalysed by Rhodium, Palladium, Iridium, and Platinum Wires


Studies of buta-1,3-diene hydrogenation over Rh, Pd, Ir, and Pt wires showed that C₅H₁₀ compositions depended on temperature but not on activity, initial Pₐ or conversion up to 50%. C₅H₁₀ yield was zero on Pd and 1–15% on the other wires. But-1-ene was the main product; trans-cis ratios for but-2-ene were determined. Chemisorption of buta-1,3-diene by interaction of only one double bond became more important as the temperature rose. Hydrogenation activity of clean Ir was replaced by hydrogenolysis as C residues accumulated on it. CH₄ was the sole product of hydrogenolysis at 245°C on Ir of C₅H₁₀ to C₅H₁₀–C₅H₁₀, etc. Comparing wires with Al₂O₃-supported catalysts, reactions seem characteristic of the metal rather than of the type of catalyst.

Homogeneous Catalysis

Homogeneous Catalysis in the Reactions of Olefinic Substances. XI. Homogeneous Catalytic Hydrogenation of Short-chain Olefins with Dichlorobis(triphenylphosphine)platinum(II)-Tin(II) Chloride Catalyst


Studies of homogeneous hydrogenation of short-chain olefins with PtCl₆/(PPh₃)₂ and SnCl₄, 2H₂O catalyst mixtures showed that mono-olefins hydrogenate rapidly only when the double bond is terminal. Reduction of hexadiene and pentadiene isomers does not stop necessarily at the monoene stage. Dienes react most when both double bonds are terminal. Conjugation is not a necessary step before hydrogenation; short-chain conjugated diene isomers inhibited further reaction. Long-chain conjugated dienes are reduced since their larger size prevents formation of stable catalyst-diene complexes. Unsaturated nitriles are hydrogenated when the double bond is terminal; substituent groups on the β-C atom do not hinder this and the CN⁻ group remains intact.

A Palladium-catalysed Synthesis of Benzyl Esters from Methylenebenzenes


Liquid phase production of benzyl esters from methylenebenzenes takes place at moderate temperatures using Pd(OAc)₂-Sn(OAc)₂ catalyst and 1 atm air, e.g. toluene in CH₂COOH gives benzyl acetate. The secondary oxidation product benzyldiene diacetate is formed at high conversions. Other methylenebenzenes behave similarly. Xylenes undergo selective diacetoxylation in CH₂COOH to give α,α'-diacetates rather than α,ω-diacetates.

Palladium-catalysed Reactions of Unsaturated Compounds in Non-aqueous Solvents. Synthesis of Vinyl Acetate via Palladium Salt/Ethylene Complexes


The rate of the reaction of C₅H₁₀ with Pd(OAc)₂ in CH₂COOH to produce vinyl acetate increases considerably on addition of small amounts of NaOAc, LiCl or LiCl, Fe(OAc)₃ to the system. The reaction is first order with respect to both Pd(OAc)₂ and the additions. When using PdCl₄ and NaOAc the rate is proportional to them.
Catalytic Asymmetric Hydrogenation Employing a Soluble, Optically Active, Rhodium Complex


A catalyst precursor which contains optically active tertiary phosphine ligands is prepared by dissolving RhL₃Cl₃ complexes with L = tertiary phosphine in 1:1 v/v C₆H₆ : C₆H₅OH containing triethylamine and pressurising with H₂. Examples of its use are described.

Catalysis of Hydrogen Transfer by a Method Hypothetically Similar to Fermentation. VI. High-activity Hydrogenation Catalysts on the Basis of π-Complexes of Rhodium(I) with Amino Acids


Studies of Rh complex catalysts with N-phenylanthranilic acid and L-tyrosine showed that low-valent compounds are stabilised at the expense of reactions with aromatic rings and carboxyl groups. Both in solid and solution state the complex is supposedly the dimer \( \text{H}_2\{\text{Rh}(\text{phen})_2\text{Cl}_2\} \) but \( \text{H}_2 \) decomposes it to the monomer. The Rh complexes catalyse D exchange with \( \text{H}_2\text{O} \). A hydrogenation mechanism for trans-stilbene is suggested. \( \text{H}_2 \) is derived during hydrogenations of fumaric acid and acetylene derivatives by the cis-scheme.

