

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

The Properties of Platinum-Cobalt Magnets Produced by Powder Metallurgy

H. C. ANGUS, *Powder Metallurgy*, 1964, 7, (13), 1-12
Co-Pt alloy magnets prepared from Pt and Co powders are superior to those prepared by melting. Fabrication and testing are described. Careful heat treatment is vital. The equiatomic stoichiometric alloy gives the best results. Energy products $> 10^7$ gauss-Oe and coercive forces up to 4900 Oe have been obtained.

The Magnetic Structure of CoPt

B. VAN LAAR, *J. Physique*, 1964, 25, (5), 600-603
X-ray diffraction showed that tetragonal CoPt has $a = 2.677$ Å, $c = 3.685$ Å. Magnetic moments point along the c -axis. Co at (0, 0, 0) and Pt at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) are coupled ferromagnetically.

Ordering in CoPt-CrPt and CoPt-MnPt Alloys

J. C. WOOLLEY, J. H. PHILLIPS and J. A. CLARK, *J. Less-Common Metals*, 1964, 6, (6), 461-471

Ordering effects in the Co-Cr-Pt system were studied by taking CoPt-CrPt alloys with equal increments of composition and determining lattice parameter values for ordered and disordered structures, and by X-ray methods estimating ordering temperatures and the type of ordering reaction. Similar studies on the Co-Mn-Pt system showed that alloys containing > 20 at.% Mn do not have the CoPt-type ordering reaction.

Relations between the Structures of Phases in the System Platinum-Molybdenum

H. P. ROOKSBY and B. LEWIS, *J. Less-Common Metals*, 1964, 6, (6), 451-460

Crystal structure changes occurred in Pt-coated Mo wire above 800°C as Mo diffused into Pt, forming successively the intermediate phases β -Pt₃Mo, γ -Pt₃Mo, δ -Pt₃Mo₂ and ϵ -PtMo₃.

The System Platinum-Aluminium

R. HUCH and W. KLEMM, *Z. anorg. allgem. Chem.*, 1964, 329, (1-6), 123-135

X-ray and thermal analyses revealed the intermetallic phases PtAl₄, PtAl₃, PtAl₂, Pt₅Al₃, PtAl, Pt₃Al₂, Pt₅Al₃, Pt₃Al and Pt₁₃Al₃. Pt₂Al₃ has hexagonal Ni₂Al₃-type structure with $a = 4.209$, $c = 10.35$ Å. Pt₅Al₃ has rhombic Th₅Ge₃ structure with $a = 5.41$, $b = 10.70$, $c = 3.95$ Å. Pt₃Al has cubic Cu₃Au-type structure with $a = 3.876$ Å. Molecular volumes are discussed. Pt-rich alloys contract strongly; Al-rich alloys dilate strongly.

Lattice Constants and Thermodynamic Parameters of the Hydrogen-Platinum-Palladium and Deuterium-Platinum-Palladium Systems

A. MAELAND and T. B. FLANAGAN, *J. Phys. Chem.*, 1964, 68, (6), 1419-1426

Absorption isotherms at 25°C and thermodynamic parameters of D₂ absorption were measured for 0, 2.79, 5.73, 8.80 and 12.03% Pt-Pd alloys. The effect of D₂ content on the relative resistance of the alloys was compared with data from the H-Pt-Pd system.

The Palladium-Uranium Phase Diagram up to 25 at.% Uranium

G. P. PELLIS, *J. Inst. Metals*, 1964, 92, (12), 416-418

X-ray diffraction and metallographic studies of U-Pd alloys with < 25 at.% U showed two eutectoidal transformations: at 13.5 at.% U, 694°C giving Pd₁₇U₂ and Pd₁₁U₂; at 15.5 at.% U, 1015°C giving Pd₁₁U₂ and Pd₅U. Pd₅U formed peritectically at 18.8 at.% U, 1440°C. Pd₁₇U₂, Pd₁₁U₂ and Pd₅U₂ have non-cubic structure. They and Pd₄U, formed peritectically at 21 at.% U, 1525°C with Cu₃Au-type structure, all have small solubility ranges. Pd₃U was detected above 20.8 at.% U. The variation of electrical resistivity with composition was determined up to 15.5 at.% U.

Melting Equilibrium in the Ternary System Cobalt-Manganese-Palladium

G. ZWINGMANN, *Metall*, 1964, 18, (7), 708-710

Thermal analysis and metallographic examination of the Co-Mn-Pd system showed that the two Mn-Pd eutectics are joined by a continuous series of eutectics in the ternary region with temperature minima at 1140 and 1210°C on either side of a maximum at 1330°C. Less than 3% Co is soluble in β -phase alloys.

