

# ABSTRACTS

## of current literature on the platinum metals and their alloys

### PROPERTIES

#### Vapour Pressures of Liquid Titanium (2008 to 2379K) and Liquid Platinum (2045 to 2442K)

R. K. KOCH, E. D. CALVERT, C. R. THOMAS and R. A. BEALL, *U.S. Bur. Mines Rept Invest.* 7271, 1969 (July), 14 pp.

Two series of vapour pressure determinations were made on liquid Pt in a 2 kW electron beam furnace using a water-cooled Cu crucible and a disappearing filament pyrometer. Results were  $\log p(\text{atm}) = 8.240 - 30,460/T$  for 2086–2420K and  $\log p(\text{atm}) = 7.795 - 29,580/T$  for 2045–2442K respectively and mean standard heats of sublimation were 133.3 and 133.8 kcal/mole respectively.

#### Short-time Creep and Breaking Strength of Platinum-Rhodium Alloys

E. I. RYTVIN and V. V. MALASHKIN, *Metalloved. term. Obrabot. Metal.*, 1969, (6), 57–59

Studies of creep rate and breaking point of 15, 20, 30, and 40% Rh-Pt were extended above 1550°C by tests at 1500, 1600 and 1700°C under strain 1 kg/mm<sup>2</sup>. It appears that 15–20% Rh-Pt can be used to 1500, 20–30% Rh-Pt to 1600, and 30–40% Rh-Pt to 1700°C. The contributions of deformation between and inside the metal grains vary with Rh content and temperature so that 15–20% Rh-Pt fractures at 1600°C with necking, but 30–40% Rh-Pt fractures at 1500°C without necking.

#### Intergranular Deformation during Creep of Platinum-Rhodium Alloys

I. I. NOVIKOV, F. S. NOVIK, E. I. RYTVIN, S. S. PRAPOR and L. P. SHIPULINA, *Izv. Vyssikh Ucheb. Zaved., tsvet. Metall.*, 1969, (3), 140–143

7, 10 and 15% Rh-Pt were studied at 1350, 1400 and 1500°C under stresses of 0.2, 0.5 and 1.3 kg/mm<sup>2</sup>. The contributions of intergranular and intragranular deformations to the elongation of the alloys were evaluated and point to a mechanism for creep of these alloys.

#### Constitution of Some Mixtures of Platinum with $\beta$ -Elements ( $\beta = \text{Sn, Sb, Te}$ )

S. BHAN, T. GÖDECKE and K. SCHUBERT, *J. less-common Metals*, 1969, 19, (2), 121–140

An investigation by thermal analysis and X-ray diffraction of the phase diagrams of the Pt-Sb, Pt-Sn-Sb and Pt-Te systems revealed several new phases. Specific mention is made of the structures of Pt<sub>3</sub>Sb<sub>2</sub>, PtSn<sub>1.3</sub>Sb<sub>0.7</sub>, PtSnSb, PtSn<sub>1.2</sub>Sb<sub>1.8</sub>, PtTe, Pt<sub>3</sub>Te<sub>4</sub>, and Pt<sub>2</sub>Te<sub>3</sub>, which are discussed in terms of spatial correlation of electrons.

#### Dissociation Energy of Pd<sub>2</sub>

S.-S. LIN, B. STRAUSS and A. KANT, *J. chem. Phys.*, 1969, 51, (5), 2282–2283

The dissociation energy of Pd<sub>2</sub> was determined using mass spectrometric and Knudsen effusion techniques and is given as 16.9 kcal, calculated using the Third Law method.

#### Hydrogen Permeation through Alpha-Palladium

S. A. KOFFLER, J. B. HUDSON and G. S. ANSELL, *Trans. Metall. Soc. AIME*, 1969, 245, (8), 1735–1740

Permeability  $J$  of H<sub>2</sub> through  $\alpha$ -Pd, measured by a low pressure permeation technique in conditions where bulk diffusion was the rate-controlling process, is derived from  $J = 1.80 \times 10^{-8} P^{1/2} \exp(-3745/RT) \text{ cm}^3(\text{stp})/\text{sec}/\text{cm}^2/\text{cm}$  for  $P_{\text{H}_2} = 2.9 \times 10^{-5}$  to  $5.0 \times 10^{-8}$  cm Hg and  $T = 300$ – $709$ K. These data in conjunction with previous solubility data give the diffusivity of H<sub>2</sub> through Pd as  $D = 4.94 \times 10^{-8} \exp(-5745/RT) \text{ cm}^2/\text{sec}$ . Substructure defects had no effect at these temperatures. The ratio of grain boundary diffusivity to bulk diffusivity was  $< 10^5$ .