Selective Homogeneous Hydrogenation of Alk-1-enes Using Hydridocarbonylris-(triphenylphosphine)ruthenium(II) as Catalyst


RhH(CO)(PPh₃)₃ efficiently catalyses homogeneous hydrogenation of unsaturated \( \text{RCH} = \text{CH}_2 \) compounds. For hex-1-ene and dec-1-ene in \( \text{C}_6\text{H}_6 \) solution the rate law is rate = \( k_1 \text{Kc [S][A}/(1 + \text{K}_1 [S]) \) where \([S]\) and \([A]\) are respectively concentrations of alk-1-ene and catalyst, \( \text{C} \) is \( \text{H}_2 \) concentration in solution, \( \text{K}_1 \) is the formation constant for an alkene intermediate complex, and \( k_1 \) is the rate constant for the rate-determining \( \text{H}_2 \) activation step. High selectivity for reduction of alk-1-ene is due to steric factors caused by the bulky triphenylphosphine groups.

Hydroformylation of Alkenes by Use of Rhodium Complex Catalysts


The inhibition period of trans-RhX(CO)(PR₃)₃ catalysts, where \( X \) - halogen and \( R = \text{aryl} \), is removed by addition of hydrogen halide acceptors and the halide complex forms a hydrido-species by hydrogenolysis. The principal catalytic species seems to be RhH(CO)(PPh₃)₂ formed by CO addition to RhH(CO)(PPh₃)₃, which is also formed by dissociation when RhH(CO)(PPh₃)₃ is dissolved in \( \text{C}_6\text{H}_6 \) or other solvents. Rapid hydroformylation of alkenes occurs at 250°C, 1 atm with RhH(CO)(PPh₃)₃ catalyst, giving a ratio of ~20 for the formation of straight- and branched-chain aldehydes from alk-1-enes. H₂ exchange and isomerisation of alkenes with RhH(CO)(PPh₃)₃ are described.

The Preparation and Reactions of Hydrochlorotris(triphenylphosphine)ruthenium(II) Including Homogeneous Catalytic Hydrogenation of Alk-1-enes


RuClH(PPh₃)₃\( \text{C}_6\text{H}_6 \) was prepared from RuCl₂(PPh₃)₃ and \( \text{H}_2 \) in ambient conditions in the presence of a base such as triethylamine. RuBrH(PPh₃)₃, \( \text{C}_6\text{H}_6 \), RuClH(C₆H₅)(PPh₃)₃, [RuClH(bipy)(PPh₃)₃] and RuH₂(CO)(PPh₃)₃ were also prepared. RuClH(PPh₃)₃ is the most active catalyst yet discovered for homogeneous hydrogenation of alk-1-enes in \( \text{C}_6\text{H}_6 \) or \( \text{C}_6\text{H}_5\text{CH}_3 \). It is highly specific but kinetic study is difficult and slow poisoning occurs.

Carbonylation of Acetylene with [Ru(CO)]₃ as Catalyst


Hydroquinone was prepared by carbonylation of \( \text{C}_6\text{H}_5\text{H}_2 \) under anhydrous conditions, in either tetrahydrofuran or dioxan as solvent, in the presence of [Ru(CO)]₃. Highest yields occurred at \( \text{pH}_2 = 5–10 \text{ atm.} \) Yields up to 65% hydroquinone were obtained by reacting \( \text{C}_6\text{H}_5\text{H}_2 \) with CO and \( \text{H}_2\text{O} \) or alcohols in the presence of [Ru(CO)]₃ at 150–250°C and relatively low \( \text{pCO} \).

FUEL CELLS

Electrocatalysts for the Direct Electrochemical Oxidation of n-Octane in Fuel Cells


Activity of supported and unsupported Pt prepared in various ways was compared with that of commercial Pt black. An increase in the specific area of a C substrate gave a corresponding increase in electrocatalytic activity up to at least 200 m²/g. Some types of Pt/C had 6–18 times the activity of Pt black. No current or voltage cycling occurred with 36 mol.% HF electrolyte at 105°C in contrast to other acid electrolytes.

Structure and Performance of Hydrophobic Gas Electrodes


Electron micrography showed that a catalyst pre-
pared by mixing Pt black with a dispersion of PTFE and applying it to a metal screen before drying and curing at 300°C consists of porous aggregates of Pt intermingled with PTFE. Performance is very dependent on microstructure. Whereas hydrophilic electrodes become flooded with electrolyte hydrophobic electrodes become full of gas and the whole thickness of the electrode is effective. The effect of catalyst surface area was studied using graphite powder as the catalyst.

CHEMICAL TECHNOLOGY

The Separation of Hydrogen from Ammonia Synthesis Exhaust Gases by the Method of Diffusion through Palladium


NH₃ synthesis is more economic when H₂ in the exhaust gas is purified and when Ar is recovered. Tests on such gas and on pure N₂-H₂ mixtures compared pure Pd and 5%-10% Ni-10% Ag-Pd foils for H₂ purification by diffusion at 400 and 500°C. Both gas mixtures gave similar results. Ag dusted on Pd foil activated the latter for H₂ diffusion.