The Thermal Decomposition of Rhodium (III) Oxide and the Influence on Alloying with Platinum and Palladium

N. G. SCHMAHL and E. MINZL, *Z. phys. Chem. (Frankfurt)*, 1964, 41, (1-2), 78-96

The decomposition of Rh₂O₃ at 900-1100°C was studied. RhO and Rh₂O were not detected but RhO₂ evaporated from Rh. The temperature dependence of the layer on Rh affected by O₂ was studied. Pt powder additions to Rh₂O₃ showed that the O₂-pressure from decomposition was a function of Rh-Pt alloy composition but was only slightly temperature-dependent. Results were discussed in relation to NH₃-oxidation at Rh-Pt contacts and to thermocouple oxidation. The Rh-Pd-O₂ system was also tested.

The Constitution Diagram Tantalum-Rhodium

B. C. GIESSEN, H. IBACH and N. J. GRANT, *Trans. Met. Soc. A.I.M.E.*, 1964, **230**, (1), 113-122

The system was studied by X-ray and metallographic methods and by thermal analysis. Five intermediate phases were detected: σ , tetragonal FeCr-type; α_1 , orthorhombic; α_2 , orthorhombic Co_2Si -type; α_3 , structure unknown, α -TaRh₃, cubic AuCu₃-type. σ , α_1 , α_2 and α_3 melt peritectically and α -TaRh₃ has a maximum melting point.

New Intermediate Phases in Systems of Nb or Ta with Rh, Ir, Pd or Pt

B. C. GIESSEN and N. J. GRANT, *Acta Cryst.*, 1964, **17**, (5), 615-616

The existence of 18 new phases in these systems is reported, together with data on their crystal structures.

The Osmium-Iridium Equilibrium Diagram

R. D. REISWIG and J. M. DICKINSON, *Trans. Met. Soc. A.I.M.E.*, 1964, **230**, (3), 469-472

The Os-Ir equilibrium diagram exhibits a peritectic temperature of about 2660°C with a miscibility gap between 42 and 63 wt.% Os. Two-phase specimens near the boundaries of the miscibility gap led to the discovery of Widmannaeschen figures and accounted for a previously suspected transformation. (7 figs.)

The Ruthenium-Iridium Alloys

E. RAUB, *Z. Metallkunde*, 1964, **55**, (6), 316-319

The high mutual solubility of Ru and Ir was indicated by X-ray and metallographic studies, with the binary phase at 2000°C extending from 46 to 52 at.% Ir. Ir-rich solid solutions showed greater temperature dependence of the solubility curve. Completely homogeneous supersaturated alloys cannot be obtained by cooling from high temperatures. Secondary spectral bands for Ru-rich phase alloyed with 55 at.% Ir are due to spinodal decomposition to an extent depending on the treatment.

The Palladium-Iridium Alloys

E. RAUB and E. RÖSCHEL, *Ibid.*, 320-321

X-ray and metallographic studies confirmed that Pd-Ir solid solutions do not form from the melt by a peritectic reaction. A continuous series of solid solutions exists from the miscibility gap to the liquid state.

The Structure of Solid Iron-Iridium Alloys

E. RAUB, O. LOEBICH and H. BEESKOW, *Ibid.*, (7), 367-370

An h.c.p. phase in the Fe-Ir system was found by X-ray diffraction. Transformation occurred at about 470°C, 19 at.% Ir. Maximum formation temperature was 625°C, 38 at.% Ir. The phase showed a wide range of homogeneity.

The Constitution Diagram Tungsten-Ruthenium

E. J. RAPPERPORT and M. F. SMITH, *Trans. Met. Soc. A.I.M.E.*, 1964, **230**, (1), 6-11

The system was studied by X-ray and metallographic methods and by electron microprobe analysis. Terminal solid solutions have 23 at.% maximum solubility of Ru in W at 2300°C and 48 at.% W in Ru at 2205°C. Solubilities decrease at lower temperatures. σ -phase W_3Ru_2 forms peritectically at 2300°C and decomposes eutectoidally at 1667°C to α -W and β -Ru. An eutectic occurs at 45 at.% Ru, 2205°C and yields σ -phase and β -Ru.

Vapour Pressures of Ruthenium and Osmium

N. J. CARRERA, R. F. WALKER and E. R. PLANTE, *J. Res. Nat. Bur. Stds., Pt. A*, 1964, **68A**, (3), 325-330

A modified Langmuir method with a microbalance technique measured the vapour pressures of Ru and Os and their heats of sublimation at 298°K. For Ru: $\log P_{\text{atm}} = -7.500 - 32,769/T$ at 1940-2377°K; $\Delta H_s(298) = 156.1 \pm 1.5$ kcal/mole; the boiling point is $4150 \pm 100^\circ\text{K}$. For Os: $\log P_{\text{atm}} = 7.484 - 39,880/T$ at 2157 - 2592°K; $\Delta H_s(298) = 189.0 \pm 1.4$ kcal/mole; b.p. is $5300 \pm 100^\circ\text{K}$.