#### On the Role of Silver Atoms in the Absorption of Hydrogen by Palladium-Silver Alloys

R. BURCH, *Solid state Commun.*, 1969, 7, (18), 1313–1317

Examination of the relationship between solubility of H<sub>2</sub> and Ag content for Pd-Ag alloys over a range of temperatures and pressures showed that the reduction in bonding potential of Pd for H<sub>2</sub> is a constant fraction of the Ag:Pd at. ratio.

#### Investigation of Alloys of the PdAl-Ag System

L. A. PANTELEIMONOV, D. N. GUBIEVA and L. I. PARSHAKOVA, *Vest. moskov. Univ., Ser II, Khim.*, 1969, 24, (4), 85–87

Thermoanalytical, microstructural and microhardness studies of the PdAl-Ag system indicated the limited solubilities of the components in both liquid and solid states.

#### Localised Magnetic Moments on Iron Atoms in Solid Solutions of the Palladium-Copper System

L. A. UGODNIKOVA and YU. N. TSOVKIN, *Fiz. Metal. Metalloved.*, 1969, 28, (2), 223–228

Studies of the relation between temperature and magnetic susceptibility of 1% solutions of Fe in Pd-Cu showed that the minimum magnetic moment of Fe is  $3.8 \pm 0.2 \mu_B$  in 40% Cu-Pd.

### Iron-Palladium Fine Particles Prepared by Evaporation Method

A. IGA, Y. TAWARA, T. SAKAKIBARA and A. TASAKI, *Japan J. appl. Phys.*, 1969, 8, (8), 1057

Fe-Pd alloys were evaporated in an atmosphere of pure Ar at 15 Torr and formed into fine particles whose sizes ranged from 300 to 700 Å and which were found to be in the f.c.c. disordered phase. The alternative ordered f.c.t. phase could then be obtained by heating the evaporated particles at a temperature below the critical temperature of composition. The lattice parameter for disordered Fe-Pd was 3.820 Å; for the ordered alloy parameters were  $a=3.86-3.88$ ,  $c=3.68-3.71$  Å,  $c/a=0.950-0.960$ , depending on the annealing temperature.

### The Effect of Magnetic and Configurational Disorder on the High Temperature Heat Capacity of a Ni-50 at. % Pd Alloy

R. E. BINGHAM and C. R. BROOKS, *J. Phys. Chem. Solids*, 1969, 30, (10), 2365-2370

Heat capacity - temperature curves at 400-920K for 50 at. % Pd-Ni solid solution, measured after various heat treatments, show quite measurable deviations from a smooth curve. A rise in the heat capacity beginning below 400K and finishing ~520K is associated with ferromagnetic disordering. Anomalous behaviour above 520K is due to non-random atom arrangements in the alloy, induced by heat treatment.

### Formation, Stability and Structure of Palladium-Silicon Based Alloy Glasses

H. S. CHEN and D. TURNBULL, *Acta Metall.*, 1969, 17, (8), 1021-1031

A report on Pd-Si based alloy glasses formed by quenching a number of different melts to room temperature at various cooling rates, typically in the order of  $10^6$  deg C/sec. Both binary and ternary alloys are discussed, and experimental details are given, including results of X-ray and electron microscope investigations, thermal properties and electrical resistivity.

### A Study of Some $\alpha$ Palladium-Scandium, -Zirconium and -Gadolinium Alloys

M. NORMAN and I. R. HARRIS, *J. less-common Metals*, 1969, 18, (4), 333-345

A report on the room-temperature lattice spacings of some  $\alpha$ Pd-Sc,  $\alpha$ Pd-Zr and  $\alpha$ Pd-Gd alloys, and the room-temperature magnetic susceptibilities of some  $\alpha$ Pd-Sc and  $\alpha$ Pd-Zr alloys. Comparison is made with  $\alpha$ Pd-Y,  $\alpha$ Pd-Ce,  $\alpha$ Pd-In and  $\alpha$ Pd-Sn.

### Thermodynamics of the First Order Transition in FeRh

J. M. LOMMEL, *J. appl. Phys.*, 1969, 40, (9), 3880-3881

Bulk samples of the compound FeRh undergo a sharp transition which is thermodynamically

of the first order between the antiferromagnetic and ferromagnetic states. The critical temperature at which this transition occurs is field-dependent, and the critical field for inducing the transition is related to the square of the temperature. Results are given for 77-370K and for fields up to 250 kOe.