TEMPERATURE MEASUREMENT

The Effect of Stress on the Thermal EMF of Platinum-Platinum/Rhodium Thermocouples


Variations in thermal e.m.f. with stress of Pt and 13% Rh-Pt wires with junctions at 20 and 550°C are -47 and -12 pV deg C⁻¹kg⁻¹cm⁻² respectively. The thermal e.m.f. hysteresis loop of some metal-sheathed mineral-insulated thermocouples is explained; the maximum discrepancy from this loop is 250μV at 550°C by calculation, 14μV by experiment on a single thermocouple. Mechanical hysteresis of the loop may cause fracture. A reliable thermocouple of this type needs matching expansion coefficients of sheath and thermocouple.

Comparison of Platinum Resistance Thermometers between 63K and 373.15K. Part I


Twelve Pt resistance thermometers were compared with a reference one at 63-273.15°C and at 373.15°C using a constant temperature bath with the thermometers inserted in a Cu block immersed in liquid iso-C₅H₁₂, C₆H₁₄, O₂, or N₂ and the differences of the reduced resistances W = R(t)/R(0°C) of them were determined. The number of calibration points to determine the W-T relation was studied and discussed.

A Direct-reading Bridge for a Platinum Resistance Thermometer


A Wheatstone bridge for a Pt resistance thermometer was modified so that the angle of rotation of a linear potentiometer is proportional to the temperature with bridge sensitivity fairly independent of temperature. Although not intended for high precision thermometry, irrespective of the inaccuracy of the thermometer itself the reading accuracy is to better than ±0.1 deg C at 0-500°C and the bridge can be used for both temperature control and temperature measurement.

NEW PATENTS

METALS AND ALLOYS

Methods of Improving the Mechanical Properties of Metals and their Alloys

JOHNSON MATTHEY & CO. LTD

British Patent 1,134,492

Pt metal alloy articles are given greater strength by cold working and annealing to give oriented recrystallisation.

Improvements in and Relating to the Treatment of Platinum Group Metals and Alloys

JOHNSON MATTHEY & CO. LTD

British Patent 1,139,897

An alloy having properties of oxidation resistance and high mechanical strength is made by alloying Pd with a minor amount of Cr capable of forming a stable refractory compound or alloying Rh or Pt (or Rh, Pt with another Pt-metal) with a minor amount of an element capable of forming a stable refractory compound (the element may be Be, Mg, Al, Si, Th, U or a transition metal) and heating (1000°C) the alloy in a gas (e.g. air or O₂) to form the refractory compound (e.g. oxide) in the alloy.

CHEMICAL COMPOUNDS

New Chemical Compounds

IMPERIAL CHEMICAL INDUSTRIES LTD

British Patent 1,138,867

These new chemical compounds are Pt group
metal alkyl carbonyl halides of formula \( \text{R. M. COX} \), where \( R \) is alkyl, \( X \) is halogen and \( M \) is Group VIII noble metal, e.g. \( \text{C}_2\text{H}_5\text{Pt.COCI} \). They are made by reacting \( \text{MX} \) with \( \text{HCOOH} \) and an olefine. No uses are given for the products.

**Osmium Carbonyl**  
**JOHNSON MATTHEY & CO. LTD**  
**British Patent 1,140,616**

Os carbonyls are prepared by heating (110-175°C) a solution of \( \text{OsO}_4 \) in a hydrocarbon solvent (e.g. xylene) inert to \( \text{OsO}_4 \) under super-atmospheric pressure (10-300 atm) in the presence of CO. The method yields \( \text{Os}_2(\text{CO})_8 \) and Os oxy-carbonyl.

**ELECTROCHEMISTRY**

**Method of Producing a Platinum Group Metal or Alloy Electrode**  
**AJINOMOTO CO. INC.**  
**British Patent 1,134,620**

Better Pt group metal plating adherence to clean surfaces, such as Ti surfaces, is obtained by first electroplating to deposit an alloy of a Pt group metal(s) and non-Pt group metal(s) and then dissolving out the latter from the plated coating. The final Pt alloy or Pt group metal is then electroplated on to the surface.