Some Experiments on the Osmium-Carbon and Ruthenium-Carbon Systems

B. JEANTET and A. G. KNAPTON, *Plansseber. Pulvermet.*, 1964, **12**, (1), 12-18.

Attempts to prepare carbides of Os and Ru were unsuccessful. Doubt is cast on the report of their preparation by Kempter and Nadler.

Mechanical Properties of Several Nickel-Platinum-Group Metal Alloys

W. L. PHILLIPS, *Trans. Met. Soc., A.I.M.E.*, 1964, **230**, (3), 526-529

Tension tests at 25, 500, 800 and 1000°C and stress-rupture tests at 650 and 800°C on 0.5, 2.0 and 6.0 at.% Os-, Pd-, Ru-, and Rh-Ni alloys showed that room- and elevated-temperature tensile strengths, as well as stress-rupture life, increase at the same Pt-metal content in the order Pd, Rh, Ru, Os. Ductility decreases with increasing Pt-metal content or with temperature at a given concentration of Pt-metal. These results are discussed in relation to solid-solution theory.

Specific Heats and Magnetic Susceptibility of Superconducting Binary Complex Phases of Transition Metals

E. BUCHER, F. HEINIGER and J. MÜLLER, *Phys. kondens. Materie*, 1964, **2**, (3), 210-240

Measurements are described and results presented for 15 phases with σ - and χ -structures both in the normal and in the superconducting states. Among the alloys are phases from the systems Nb-Os, Nb-Rh, Nb-Ir, Nb-Pd, Nb-Pt, Mo-Ru, Mo-Os and W-Ir.

ELECTROCHEMISTRY

A Simple Method for Determining the Cleanliness of a Platinum Anode

S. SCHULDINER and T. B. WARNER, *J. Phys. Chem.*, 1964, **68**, (5), 1223-1224

The linearity of the voltage-time curve in the atomic O adsorption region can serve as a reliable index of electrode cleanliness. Oscilloscope traces illustrate this for a Pt bead electrode in 1 M H₂SO₄. The true area of the clean Pt electrode can be derived also.

The Relative Electrocatalytic Activity of Noble Metals in the Oxidation of Ethylene

H. DAHMS and J. O'M. BOCKRIS, *J. Electrochem. Soc.*, 1964, **111**, (6), 728-736

Complete anodic oxidation of C₂H₄ to CO₂ occurred at Pt, Ir, and Rh electrodes but on Au and Pd the main products were aldehydes and acetone with hardly any CO₂. The electrolyte was 1 M H₂SO₄ at 80°C and the cell is described. The orders of reactivity for the two groups of electrocatalysts were Pt > Rh > Ir and Pd > Au.

The Mechanism of the Electro-Oxidation of Acetylene on Platinum

J. W. JOHNSON, H. WROBLOWA and J. O'M. BOCKRIS, *Ibid.*, (7), 863-870

Parameters for C₂H₂ oxidation on platinised Pt gauze electrodes were determined at 80°C in solutions of H₂SO₄+Na₂SO₄ and NaOH of constant ionic strength. Reaction rates depended on potential, pH, and pC₂H₂. Coulombic efficiency, measured as CO₂ production in acidic solutions and C₂H₂ production in alkaline solutions, was 100 ± 1% in acid, 95 ± 5% in alkali. Heats of activation and passivation effects were also measured.

Hydrogenation of Ethylene at Palladised Palladium and Platinised Platinum Electrodes

L. D. BURKE, C. KEMBALL and F. A. LEWIS, *Trans. Faraday Soc.*, 1964, **60**, (5), 913-918

Hydrogenation of Acetylene at Palladised Palladium and Platinised Platinum Electrodes

L. D. BURKE, F. A. LEWIS and C. KEMBALL, *Ibid.*, 919-929

Electrocatalytic hydrogenation of C₂H₄ and of C₂H₂ dissolved in aqueous solutions of HCl and NaOH was measured at 25 and 50°C and results compared, using H₂ preadsorbed on Pd as well as electrolytic H₂. C₂H₆ was produced from C₂H₄ and C₂H₆ and C₂H₄ were produced from C₂H₂, as shown by gas chromatography. Electrolytic H₂ was most efficient with C₂H₂ at palladised Pd electrodes in alkaline solution. C₂H₄ was reduced to C₂H₆ at a rate dependent on olefin diffusion through the Brunner-Nernst boundary layer on the electrode surface.

ELECTRODEPOSITION AND SURFACE COATINGS

Vapour Deposition of Pure Ruthenium Metal from Ruthenocene

D. E. TRENT, B. PARIS and H. H. KRAUSE, *Inorg. Chem.*, 1964, **3**, (7), 1057-1058

99.99% pure Ru film was deposited from bis-(cyclopentadienyl) ruthenium at 595°C in a stream of H₂ on the inside of a Vycor tube in which the reaction took place. Ruthenocene, which has an appreciable vapour pressure at relatively low temperatures, was carried by the gas stream to the point of deposition. A non-uniform deposit formed on the graphite susceptor used for heating.