### New $A_3B_5$ Phases of the Titanium Group Metals with Rhodium

B. C. GIESSEN, R. WANG and N. J. GRANT, *Trans. Metall. Soc. AIME*, 1969, 245, (6), 1207-1210

A report on the existence and isomorphism of  $Ti_3Rh_5$  and  $Hf_3Rh_5$ , both shown to be of the orthorhombic  $Ge_3Rh_5$  type; an analogous phase with Zr does not exist. Lattice parameters and refined positional parameters are given, together with details of experimental work based on X-ray and other crystallographic methods.

### The Hafnium-Iridium System

M. I. COPELAND and D. GOODRICH, *J. less-common Metals*, 1969, 18, (4), 347-355

A report from the U.S. Bureau of Mines on Hf-Ir phase relations by metallography, thermal analysis, electron beam microprobe and X-ray diffraction techniques. Four intermediate phases ( $Hf_3Ir$ ,  $Hf_5Ir_3$ ,  $HfIr$ , and  $HfIr_3$ ) were identified, together with a number of eutectic and eutectoid alloys of Hf and Ir.

## CHEMICAL COMPOUNDS

### Some Acid Properties of $H_2PtCl_6$

R. W. MAATMAN and C. J. ADDINK, *J. Catalysis*, 1969, 15, (2), 210-213

A method of determining the acid content of  $H_2PtCl_6$  involves its titration with NaOH using an excess of  $Cl^-$  to repress exchange.  $H_2PtCl_6$  was shown to be a very strong acid by plots of pH titrations, by comparison of pH values using the same electrodes for solutions of  $H_2PtCl_6$  and of  $H_2SO_4$  of the same concentration, and by its reaction with NDA (4-nitrodiphenylamine), a very weak base.

### Two New Ternary Copper-Platinum Oxides

O. MULLER and R. ROY, *J. less-common Metals*, 1969, 19, (3), 209-214

Two new phases synthesised at 890°C,  $p_{O_2}=200$  atm are the solid solution  $Cu_{1-x}Pt_xO$ , which has tetragonal PtS structure and  $x=0.135-0.355$ , and  $CuPt_3O_6$ , which has a primitive orthorhombic cell with  $a=11.588$ ,  $b=6.126$ ,  $c=3.109$  Å. These phases are black and very insoluble.

### Cationic Transition Metal-Olefin Complexes

B. F. G. JOHNSON, J. LEWIS and D. A. WHITE, *J. Am. Chem. Soc.*, 1969, 91, (18), 5186-5187

A number of cationic olefin complexes with Pd, Pt and Rh were derived by treating enyl complexes of the metals with electrophilic agents such as

$\text{Ph}_3\text{CBF}_4$  or  $\text{HBF}_4$ . Four reaction schemes are described. These provide a general route for preparation of a wide variety of cationic derivatives.

### Chloride Complexes of Rhodium(III) in Aqueous Solutions

V. I. SHLENSKAYA, O. A. EFREMENKO, S. V. OLEINIKOVA and I. P. ALIMARIN, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, (8), 1643-1646

Ru chloride complex formation in aqueous solutions proceeds in stages and is reversible. Total and partial (stage) stability constants were calculated from spectrophotometric data derived from Ru perchlorate solutions.

### The Reaction of Iridium and Rhodium with Refractory Carbides and Borides

R. A. MERCURI and J. M. CRISCIONE, *Abstr. Papers, 158th Mtg, Am. Chem. Soc.*, 1969, (Sept.), INOR 33

Ir and Rh when heated to  $\sim 1200^\circ\text{C}$  and mixed intimately with Hf and Zr carbides yield C and noble metal-rich compounds; e.g. HfC and Ir yield  $\text{HfIr}_3$  and C. Ir and Rh react at  $1160$ – $1230^\circ\text{C}$  with Zr and Hf borides to yield cubic phases as 1:3 transition metal: noble metal, held in noble matrices.

### Photochemical Oxidation of Nitrogenamine Ru(II) Compounds

C. SIGWART and J. T. SPENCE, *J. Am. Chem. Soc.*, 1969, 91, (14), 3991-3992

A study of nitrogenaminerruthenium(II) compounds as possible models for biological  $\text{N}_2$  reduction. Experiments included exposure of a solution of deoxygenated  $\text{Ru}(\text{NH}_3)_5\text{N}^{2+}$  to UV light and the subsequent appearance of a Ru(III) species; solutions of the dimer  $\text{Ru}(\text{NH}_3)_6\text{N}_2\text{Ru}(\text{NH}_3)_6^{4+}$  behaved similarly. Photochemical oxidation was found to proceed equally well in acidic, neutral or basic conditions. Work continues to identify the reduction product and to confirm the suspected reduction of the bound  $\text{N}_2$  after photolysis.