**Production of Gases by the Electrolysis of Water**  
**ALLIS-CHALMERS MFG CO.**  
**British Patent 1,139,614**

\( \text{H}_2 \) and \( \text{O}_2 \) are generated electrolytically at porous electrodes and diffused into separate chambers. The aqueous electrolyte saturates an electrolyte matrix and fresh electrolyte is passed through only one of the gas chambers. The gas in the other chamber is maintained at sufficient pressure to prevent inward leakage of electrolyte. The \( \text{H}_2 \)-generating electrode may be coated with a catalytic deposit of \( \text{Pt}, \text{Ir}, \text{Pd}, \text{Rh}, \text{Ru} \) or \( \text{Os} \).

**Electrolysis of Alkali Chloride by Mercury-Method**  
**ASAHI KASEI K.K.**  
**U.S. Patent 3,409,533**

Aqueous alkali chloride is electrolysed in a cell using a Pt-plated \( \text{Ti} \) anode and Hg cathode and operates at specified voltage, current-density and efficiency.

**Electrochemical Cell for Separation of Gaseous Mixture**  
**ALLIS-CHALMERS MFG CO.**  
**U.S. Patent 3,410,783**

An electrochemically active gas is separated from electrochemically inert gases by electrochemical reduction of the former to a solvated species at an activation electrode (porous Ag), transported through the electrolyte to the regeneration electrode (e.g. a Pt/Pd catalysed porous Ni electrode) and regenerated.

**Vacuum-metallised Electrode**  
**NATIONAL RESEARCH CORP.**  
**U.S. Patent 3,410,785**

A Ti electrode for electrochemical systems is vacuum coated with Pt < 0.0001 inch in thickness. This affords high resistance to flaking upon reversal of electric current in the electrochemical system.

**ELECTRODEPOSITION AND SURFACE COATINGS**

**Ceramic Pigments**  
**JOHNSON MATTHEY & CO. LTD**  
**British Patent 1,135,057**

A grey ceramic pigment for ceramic, glass and enamelled metal decoration contains elementary Ru, preferably mixed with a suitable carrier.

**Platinum Coating Process and Platinum Coated Materials**  
**JOHNSON MATTHEY & CO. LTD**  
**British Patent 1,135,514**

Catalytically active adherent Pt or combinations of at least 50 wt\% Pt with other Pt group metals are deposited, especially on fuel cell electrodes, by forming a dispersion of the relevant oxide or oxides of Pt group metals in a 2–5 C aliphatic alcohol. The oxides can be precipitated on the surface to be coated by adding a \( \text{H}_2\text{O} \)-soluble inorganic salt to the dispersion. The platinised substrate is then processed in the usual way.

**JOINING**

**Brazing Alloy for Joining Graphite to Graphite and to Refractory Metals**  
**U.S. ATOMIC ENERGY COMMISSION**  
**British Patent 1,133,309**

Graphite is joined to graphite or to Mo, W or their alloys using a brazing alloy containing 30–45 wt\% Ni, 43–68 wt\% Pd and 2–12 wt\% Cr.

**High Temperature Brazing Alloys for Tungsten and Tantalum**  
**U.S. ATOMIC ENERGY COMMISSION**  
**British Patent 1,136,980**

The alloy comprises 35–45 wt\% Ir and 65–55 wt\% W, optionally with 1–10 wt\% of the W replaced by Re.

**HETEROGENEOUS CATALYSIS**

**Selective Hydrogenation of Small Amounts of Acetylene in Ethylene of Gases Rich in Ethylene**  
**BADISCHE ANILIN-\& SODA-FABRIK A.G.**  
**British Patent 1,133,253**

The catalyst contains 0.01–1.0 wt\% PdSiO₄ having an internal surface area of 250–400 m²/g.
Simultaneous Preparation of Saturated Aliphatic Hydrocarbons Containing 1–4 C Atoms and Benzene with its Homologues from Light Virgin Naphtha

STAMICARBON N.V.  
**British Patent 1,133,263**

This process is catalysed by a dehydrogenation catalyst comprising 0.1–21% Pt on Al₂O₃ and/or SiO₂.

Preparation of Dinitriles from Acrylonitrile

E. I. DU PONT DE NEMOURS & CO.  
**British Patent 1,133,900**

The acrylonitrile is heated at 100–200°C and 3.5–635 Kg/cm² in the presence of metallic Ru, and gaseous H₂.

Hydrocatalytic Conversion of Hydrocarbons

BRITISH PETROLEUM CO. LTD  
**British Patent 1,134,014**

The selective hydrocracking of n-paraffins is catalysed by a Group VI or VIII metal or oxide deposited on a decationised mordenite having a SiO₂:Al₂O₃ ratio of 14:1. Pt is a suitable metal.