LABORATORY APPARATUS AND TECHNIQUE

The Weight Constancy of Rhodium and Iridium Vessels during Analytical Operations

G. REINACHER, *Werkstoffe u. Korrosion*, 1964, **15**, (6), 451-457

Rh and Ir crucibles plated with Pt and unplated were tested in various analytical operations. Unplated vessels were tarnished after heating at 800-1000°C. Rh had gained some weight at 1000°C but Ir tended to lose it by 900°C. Both resisted attack by HNO₃ and HCl better than Pt. KHSO₄ fusion at 400°C had no effect but, at 600°C, Rh was attacked. Rh resisted attack during NaHCO₃ fusion better than Ir. Vessels covered with Pt had the usual good resistance of Pt.

CATALYSIS

Chemisorption and Surface Chemistry of Ethylene on Supported Platinum Catalysts

P. J. LUCCHESI, J. L. CARTER and J. H. SINFELT, *J. Am. Chem. Soc.*, 1964, **86**, (8), 1494-1497

Comparisons of C₂H₄ chemisorption and surface chemistry on Al₂O₃ and 0.6 and 1.0 wt. % Pt/Al₂O₃ catalysts showed that identical species formed on them with different reactivities. H₂ treatment removed adsorbed species more easily from Pt/Al₂O₃ than from Al₂O₃, suggesting that migration of reactive species between Pt and Al₂O₃ centres may be an important mechanism. Desorption products of this treatment were mainly C₂H₆ and *n*-C₄H₁₀ at 100-150°C, with more CH₄ and C₃H₈ at higher temperatures.

Reactions of Some C₉ Aromatics on Platinum-Alumina Catalysts

F. E. SHEPARD and J. J. ROONEY, *J. Catalysis*, 1964, **3**, (2), 129-144

When *n*-propylbenzene, ω -methylstyrene, and *o*-ethyltoluene reacted with excess H₂ over Pt/ γ -Al₂O₃ in the range 337 to 490°C and when indane reacted at 337, 392, and 434°C, equilibrium

between olefins and corresponding paraffins by hydrogenation and dehydrogenation occurred rapidly. Dehydrocyclisation of the substituted benzenes gave indane, the C₉ ring of which was hydrogenolysed to give the isomeric alkylbenzene without reaching equilibrium. Product analyses and tests on catalysts with varying composition, sintering and thiophene poisoning showed that the reactions depended on the state of the supported Pt.

Hydrogenolysis of Cyclopentane Hydrocarbons in the Presence of Platinum on Alumina

I. V. GOSTUNSKAYA, HO CHIN-FYN and B. A. KAZANSKII, *Izv. Akad. Nauk. S.S.S.R., Ser. Khim.*, 1964, (5), 832-836

The hydrogenolysis of cyclopentane, methylcyclopentane, and ethylcyclopentane was studied using 9.8% Pt/Al₂O₃ catalyst at 230 to 280°C. Apparent activation energies were determined; for the alkylcyclopentanes these were lower than for cyclopentane itself. The products were linear and branched alkanes.

Hydrogenolysis of Cyclopentane Hydrocarbons in the Presence of Platinum Supported on Silica Gel

Ibid., (6), 1073-1077

The apparent activation energies of hydrogenolysis of methyl- and ethylcyclopentanes on Pt/SiO₂ at 210-260°C are less than that for cyclopentane. The deactivating effect of alkyl groups on 5-membered rings was clearly apparent.

Catalytic Conversion of Cyclopentane and its Homologues in the Presence of Platinum Supported on Aluminosilicate

Ibid., 1078-1082

Conversions over Pt/SiO₂-Al₂O₃ were studied at atmospheric pressure in the 200-270°C range. At 200-235°C hydrogenolysis of cyclopentane and methylcyclopentane was selective and the apparent activation energy of the reaction could be calculated. Ethylcyclopentane was not selectively hydrogenolysed but most of it was isomerised to methylcyclohexane. The temperature coefficient of isomerisation was less than that of dehydrogenation of methylcyclohexane. At 230-270°C, there was less hydrogenolysis of ethylcyclopentane as the temperature rose.

Desorption of Hydrogen from Platinum Catalysts

Y. KUBOKAWA, S. TAKASHIMA and O. TOYAMA, *J. Phys. Chem.*, 1964, 68, (5), 1244-1245

1.15 wt.% Pt/Al₂O₃, Pt/SiO₂, and Pt black catalysts all have nearly the same minimum and maximum heats of adsorption and exhibit two types of adsorption of H₂. The activation energy of desorption E for 1.15 wt.% Pt/Al₂O₃ was almost constant at 10 kcal/mole below room temperature and rose to 23 kcal/mole at about 300°C. H₂ was

chemisorbed on the catalyst at 300°C, the catalyst was cooled in H₂ to -52°C and then heated in stages. At -52°C the H:Pt ratio was nearly 1, indicating high Pt dispersion.