### Formation of Metal Ion-Nitrene Complexes

L. A. P. KANE-MAGUIRE, F. BASOLO and R. G. PEARSON, *Ibid.*, (16), 4609-4610

A report on the formation of nitrene co-ordinated to Ru ion via the catalytic action of an acid, e.g.,  $\text{H}_2\text{SO}_4$ , on Ru(II) azide complexes.

## ELECTROCHEMISTRY

### The Adsorption of Water on Platinum Electrodes in Aqueous Electrolytes

J. W. SCHULTZE, *Ber. Bunsenges. Phys. Chem.*, 1969, 73, (5), 483-491

Potentiostatic tracer studies on  $\text{H}_2\text{O}$  adsorption on smooth Pt electrodes in  $\text{H}_2\text{SO}_4$  HTO solution showed that an approximate monomolecular

$\text{H}_2\text{O}$  layer is formed in the double-layer region, and a similar layer is adsorbed on the oxide layer built up at higher potentials. In acid and neutral solutions the exchange  $\text{PtOTH} + \text{H}_2\text{O} \rightarrow \text{PtOH}_2 + \text{HTO}$  is rate determining but in alkaline solutions the exchange occurs by  $\text{PtOTH} + \text{OH}^- \rightarrow \text{PtOH}^- + \text{HTO}$ .

### An Electrochemical and Electron Microscopic Study of Activation and Roughening of Platinum Electrodes

T. BIEGLER, *J. Electrochem. Soc.*, 1969, 116, (8), 1131-1137

A report on the factors governing the behaviour of Pt electrodes during anodic-cathodic cycling in 1 M  $\text{H}_2\text{SO}_4$ ; in particular, details of the activation and roughening of Pt electrodes, thought to occur through weakening of Pt interactions due to the formation of strong Pt-O chemisorption bonds.

### Cyclic Voltammetry of Mixed Metal Electrodes

J. S. MAYELL and W. A. BARBER, *Ibid.*, (10), 1333-1338

Repetitive potentiostatic triangular voltage sweeps cause significant changes in surface structure and catalytic activity of mixed metal electrodes, e.g., with a Pt-Rh black electrode each successive cycle causes a decrease in the Pt oxidation and reduction peaks with a proportionate increase in Rh oxidation and reduction peaks. Complete elimination of Pt peaks is related to resistance of the electrode to CO poisoning. A mechanism for these phenomena involves migration and redistribution of Rh. Pd-Rh, Pt-Ru and Au-Rh electrodes exhibit similar characteristics.

### Diffusion of Oxygen through a Platinum Diaphragm

J. P. HOARE, *Ibid.*, 1390-1392

A thin Pt foil, mounted in a cell between two compartments containing 2 N  $\text{H}_2\text{SO}_4$ , was anodised on the polarisation side and  $\text{O}_2$  was detected on the diffusion side by the increase in potential to an  $\alpha$ -Pd reference electrode in the  $\text{N}_2$ -stirred acid solution. When the foil became a cathode, the potential on the diffusion side became less noble. Diffusion coefficient at  $24^\circ\text{C}$  from cathodised foil data was  $1.8 \times 10^{-11} \text{ cm}^2 \text{ sec}^{-1}$  and from anodised foil data was  $4.4 \times 10^{-11} \text{ cm}^2 \text{ sec}^{-1}$ .

### Studies of Anodic and Cathodic Polarisation of Palladium in Cyanide Solutions

I. A. KAKOVSKII, V. A. SVETLOV and B. D. KHALEZOV, *Izv. Vysshikh Ucheb. Zaved., tsvet. Metall.*, 1969, (3), 51-57

Galvanostatic studies on the anodic and cathodic polarisation of Pd in cyanide solutions saturated by  $\text{O}_2$  or air, using the rotating disc, show as much passivation of Pd as with less cyanide and lower temperature with more  $\text{O}_2$  and agitation. If the critical value of outer anode current is

exceeded the potential drops sharply, i.e., passivation increases.  $O_2$  is reduced to hydroxyl during cathodic polarisation. These studies explain the dissolution of Pd in cyanide solutions.