Catalysts

JOHNSON MATTHEY & CO. LTD  
**British Patent 1,134,111**

Catalysts for oxidation, reduction and other chemical reactions are intimate homogeneous mixtures (not pure mechanical mixtures) of one or more oxides of a Pt metal (excluding Os) and one or more oxides of Fe, Co, Ni and Cu.

A Process for Starting up a Reactor for the Catalytic Conversion of Hydrocarbons or a Hydrocarbon Mixture

SHELL INTERNATIONAL RESEARCH M.I.N.V.  
**British Patent 1,134,144**

A process for starting up a reactor containing a catalyst comprising Pt and halogen for the catalytic conversion of hydrocarbons or a hydrocarbon mixture, in which a fresh catalyst or a catalyst regenerated with the aid of O₂, steam and halogen (the Pt being present on the catalyst as a Pt-halogen compound or complex) is first dried by means of a preferably previously dried oxidative gas or gas mixture at a temperature of at least 480°C and at most 570°C till the H₂O content of the reactor off-gas is less than 150 ppmv. The catalyst, whether in the presence of the hydrocarbon feed to be converted or not, is subsequently reduced by means of dry H₂ at a temperature of 500°C.

Process for Reducing the Polymerisation and/or Condensation Tendency of Unsaturated Benzines Rich in Aromatic Substances

VEB LEUNA-WERKE WALTER ULRICH  
**British Patent 1,134,599**

Petrol fractions are stabilised by hydrogenation using a noble metal catalyst, such as Pd, deposited on a mixture of gibbsite and 1–20%; kaolin which has a surface area of more than 150 m²/g.

Fluoropyridines

NATIONAL RESEARCH DEVELOPMENT CORP.  
**British Patent 1,134,651**

Trifluoro- or tetrafluoropyridines can be obtained by hydrogenating chlorofluoropyridines, e.g. using PdC as catalyst.

Paraffinic Jet Fuel by Hydrocracking Wax

ESSO RESEARCH & ENGINEERING CO.  
**British Patent 1,137,639**

Jet fuel is produced by cracking a paraffinic wax feedstock over a catalyst, such as Pd on a zeolite, at 300–900°F, 500–3000 psig and 0.1–10 v/v% with added H₂.

Preparation of Dicarboxylic Acids

E. I. DU PONT DE NEMOURS & CO.  
**British Patent 1,138,131**

Cyclic olefins are oxidised to dicarboxylic acids by HNO₃ in the presence of an Os-V catalyst, e.g. in OsO₄·V₂O₅ or in metal form.

Preparation of Chlorine-substituted Aromatic Amines

GENERAL ANILINE & FILM CORP.  
**British Patent 1,138,567**

These amines are produced by the catalytic hydrogenation of corresponding chloroaromatic nitro compounds using a new catalyst system. This comprises (a) 0.05–0.08% of 1–5% Pt black or Pt or Pd on C or Al₂O₃, and (b) 0.05–0.5% triphenyl or tritolyl phosphite.

Preparation of Unsaturated Organic Esters

NATIONAL DISTILLERS & CHEMICAL CORP.  
**British Patent 1,139,210**

The contact catalysts in a process for the preparation of an unsaturated organic ester from an alkene and an O₂-containing gas comprise (a) a Pd- or Pt-group metal or metal compound supported on C, and (b) a Pd- or Pt-group metal or metal supported on Al₂O₃.

Oxidation of Ammonia

INVENTA A.G.  
**British Patent 1,139,849**

NH₃ is oxidised by mixing with O₂ in volume ratio NH₃ : O₂ of 1 : 1.10–1.27 and passing the mixture with steam over a Pt or Pt-Rh catalyst at a specified flow velocity at 800–950°C. The catalyst may be a Pt-Rh grid containing 90% Pt, 10%, Rh.

Preparation of Aryl Thiols

UNIROYAL INC.  
**U.S. Patent 3,399,238**

C₆H₆ and p-toluene thiols are produced by the hydrogenation of the corresponding aryl sulphuric acid over a PtS catalyst.

Platinum Metals Rev., 1969, 13, (2) 81
Production of 1-Naphthol
UNION CARBIDE CORP. U.S. Patent 3,402,210
The dehydrogenation of 3,4-dihydro-1-(2H)-naphthalenone is catalysed by a supported mixture of 0.25-5 wt% Pt metal and 0.25-1.5 wt% of Nd in the form of an inorganic compound, e.g. NdCl₃.