On the Hydrogenation of Dimethylenecyclobutane

YA. M. SLOBODIN and A. P. KHITROV, *Zh. Obshch. Khim.*, 1964, 34, (6), 1727-1728

During the hydrogenation over PtO₂ of 1,2-dimethylenecyclobutane, *cis*- and *trans*-1,2-dimethylcyclobutane were formed. Similar hydrogenation of 1,3-dimethylenecyclobutane caused some breaking of the 4-membered ring and the formation of 2-methylpentane.

Catalytic Reduction of Aromatic Nitrocompounds. XIV. Reduction of Nitrobenzene on Platinum Black

V. P. SHMONINA, *Ibid.*, 2020-2026

Nitrobenzene was reduced over Pt black in tests in the range 0-50°C, 40-80% C₂H₅OH solution. Addition of 0.1 N KOH or 0.1 N HCl to the solution retarded the reaction.

Tritium-labelling of Natural Products

R. MAURER, M. WENZEL and P. KARLSON, *Nature*, 1964, 202, (4935), 896-898

Tritiation of pure digitogenin by the charcoal adsorption method combined with Pt catalysis was almost 100 times faster than by the Wilzbach technique at room temperature and gave specific activities three times better than with charcoal adsorption alone. Digitogenin in C₆H₆/C₂H₅OH was shaken with 10% Pt/C, exposed to 2c T₂ for 7.5h, separated and tested.

Shifts of Double Bonds in Hexenes in the Presence of Platinum Catalysts

N. B. DOBROSERDOVA, G. S. BAKHMET'EVA, A. I. LEONOVA, I. V. GOSTUNSKAYA and B. A. KAZANSKII, *Neftekhimiya*, 1964, 4, (2), 215-218

Catalytic isomerisation under partial hydrogenation conditions by Pt black and Pt/C was studied on hexenes with double bonds in the α -position (hexene-1; 2-, 3- and 4-methylpentene-1; 2,3-dimethylbutene-1). Different forms of H₂ are believed to cause double-bond transfer and hydrogenation. Isomerisation increases when more H₂ dissolves in the catalyst metal; hence Pd is more active than Pt.

Catalytic Conversions of Spiro-(5, 6)-dodecane on a Platinum Catalyst

N. V. ELAGINA, A. K. MIRZAEVA, KH. E. STERIN, A. V. BOBROV and B. A. KAZANSKII, *Ibid.*, 241-245

66% of spiro-(5, 6)-dodecane was converted over Pt/C at 320°C. C-C bond rupture occurred at the quaternary C atom, followed by isomerisation and dehydrogenation. Principal product was diphenyl, produced by dehydrogenation via dicyclohexyl. Minor products were *n*-hexylbenzene, benzocycloheptane and 1, 2-benzobicyclo-(0,3,3)-octane.

On a Series of Hydrogen Additions to Double Bonds of 4-Vinylcyclohexane-1 on Pt- and Ni Catalysts

L. KH. FREIDLIN, A. F. PLATE, I. F. ZHUKOVA and B. A. BELINKOVA, *Ibid.*, (3), 382-385

When 4-vinylcyclohexene-1 was hydrogenated over Pt/C and Raney Ni the first double bond affected was that outside the ring. Product ratios of 4-ethylcyclohexene-1 and ethylcyclohexane were ~3:1 on Pt/C and ~9:1 on Raney Ni.

Catalytic Conversion of 1,1-Dimethyl-cyclohexane on Platinum Catalyst at Elevated Temperature and Hydrogen Pressure

S. I. KHROMOV, D. CHULTEM and E. S. BALENKOVA, *Ibid.*, 413-416

Toluene was the principal product of conversion of 1, 1-dimethylcyclohexane over 1% Pt/C at 320 and 460°C, and 20 atm H₂. Meta- and ortho-xylene were the chief products over 1% Pt/Al₂O₃ at 400-460°C, and 20 atm H₂.

Catalytic Conversion of *n*-Amylbenzene on Platinum Catalyst

A. K. MIRZAEVA, N. V. ELAGINA, KH. E. STERIN, A. V. BOBROV and B. A. KAZANSKII, *Ibid.*, 417-420
n-Amylbenzene was dehydrogenated over 15% Pt/C at 320°C and converted into α -ethylindane, α -methyl-naphthalene, β -methyl-naphthalene and naphthalene, which were determined by chromatography.

Olefin Isomerisation with Noble Metal Catalysts

J. FALBE and F. KORTE, *Brennstoff-Chem.*, 1964, 45, (4), 103-105

Pd/C and Pt/C were shown to be good catalysts for the isomerisation of butene-2 and pentene-2 to mixtures of the corresponding olefin isomers. The amount of isomerisation of pentene-2 using RhCl₃ and IrCl₃ as catalysts during the formation of CO-compounds of Rh and Ir was also studied.