### Mechanism of Dissolution of Palladium in Chlorinated Hydrochloric Acid Solutions

A. D. KOVYLAYEV and M. D. IVANOVSKII, *Ibid.*, 58-61  
Rotating disc studies of Pd dissolution in chlorinated HCl solutions at 20-80°C, 300-1500 rev/min, 0-10 g.mole/l HCl suggest an electrochemical dissolution mechanism which is autocatalytic and has two stages. At first  $Cl_2$  causes cathodic depolarisation; in the second stage  $[PdCl_6]^{2-}$  is reduced at Pd electrodes with less overvoltage than for reduction of  $Cl_2$ .

### Electrochemical Preparation of Rhodium(0) Complexes

D. C. OLSON and W. KEIM, *Inorg. Chem.*, 1969, 8, (9), 2028-2031

Two new Rh(0) complexes,  $Rh((C_6H_5)_3P)_4$  and  $Rh((C_6H_5)_2PCH_3)_4$ , were prepared by electroreduction in 85% acetonitrile-15% toluene of  $((C_6H_5)_3P)_3RhCl$  and  $((C_6H_5)_2PCH_3)_3RhCl$ , respectively.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Epitaxial Deposition of Platinum on Iridium at Low Temperatures

W. R. GRAHAM, F. HUTCHINSON, J. J. NADAKAVUKAREN, R. A. REED and S. W. SCHWENTERLY, *J. appl. Phys.*, 1969, 40, (10), 3931-3936.

Pt evaporated on a clean Ir surface at temperatures as low as 200K produces epitaxial layers, as shown by field ion microscopy. If the Ir surface has been exposed to the atmosphere after forming, the temperature required for epitaxy rises to ~375K. Even this temperature is well below that required for high mobility of the incoming atoms over the surface, as assumed in present theories of the formation of epitaxial layers.

### Electrodeposition of a Silver-Palladium Alloy

L. DOMNIKOV, *Metal Finish.*, 1969, 67, (9), 58-59, 65

Conditions are described for the electrodeposition of a Ag-Pd alloy from a  $CN^-$  bath. The structure sensitive properties of the deposits were studied and are compared with X-ray analysis results.

### Direct Activation of Polymers for Electroless Deposition

L. T. ROMANKIW, *Extended Abstr.*, 136th natl Mtg. *Electrochem. Soc.*, 1969, (Oct.), abstr. 135

A technique was developed which avoids intentional roughening of the polymer surface yet provides satisfactory adhesion of the plated film. A Pd salt as activator was dissolved in a solvent

compatible with the monomer and the mixture was applied to the surface to be metallised. Reduction to Pd occurred either during or after polymerisation of the monomer. Pd on the surface initiates electroless deposition and is believed to be embedded in the polymer.  $NiPdCl_6$  dissolved in dimethylacetamide rendered polyimide capable of being metallised by Cu. 0.4-2.0% Pd in the polymer gave optimum results.

### Palladium Chloride Activation of Plastic Surfaces prior to Metallisation

K. PETROV, G. PASSABOV, E. DOBREV and M. ENTSHEVA, *Kunststoffe*, 1969, 59, (4), 229-232

Studies with  $^{102}Pd$  of the activation before metallisation of polystyrene and polyamide with HCl-PdCl<sub>2</sub> solutions showed that surface activation is a sorption process, maximum sorption of  $Pd^{2+}$  occurring at 2 g/l Pd, pH2, 20°C, 20 min immersion. Satisfactory activation can occur in more dilute solutions over shorter times.

### Electrodeposition of Rhodium from a Molten Sodium Cyanide Electrolyte

G. R. SMITH, C. B. KENAHAN, R. L. ANDREWS and D. SCHLAIN, *Plating*, 1969, 56, (7), 805-808

A method of electrodepositing protective coatings of Rh up to 7.8 mils thick from a fused salt electrolyte made by dissolving Rh in molten NaCN. Plating is done in a special cell at 600°C under an atmosphere of Ar. The anode is either Rh or graphite. The cathode is one of several substrate materials suitable for plating, e.g., W and Mo, which so treated are protected from oxidation up to 600 and 700 deg C above their normal oxidation temperatures.

### Ruthenium Plating

G. A. CONN, *Ibid.*, (9), 1038-1040

Tests on the plating of Au-plated Cu cathodes with Ru, using  $RuNOCl_3 \cdot 5H_2O$  and sulphamic acid as plating solution showed the effects of Ru content, current density, sulphamic acid concentration, and temperature on the plating efficiency. A temporary increase of efficiency occurs by control of temperature, by anodic reactions and by control of complexing agent concentration to cause the metal complex to shift from a non-plateable to a plateable state. The physical properties of Ru plating are affected by the methods used to achieve increased plating efficiency. Periodic stopping of the plating current reduces stress in the deposit.