Hydrocracking Catalyst
STANDARD OIL CO. U.S. Patent 3,403,094
The catalyst comprises a known active Group VIB or VIII metal such as Pt deposited on a fluorided SiO₂-Al₂O₃ cracking catalyst and promoted with an alkali metal or alkaline earth metal.

Group VIII - Aluminosilicate Catalyst
PULLMAN INC. U.S. Patent 3,403,108
An improved catalyst for unsaturated ester production consists of an alkaline metal aluminosilicate with about 0.1-15 wt% of a Group VIII metal having an atomic number of at least 44 and a Fe(III), Cu, Cr or W halide, e.g. PdCl₂ and CuCl₂ on a zeolite.

Selective Hydrogenation of Olefins
SINCLAIR RESEARCH INC. U.S. Patent 3,404,192
The hydrogenation of straight chain olefins in the presence of branched olefins is catalysed by a Pt catalyst produced by treating a deactivated zeolite with H₂PtCl₆.

Hydrocracking Process
UNION OIL CO. OF CALIFORNIA U.S. Patent 3,405,056
When the H₂S concentration is low, the catalyst for hydrocracking may be a zeolite promoted with a partially (coke) - deactivated Group VIII noble metal (especially Pd).

Hydroxylammonium Salts
These salts are produced by the reduction of NO with H₂ in the presence of noble metal catalysts, e.g. Pt/C, which are periodically or continuously treated with O₂ to maintain the catalyst selectivity and activity.

Oxidation of Alcohols to Carboxylic Acids
SHELL OIL CO. U.S. Patent 3,407,220
Saturated aliphatic straight chain primary alcohols are selectively oxidised to the corresponding carboxylic acids in the presence of branched chain acids by using finely dispersed Pt as the catalyst.

Production of Methyl Pentamethylenediamine in Two Stages
NATIONAL DISTILLERS & CHEMICAL CORP. U.S. Patent 3,408,397
An apropiated dinitrile is reduced over a Pd or Pt catalyst and then the product is reacted with NH₃ and/or a tertiary amine in the presence of a catalyst containing Ru, Ni or Co.

Treatment of Combustible Wastes
UNIVERSAL OIL PRODUCTS CO. U.S. Patent 3,409,390
Noxious exhaust gases are oxidised by contacting under oxidising conditions with a catalytic composite essentially of Al₂O₃, a Pt-metal (0.01%-1% by wt) and an alkali earth component (>1%).

Catalytic Isomerisation of Saturated Hydrocarbons
UNIVERSAL OIL PRODUCTS CO. U.S. Patent 3,409,682
The catalyst for isomerisation of saturated hydrocarbons comprises at least one active catalytic component, preferably Pt, on an Al₂O₃ support in which not more than 20% of a finely divided crystalline aluminosilicate is dispersed.

Catalytic Isomerisation of Xylene
UNIVERSAL OIL PRODUCTS CO. U.S. Patent 3,409,685
Alkyl aromatic hydrocarbons are isomerised in contact with a Group VIII metal catalyst (e.g. Pt) on an Al₂O₃/alumino-silicate matrix and also in contact with about 0.001-2.0 wt% of an S-containing isomerisation promoter. See also U.S. Patent 3,409,686.

Dehydrogenation of Cycloparaffinic Hydrocarbons
UNIVERSAL OIL PRODUCTS CO. U.S. Patent 3,409,690
The catalyst for dehydrogenating cyclo-paraffinic hydrocarbons to aromatic hydrocarbons comprises a refractory inorganic oxide (e.g. Al₂O₃) containing at least one metal (e.g. Pt) from Group VIII of the periodic table, chemically combined with a metal subfluoride (e.g. AlF) vapour. See also U.S. Patent 3,409,699.

Catalytic Olefins Isomerisation
ETHYL CORP. U.S. Patent 3,409,702
ω-Olefines (4-24C) are effectively isomerised to β-olefines in a process using a catalyst of mixtures of Group VIII metals on an inert support, e.g. Rh, Pd, Ru and Pt on charcoal.

Catalytic Reforming
UNIVERSAL OIL PRODUCTS CO. U.S. Patent 3,410,789
Gasoline or naphtha fractions are reformed in contact with a refractory inorganic oxide (Al₂O₃) containing a Group VIII metal (Pt) which has been contacted with vapours of AlF or a Si subfluoride and a S-containing component (tert-butyl mercaptan). See also U.S. Patent 3,410,790.
Catalytic Transalkylation
UNIVERSAL OIL CO. U.S. Patent 3,410,921
A polyalkylated aromatic compound is trans-
alkylated by reacting the compound in admixture
with H₂ with alkylatable aromatic compound in
contact with a catalyst. The catalyst is preferably
a Group VIII metal (e.g. Ni, Pt, Pd; especially
Pt) on an alumino-silicate support under trans-
alkylating conditions.