Stereoisomeric Conversion of Individual *cis*- and *trans*-3-Methylpentene-2 in Liquid Phase Catalytic Hydrogenation Conditions

I. V. GOSTUNSKAYA, A. I. LEONOVA and B. A. KAZANSKII, *Neftekhimiya*, 1964, 4, (3), 379-381
Isomerisation of each of *cis*- and *trans*-3-methylpentene-2 in alcoholic solution increased with catalysts in the order Pt < Ni < Pd. Low boiling-point isomers reacted faster than those of higher boiling-point. Minor products included 3-methylpentane and 2-ethylbutene-1.

Homogeneous Catalysis. I. Double Bond Migration in *n*-Olefins, Catalysed by Group VIII Metal Complexes

J. F. HARROD and A. J. CHALK, *J. Am. Chem. Soc.*, 1964, 86, (9), 1776-1779

Catalysis of double bond migration in linear olefins by Pt metal complexes yielded equilibrium

distribution of isomers. The effects on reaction rates, cocatalysts, and isomer distribution of the metal ions, their oxidation state, and their ligand attachments were studied. When suitable cocatalysts were present, 1-hexene was isomerised by dichlorobis(ethylene)dichlorodiplatinum(II), RhCl₃·3H₂O isomerised 1-hexene, *cis*- and *trans*-2-heptene, Pd(II) complexes catalysed similar reactions until reduced to Pd, and IrCl₃ behaved like Pt(II).

On the Mechanism of Hydrogenation of Dienes with Linked Double Bonds on Palladium Catalyst

L. KH. FREIDLIN and E. F. LITVIN, *Neftekhimiya*, 1964, 4, (3), 374-378

The composition of olefins derived from hydrogenation over Pd black of isoprene, 2,3-dimethylbutadiene, 3-methylbutene-1, and 2,3-dimethylbutene-1 depended on the point of H₂ addition or on the amount of isomerisation before desorption at the catalyst. Olefins produced were not isomerised in the presence of the diene.

Study of the Partial Catalytic Hydrogenation of Nitrocyclohexene

P. GUYER and H. J. MERZ, *Chimia*, 1964, 18, (4), 144-146

When nitrocyclohexene was hydrogenated in the presence of Pd/C, the double bond was attacked 7.8 times more quickly than with Pt/C, but with Pt/C the NO₂ was reduced 1.8 times more quickly than with Pd/C. Hydrogenation of nitrocyclohexene with Pd/C therefore leads principally to cyclohexylhydroxylamine but with Pt/C the reaction can be selective for cyclohexanonoxime.

The Activation on Palladous Chloride by Metal Ions in the Homogeneous Hydrogenation of Ethyl Crotonate

E. B. MAXTED and S. M. ISMAIL, *J. Chem. Soc.*, 1964, (May), 1750-1752

10⁻⁴M aqueous solutions of acetates of Cu, Ni, Zn, Ag, Hg, Cd, Na and Ca, and of chlorides of Cu, Ni, Co, Al, Mg, Ce and Cr were tested as promoters of 1% PdCl₂ solution as catalyst for the hydrogenation of ethyl crotonate. Activation was successful at as low as 30°C, 1 atm. Na⁺ was most active, increasing the activity of PdCl₂ by up to seven times. Decrease in activity and the precipitation of Pd as the reaction proceeded indicated a homogeneous reaction in which individual Pd atoms in PdCl₂ are catalysts.

Investigations of the Hydrogenation Reactions of Olefins and Dienes in the Presence of Rhodium Black

L. KH. FREIDLIN, E. F. LITVIN and L. M. KRYLOVA, *Neftekhimiya*, 1964, 4, (2), 185-189

Rh black catalysed liquid phase hydrogenations of dienes, (*cis*-piperylene, isoprene and 2,3-dimethyl-

butadiene) and olefines (pentene-1, *cis*- and *trans*-pentene-2, 3-methylbutene-1 and 2,3-dimethylbutene-1) with selectivity close to that of Pt black and isomerisation properties (double-bond transfer and *cis-trans* isomerisation) intermediate to those of Pd and Pt black.

Synthesis of High-Molecular-weight Paraffins from Carbon Monoxide in Aqueous Suspensions of Ruthenium

H. KÖLBEL, W. H. E. MÜLLER and H. HAMMER, *Makromol. Chem.*, 1964, **70**, 1-11

Paraffin waxes with melting points up to 131°C and mol. wt. up to 7000 were synthesised by feeding CO into an aqueous suspension of finely divided, metallic Ru at 75-200 atm, 150-260°C. $\Delta H = 57.2$ kcal/mole wax. 100% CO-conversion was possible. CO₂, CH₄ and H₂ were byproducts. H₂O acted as reactant, suspension liquid, coolant and heat transfer medium.