## HETEROGENEOUS CATALYSIS

### Comparison of the New Platinum Reforming Catalyst of Czechoslovak Production with Foreign Catalysts

O. SVAJGL and H. KOSTKOVA, *Ropa Uhlie*, 1969, 11, (3), 116-126

The stability and activity of the new Czech

petroleum reforming catalyst, which is supported on a highly active  $\text{Al}_2\text{O}_3$ , is compared to the Houdry-Hüls catalyst. It is insensitive to low  $\text{H}_2$ :hydrocarbon ratio. A drying method is specified as all feeds contained  $\sim 10$  p.p.m.  $\text{H}_2\text{O}$ . Reformates have research octane numbers  $>95$  in continuous operation, at lower pressures and with higher throughput than formerly.

#### Direct Evidence for Dual-functional Cyclisation of Paraffins over Platinum Reforming Catalysts

A. J. SILVESTRI, P. A. NARO and R. L. SMITH, *J. Catalysis*, 1969, **14**, (4), 386-388

$n\text{-C}_7\text{H}_{16}$  containing 100 p.p.m. S reacts on either Pt/C or  $\text{Al}_2\text{O}_3$  to yield relatively few ring hydrocarbons but the large increase in ring production when both catalysts are mixed points to paraffin cyclisation proceeding by a dual-functional mechanism.

#### On the Dependence of the Catalytic Activity of Platinum on the Crystalline Size and Orientation

V. S. BAGOTSKY, YU. B. VASSILIEV, A. M. SKUNDIN, V. SH. PALANKER, I. I. PYSHNOGRAEVA, O. A. KHASOVA and L. S. KANEVSKY, *Abstr. Papers, 158th Mtg, Am. Chem. Soc.*, 1969, (Sept.), FUEL 18

Pt catalyst activity was investigated for electrolytic  $\text{H}_2$  and  $\text{O}_2$  evolution, anion and  $\text{CH}_3\text{OH}$  adsorption and  $\text{CH}_3\text{OH}$  oxidation. For the latter the activity of platinised Pt was much lower than that of smooth Pt. Small quantities of Pt microcrystals were deposited on smooth C and it was found that the rate of  $\text{H}_2$  evolution depended on crystal size and distance between crystallites. For small crystallites and small amounts of crystallites the rate is  $>5-7$  that on smooth Pt.

#### Kinetics of the Catalytic Conversion of Cyclodecane over Platinised Carbon

A. A. VEDENYAPIN, E. S. BALENKOVA and S. I. KHROMOV, *Kinet. Kataliz*, 1969, **10**, (4), 808-812

Kinetics of total conversion of cyclodecane over Pt/C are explained by the Frost equation. Methods for finding activation energies of the constituent processes are proposed. Activation energy of transannular  $\text{C}_5$ - and  $\text{C}_6$ -dehydrocyclisation exceeds that of the analogous reaction with paraffins, which suggests a mechanism for the transannular conversion of cyclodecane.

#### Catalytic Conversion of Spiro-(4,4)-nonane on Platinum Catalyst

N. V. ELAGINA, S. Z. FRENKEL' and B. A. KAZANSKII, *Dokl. Akad. Nauk SSSR*, 1969, **188**, (2), 358-361  
Spiro-(4,4)-nonane undergoes  $\sim 33\%$  conversion over Pt black at  $310^\circ\text{C}$  in the absence of the gases but undergoes  $\sim 75\%$  conversion in a stream of  $\text{H}_2$ . The compositions of the products are given and the reasons for them are suggested.

#### Investigation of Structures and Activity of Promoted Catalysts of the Metal-Metal Oxide Type. III. Hydrogenation of Isoprene on Pt and Pd Catalysts Promoted by Salts of Chromium, Manganese and Zinc

R. G. DAVLESUPOVA, R. Z. KHAIRULLINA and R. I. IZMAILOV, *Kinet. Kataliz*, 1969, **10**, (4), 847-851  
Comparison of Pt and Pd catalysts (on C,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ ) for the hydrogenation of isoprene showed that Cr and Mn additions to  $\text{Al}_2\text{O}_3$  increased catalytic activity and raised the content of sorbed  $\text{H}_2$ . Where the  $\text{H}_2$  is added to dienes it is independent of the nature of the support. Mn-promoted Pt/ $\text{Al}_2\text{O}_3$  catalysed more direct  $\text{H}_2$  addition to isoprene to form 2-methylbut-2-ene.