Butyraldehyde Production
JOHNSON MATTHEY & CO. LTD
German Patent 1,278,420
The hydrogenation of crotonaldehyde
in the liquid phase using a trickle column reactor is
catalysed by Pd/Al₂O₃.

HOMOGENEOUS CATALYSIS
Production of Unsaturated Compounds
IMPERIAL CHEMICAL INDUSTRIES LTD
British Patent 1,138,366
Unsaturated diesters and diethers are produced
by contacting a conjugated diene with a carboxylic
acid or an organic hydroxy compound in the
presence of a salt (not a nitrate or sulphate) or co-
ordination compound of Pd, Pt, Ni, Fe or Co,
e.g. palladous acetate, chloride or acetyl-
acetone.

Improvement in Catalytic Reactions
G. WILKINSON British Patent 1,138,601
Hydrogenation, hydroformylation or carbonyla-
tion reactions are catalysed by a complex of a Pt
metal halide or pseudohalide and either (a) an
organic nitrile or (b) a N, P, As, Sb, Bi, S or Se
compound. For example (Ph₃As)₂RhCl₃ catalyses
the hydrogenation of hexyne-1 to C₆H₁₂.

Decomposition of Formic Acid
IMPERIAL CHEMICAL INDUSTRIES LTD
British Patent 1,138,946
The selective destruction of HCOOH in the
presence of CH₃COOH is achieved by oxidation
with O₂ using a catalyst system comprising a
soluble Pt compound and a redox system, e.g.
PdCl₂, LiCl, LiOAc and Cu(OAc)₂.

Production of Unsaturated Aliphatic Nitriles
ASAHI KASEI K.K.K.
British Patent 1,139,398
An unsaturated aliphatic nitrile is produced by
contacting a gaseous mixture of an olefinic hydro-
carbon, HCN and O₂ with a catalyst selected from
Pd metal, Pd compounds and mixtures consisting
predominantly of at least one of PdCl₂, CsBr and
SiO₂. Alternatively high temperature (~300°C)
may be used while feeding in simultaneously a
gaseous mixture of halogenated aliphatic nitrile
and hydrogen halide or halogenated aliphatic
nitrile, unsaturated aliphatic nitrile and hydrogen
halide.

Improvements in or Relating to the Production
of Silicon Compounds
IMPERIAL CHEMICAL INDUSTRIES LTD
British Patent 1,140,424
Organic silicone compounds (e.g. Cl₃SiCH₂CH₂
SiCl₃) are prepared by contacting a compound
containing at least one Si-H bond with an
organic compound containing at least one
acetylenic or olefinic bond in the presence of a
catalyst of general formula RhX(R'R''R''''Y)₃
where X is an anionic element or group, R', R'',
R'''' are organic groups and Y is As, Sb or Bi,
e.g. RhCl(Ph₃P)₃.

Oxidation of Aromatic Compounds
LUMMUS CO. British Patent 1,141,238
Aromatic compounds, having at least one un-
substituted position on the ring and free from any
unsaturated substituent groups, are oxidised to
phenols in the presence of an alcohol and a
Group VIII noble metal compound, e.g. C₆H₆
in the presence of PdCl₂, CuCl₂ and ethylene
glycol gives phenol.

Production of Lactones and Ketones
IMPERIAL CHEMICAL INDUSTRIES LTD
British Patent 1,141,353
Dienes are converted to cyclic ketones and lac-
tones by reaction with CO in the presence of Pd
and acid ions. The Pd is preferably in complexed
form as in Pd₁₂(PBu₃)₂.

Production of Polynuclear Aromatic Com-
ounds
GULF RESEARCH & DEVELOPMENT CO.
U.S. Patent 3,404,207
Polynuclear compounds are produced from
aromatic compounds having at least one labile
H atom by contacting them with a noble metal
salt of an organic acid in the presence of a strong
acid; halide and nitrate ions must be absent. A
typical catalyst consists of Pd acetate and HClO₄.

Saturated Aliphatic Nitrile Production
ASAHI KASEI K.K.K.
U.S. Patent 3,407,223
These nitriles are produced by the reaction of
C₆H₄ or C₅H₄ and HCN at 200–600°C in the
presence of Pd, Rh or their salts, H₃PO₄ and
ammonium thiocyanate, Al thiocyanate or AlCl₃.