Polymethylene from Carbon Monoxide and Hydrogen

H. PICHLER, B. FIRNHABER, D. KIOUSSIS and A. DAWALLU, *Ibid.*, 1964, **70**, 12-22

Polymethylene, similar to low-pressure polyethylene, with mol. wt. up to 100,000+ was synthesised from CO and H₂ in the presence of RuO₂ at high pressures below 140°C.

Hydrogenation and Hydrogenolysis. VIII. The Ruthenium-catalysed Hydrogenation of Aromatic Compounds Containing C-O Linkage to be Easily Hydrogenolysed

Y. TAKAGI, T. NAITO and S. NISHIMURA, *Bull. Chem. Soc. Japan*, 1964, **37**, (4), 585-587

RuO₂ successfully catalysed hydrogenations of compounds in which it was desired to avoid hydrogenolysis of C-O linkages. Reactions were rapid and gave good yields of the corresponding alcohols or ethers, although slightly more hydrogenolysis occurred than with Rh and (7:3) Rh-Pt oxides as catalysts, perhaps because the latter operated at lower temperatures. Solvents were not used, except for C₂H₅OH or H₂O with benzyl alcohol, but CH₃COOH additives were used to neutralise alkaline traces in RuO₂. Reactions took place at 95-100°C, 80-100 kg/cm² H₂.

Catalysts for Selective Hydrogenation of Soybean Oil. II. Commercial Catalysts

C. H. RIESZ and H. S. WEBER, *J. Am. Oil Chem. Soc.*, 1964, **41**, (6), 400-403

Linolenic components of soybean oil are hydrogenated with high selectivity by commercial Pt, Pd, and Rh catalysts. Many of the latter had selectivities S_L of 2.4 to 2.7, but of the Ni catalysts tested only Raney Ni had $S_L > 2.0$. The Pt metal catalysts isomerised the linolenic components to the *trans*-form to the extent 7.8 - 15.4% but Ni caused only 5.2 - 7.4% isomerisation.

FUEL CELLS

Electrochemical Oxidation of Methanol in Fuel Cells

M. PRIGENT, *Rev. Inst. Fr. Pétrole*, 1964, **19**, (6), 1-54

The complete oxidation of CH₃OH is affected by the electrode potential, reactant concentration, and the state of the catalyst electrode. Studies of these parameters showed that Pt black electrodes gave the best results. Electrode properties depended on the weight of Pt deposit, on the deposition potential, and on additives. (83 references).

Structure and Activity of a Type of Sintered Electrode for Gas Cells

R. COFFRE, G. FEULLADE and B. MICHEL, *Ann. Radioélect.*, 1964, **18**, (74), 40-59

The theoretical basis of sintered fuel cell electrodes is expounded and the efficiency, activation processes, and passivation and ageing of oxygen and hydrogen electrodes are described. Au is used as catalyst on the Ni oxygen electrodes and Pd or Pt on the Ni alloy hydrogen electrodes. The latter age as Pd or Pt recrystallises.

The H₂-Cl₂ Fuel Cell. A Study of the Prospects of Power Recovery in Plants for Electrolytic Manufacture of Chlorine and Soda

G. BIANCHI and C. TRAINI, *Chim. e Ind.*, 1964, **46**, (4), 363-370 (English summary)

The capillary-inhibition H₂ electrode and the flowing-electrolyte Cl₂ electrode were porous graphite discs activated with Pt or Ir. The electrolyte was HCl solution. Ionisation occurred at room temperature and 1000 A/m² was obtained with 0.5 V at the H₂ electrode. 1000 A/m² was reached with 0.2 V at the Cl₂ electrode. Pure H₂ and dilute Cl₂ from the Deacon process could yield 500 A/m² at 0.88 V working voltage at room temperature and pressure. This represents 25% power recovery from the electrolysis but actual power recovery is less because some is used in auxiliary process equipment.

Electrochemical Oxidation of Hydrocarbons

R. JASINSKI, J. HUFF, S. TOMTER and L. SWETTE, *Ber. Bunsengesell. Phys. Chem.*, 1964, **68**, (4), 400-404

Pt-Ta screens were used in fuel cell oxidation tests at 70°C with 30% H₂SO₄ electrolyte. Current densities of 35 mA/cm² with CH₃OH fuel and 80 mA/cm² with HCOOH were achieved, both at 0.3 V. Pt black mixed with a Teflon dispersion and spread over a Ta screen was used in similar tests on CH₄, C₂H₆, C₃H₈, *n*-C₄H₁₀ and *iso*-C₄H₁₀, with O₂ as oxidant and 85% H₃PO₄ electrolyte. Such cells generated 40 mA/cm² at 0.37 V, 150°C using C₃H₈ or *n*-C₄H₁₀ fuels.