#### Hydrogenation of Methylacetylene over Platinum and Iridium Catalysts

R. S. MANN and K. C. KHULBE, *J. phys. Chem.*, 1969, **73**, (7), 2104-2110

An investigation of the reaction between methylacetylene and  $\text{H}_2$  over pumice-supported and unsupported Pt and Ir catalysts in a static system for a wide range of reactant ratios and between 20 and  $150^\circ\text{C}$ . Selectivity was found to be dependent on initial  $\text{H}_2$  temperature and pressure and independent of methylacetylene pressure. Overall activation energies were 12.4, 14.7, 8.6 and 6.2 kcal/mole for Pt/pumice, Pt powder, Ir/pumice and Ir powder, respectively.

#### Investigation of Stationary Palladium Catalysts for Hydrogenation of Oils

D. V. SOKOL'SKII, E. P. MAZIN and K. A. ZHUBANOV, *Zh. prikladnoi Khim.*, 1969, **42**, (6), 1270-1274

Stationary Pd catalysts possess adequate activity, selectivity and stability for the hydrogenation of fats, e.g., optimum conditions for hydrogenation of sunflower oil over Pd/ $\text{Al}_2\text{O}_3$  at atmospheric pressure are  $220^\circ\text{C}$  and space velocity of  $\text{H}_2$   $18\text{h}^{-1}$ .

#### Hydrogenation of Unsaturated Compounds on Palladium/Polymer Catalysts

O. A. TYURENKOVA, *Zh. fiz. Khim.*, 1969, **43**, (8), 2088-2092

Hydrogenations of allyl alcohol, *o*-nitrophenol and dimethylethynylcarbinol showed that catalysts used have the following order of activity: Pd/polyvinyl alcohol, Pd/polyacrylonitrile, Pd/anilide, Pd/polyethyleneterephthalate. The polymers enhanced the activity of Pd.

#### Mixed Adsorption Hydrogenation Catalysts. XV. Rhodium-Silver Catalysts on Silica Gel

A. A. ALCHUDZHAN, N. Z. EDIGARYAN and M. A. MANTIKYAN, *Arm. khim. Zh.*, 1969, **22**, (1), 3-9  
Studies of Rh-Ag/ $\text{SiO}_2$  catalysts with 1.0, 0.5 and 0.2 wt carrier % Rh and 20-90 at. % Ag-Rh for hydrogenation of  $\text{C}_6\text{H}_6$  show that activity-Ag content graphs for 1.0 and 0.5% Rh catalysts have both a minimum and a maximum but that

for 0.2% Rh there is a rapid decrease of activity with increased content of Ag and then a slower decrease. For 1% Rh catalysts prepared by consecutive adsorption and reduction of Rh and Ag salts, the activity decreases as Ag content increases. If Ag is adsorbed before Rh the catalysts are more active, i.e., Ag covers more active Rh in the former case.

### Olefin Isomerisation Catalysed by Group 8 Metals in Absence of Molecular Hydrogen. Part 3. Butene Isomerisation over Iridium-Alumina

S. D. MELLOR and P. B. WELLS, *Trans. Faraday Soc.*, 1969, **65**, (7), 1873-1882

Butene isomerisation catalysed by Ir/Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O was studied at 100°C and the overall relative rate constants were determined. Isomerisation occurs by an addition-abstraction mechanism, the intermediates being chemisorbed secondary butyl groups. If surface H atom availability is low, butene desorption is rate-controlling, and the products are formed in equilibrium proportions; if high, desorption is not rate-controlling and the but-1-ene isomerises predominantly to *cis*-but-2-ene due to steric factors.

### Hydrogenation of Olefins. Part 5. Hydrogenation of But-1-ene Catalysed by Iridium-Alumina

*Ibid.*, 1883-1890

But-1-ene hydrogenation and isomerisation catalysed by Ir/Al<sub>2</sub>O<sub>3</sub> was studied at 20-170°C and the kinetics were obtained. The formation of chemisorbed butyl groups was rate-determining in both processes. The rate of isomerisation declined from 150°C to a minimum at 20°C. Ir alone of Group VIII metals favours the formation of *cis*-but-2-ene.

### On the Mechanism of Isomerisation of Allyl Alcohol on Platinum Group Metals

ZH. I. BOBANOVA, G. A. BOGDANOVSKII and G. D. VOVCHEKNO, *Vest. moskov. Univ., Ser. II, Khim.*, 1969, **24**, (4), 88-91

Isomerisation of allyl alcohol on Pt, Rh and Pd blacks in 1 N H<sub>2</sub>SO<sub>4</sub> showed C<sub>2</sub>H<sub>5</sub>CHO and traces of acrolein and C<sub>3</sub>H<sub>7</sub>OH in the liquid phase in the case of Rh black. Dehydrogenation and autohydrogenation controlled this isomerisation mechanism.