Catalytic Ester Production
SHELL OIL CO.
U.S. Patent 3,407,224
The reaction of conjugated dienes and carboxylic
acids to produce 2,7-alkadienyl esters is catalysed
by a Pt, Pd or Ru compound activated by a
phenoxy anion. In an example PdCl₂ activated
by sodium phenate (NaOPh) is used to catalyse
the production of 2,7-octadienyl acetate from
butadiene and CH₃COOH.
Solutions of Noble Metal Compounds
Lummus Co. U.S. Patent 3,410,807
Stable homogeneous solutions suitable for the
catalytic oxidation of olefines, aromatic hydro-
carbons, CO and SO₂ are compounds of Group
VIII metals with a concentration of metal ion
between 0.01 and 0.0001 mol/l, mono- or poly-
hydric alcohols containing about 0.1-12% by vol.
of H₂O. The Group VIII metal compound is
preferably PdCl₂.

Catalytic Addition of Si-H to C=C and C≡C
Union Carbide Corp. U.S. Patent 3,410,886
Si-C compounds are produced by contacting a
compound containing at least one Si-H with an
aliphatic organic compound having C=C or
C≡C in the presence of a Pt (II) complex for
sufficient time to form the Si-C bond.

FUEL CELLS

Fuel Cells and other Galvanic Cells
Allmanna Svenska Elektriska A.B.
British Patent 1,133,921
Porous electrodes, e.g. made from Ni powder,
are now modified by adding 0.005-0.1% Pt
metal before sintering so that the added metal
lies in the active surface.

Fuel Cell Electrode
Standard Oil Co. of Indiana
U.S. Patent 3,405,007
Catalytic metals are deposited on porous con-
ducting supports by impregnating the support
with a compound of the metal (e.g. H₂PtCl₆)
and reducing carboxylic acid and then heating it.

Spinel-Ruthenium Catalysed Electrodes
Union Carbide Corp. U.S. Patent 3,405,010
Electrodes especially suitable for fuel cells consist
of a support treated with a heavy metal salt, an
Al salt and a Ru salt and then heated at 700-
900°C to form the required spinel. The heavy
metal may be Au and Ag, among other metals.

Hydrogen Control in Fuel Cells
H₂ is generated from carbonaceous fuel reforma-
tion for passage to a fuel cell where a permeable
Pd membrane is used to control current genera-
tion. In 3,407,095 a Pd-containing film is used.

CATHODIC PROTECTION

Anode Assembly for the Internal Cathodic
Protection of Pipes against Corrosion
W. C. Heraeus G.m.b.H.
British Patent 1,133,285
The anode is made with a surface of Ti, Ta, Nb
or an alloy of one of these metals coated with a
Pt group metal wound round helically with a
plastic insulator.

CHEMICAL TECHNOLOGY

Improvements in or Relating to Gas Per-
meable Diaphragm
Energy Conversion Ltd
British Patent 1,139,501
A gas-permeable diaphragm comprises a non-
porous gas-permeable metallic member (Pd)
adhering face to face with a non-porous sheet of
polymeric material permeable to at least the same
gases as the metal.

Hydrogen-Permeable Membrane and Hydro-
gen Permeating Assembly
Japan Gas-Chemical Co.
British Patent 1,140,952
A H₂-permeable membrane of Pd or Pd-alloy
(0.3-0.005 mm thick) is characterised by a
plurality of convexities protruding in the direction
of the thickness of the membrane and concavities
surrounding these convexities so that it has a
wavy configuration longitudinally and laterally.
The Pd-alloy may be Pd-Ag-Au.

ELECTRICAL AND
ELECTRONIC ENGINEERING

Semiconductor Devices
C.R.D. Praha, Oborovy Podnik
British Patent 1,135,068
Junction problems between semiconductor wafers
in pressure contact with electrode contact plates
are overcome by applying a layer of Rh to both
contact surfaces.

Electrical Resistance Element
International Business Machines Corp.
U.S. Patent 3,411,122
A laminated electrical resistance structure con-
­sists of an insulating base supporting a conductive
layer of a finely divided metal and metal oxide
(e.g. Pd-Ag, Pd oxide or In oxide) and a layer of
a polyimide condensation product.

TEMPERATURE
MEASUREMENT

Thermistor Compositions
E. I. Du Pont de Nemours & Co.
U.S. Patent 3,408,311
Thin film thermistors with a negative coefficient
of resistance are produced by applying and firing
(on a substrate) a mixture of finely divided Pd
mixed with up to 60% Ag and an inorganic
binder as before but now also a finely divided
mixture of Co₃O₄ and MnO₂.