TEMPERATURE MEASUREMENT

A Microfurnace for High Temperature Microscopy and X-ray Analysis up to 2150°C
W. GUTT, *J. Sci. Instrum.*, 1964, **41**, (6), 393-394
The design, calibration and testing of an Ir:60%

Ir-Rh thermocouple used as a microfurnace for microscopy and X-ray analysis to 2150°C are described. The electrically heated thermocouple acted as specimen holder, heater and thermometer. Variation was $\pm 0^\circ\text{C}$ at 2000°C over one hour and $\pm 10^\circ\text{C}$ at 1900°C over 12 hours. The cold junction had to be maintained at 0°C. Corrosion by specimens was resisted.

NEW PATENTS

Ruthenium Hydrogenation Catalyst

ENGELHARD INDUSTRIES INC.

British Patent 956,630

A catalyst of 1-5 wt.% Ru on an inert carrier is used for the hydrogenation of mono- and polyhydroxy and alkoxy aromatics using H_2 at 25-150°C and 50-200 p.s.i.g.

Halogenated Platinum Metal Catalysts

THE BRITISH PETROLEUM CO. LTD.

British Patent 956,684

A hydrogenation catalyst of improved activity is prepared by treating an alumina-supported catalyst containing 0.01-5.0 wt.% Pt or Pd with a F compound, e.g. CF_4 , to give a product containing 1.0-5.0 wt.% F.

Platinum Metal Isomerisation Catalyst

THE BRITISH PETROLEUM CO. LTD.

British Patent 956,685

A catalyst consisting of an alumina support with a surface area of at least 300 m^2/g , 0.1-2.0 wt.% of Pt or Pd, up to 1.0 wt.% Cl_2 and 1.2×10^{-4} to 3.4×10^{-4} g F_2/m^2 of Al_2O_3 surface area is used for the isomerisation of 4C and higher paraffin hydrocarbons at 250-500°C and 250-1000 p.s.i.g.

Ruthenium Hydrogenation Catalysts

C. F. BOEHRINGER & SOEHNE G.m.b.H.

British Patent 957,149

Ruthenium metal, oxide, salt or ruthenate may be used as hydrogenation catalyst in the conversion of pyridyl-(4)-ethers to piperidyl-(4)-ethers by reaction at 130-140°C and 100-200 atm. H_2 .

Semiconductor with Noble Metal Alloy Contact Element

SIGMUND COHN CORP. *British Patent 957,639*

A silicon diode semiconductor has a spring contact element made of an alloy containing, by weight, 1-10% W, 1-20% Mo and/or 1-12% Cr and balance of Rh or Pd and Pt with up to 50% Pt.

Activation of Platinum Metal Electrodes

JOHNSON, MATTHEY & CO. LTD.

British Patent 957,703

Particularly active electrodes for use in the electrolysis of brine are produced by exposing a Ti electrode plated with Pt group metal or alloy, in particular Pt, Pt-Rh or Pd-Ag, to the action of Hg vapour or alkali metal amalgam vapour, the Hg

coating being distilled off after it has been deposited to leave the surface in a highly active state.

Precious Metal Alloy Electric Switch

THE UNITED STATES TIME CORP.

British Patent 957,872

Electric switches for clocks and watches and the like have one contact made of an alloy containing 65-80% Au and 35-20% Ag, with up to 30% Ag being replaceable by Cu, and a second contact made of an alloy containing 40-60% Pd and 60-40% Ag, with up to 20% Ag replaceable by Cu.

Platinum Metal Anodes

IMPERIAL CHEMICAL INDUSTRIES LTD.

British Patent 958,413

Improved anode for the production of chlorine by brine electrolysis consists of a wire mesh supported on a pillar and strengthened by stiffeners, all parts made of Ti or its alloys, and an operative anode surface produced from Pt, Rh, Ir or an alloy of two or more of these metals applied to the wire mesh.

Palladium Plating

AUTOMATIC TELEPHONE & ELECTRIC CO. LTD.

British Patent 958,685

Pd is plated on to articles forming a cathode in a bath containing 4-100 g/l Pd, 20-160 g/l ammonium sulphate, 4-100 g/l ammonium nitrite, 0-1 g/l Ni sulphamate and NH_3 to give a pH of 6-8.

Electrolytic Cell Electrodes

IMPERIAL CHEMICAL INDUSTRIES OF AUSTRALIA & NEW ZEALAND LTD. *British Patent 959,498*

Electrodes for brine electrolysis cells, etc., have Ti electrodes whose anodic faces are coated with a Pt metal or its alloys.

Platinum Metal Hydrogenation Catalyst

ABBOTT LABORATORIES *British Patent 959,507*

Aminophenol is produced by passing a mixture of inert mineral acid, CH_3COOH and H_2O , containing 10% nitro-phenol, over a platinised or palladised charcoal catalyst.

Precious Metal Catalysts for Exhaust Purifiers

OXY-CATALYST INC. *British Patent 960,900*

Pt, Pd, Ru or Rh or their oxides are used in ex-