### Catalytic Oxidation of Methane on Zeolites Containing Rhodium, Iridium, Palladium, and Platinum

J. G. FIRTH and H. B. HOLLAND, *Trans. Faraday Soc.*, 1969, **65**, (7), 1891-1896

The complete oxidation of CH<sub>4</sub> over zeolites containing Pd, Pt, Rh and Ir was studied using a microcalorimetric technique. The results show that isolated ions of these metals can absorb CH<sub>4</sub> and O<sub>2</sub> but only with Pt competitively.

### Catalytic Decomposition of Hydrogen Peroxide by Metals and Alloys of the Platinum Group

D. W. MCKEE, *J. Catalysis*, 1969, **14**, (4), 355-364  
Kinetic studies at 27°C as a function of catalyst composition and pH of the solution for the decomposition of dilute aqueous solutions of H<sub>2</sub>O<sub>2</sub> showed that in neutral solution the order of specific activity per unit surface area of the metals was Pt>Os>Ir>Pd>Ru>Rh and that Pt-Pd, Pt-Ru and Pt-Rh had activities intermediate between those of their constituents, while Pt-Ir and Pd-Au showed maximum activity at intermediate alloy compositions. The reaction rate reached a sharp maximum at pH 10-11.

### Hydrogenation of Propylene over Group VIII Metals

R. S. MANN and T. R. LIEN, *Ibid.*, **15**, (1), 1-7

Catalytic activities of Group VIII metals supported on pumice for the C<sub>3</sub>H<sub>6</sub>-H<sub>2</sub> reaction are in the same sequence Rh>Ir>Ru>Pt>Pd>Ni>Fe>Co>Os. Orders of hydrogenation are first or slightly lower for H<sub>2</sub> and zero or slightly negative for C<sub>3</sub>H<sub>6</sub>. Activation energies have been determined.

## HOMOGENEOUS CATALYSIS

### Organic Syntheses by Means of Noble Metal Compounds. XXXIX. Palladium Catalysed Carbonylation of Propargyl Compounds

T. NOGI and J. TSUJI, *Tetrahedron*, 1969, **25**, (17), 4099-4108

Pd-catalysed carbonylation of propargyl chloride and acetylenic alcohols were carried out using PdCl<sub>2</sub> or Pd/C.

### XL. Palladium-catalysed Carbonylation of Allylic Ethers

S. IMAMURA and J. TSUJI, *Ibid.*, (18), 4187-4195

Carbonylation of allylic ethers, especially 1,4-diethoxy-2-butene was carried out using PdCl<sub>2</sub>, Pd(acac)<sub>2</sub> or Pd/C.

### A Novel Palladium(II) Chloride-promoted Addition-Rearrangement Reaction of Terminal Olefins with Diphenylacetylene

P. MUSHAK and M. A. BATTISTE, *J. Chem. Soc., D, Chem. Commun.*, 1969, (19), 1146-1147

C<sub>6</sub>H<sub>5</sub> and certain terminal olefins react with diphenylacetylene in the presence of PdCl<sub>2</sub> to produce substituted alka-1,3-dienes derived from symmetrical addition of two olefin units to the acetylenic reactant.

### Aromatic Substitution of Olefins. VII. Reactions of Lower Olefins with Benzene Catalysed by Palladium Acetate

S. DANNO, I. MORITANI and Y. FUJIWARA, *Tetrahedron*, 1969, **25**, (19), 4809-4813

Phenylation of C<sub>3</sub>H<sub>6</sub>, 1-C<sub>4</sub>H<sub>8</sub>, *trans*- and *cis*-

2-C<sub>4</sub>H<sub>8</sub> and 1,3-butadiene with C<sub>6</sub>H<sub>6</sub> was carried out using Pd(OAc)<sub>2</sub> and AcOH as catalysts.

### VIII. Substituent Effects on the Reactions of Styrene with Monosubstituted Benzenes in the Presence of Palladium(II) Salts

Y. FUJIWARA, I. MORITANI, R. ASANO, H. TANAKA and S. TERANISHI, *Ibid.*, 4815-4818

Styrene was reacted with monosubstituted benzenes (toluene, ethyl benzene) with Pd(II) salts such as Pd(OAc)<sub>2</sub> and PdCl<sub>2</sub>. Direction of substitution is influenced by the substituent.

### IX. Reactions of Olefins Containing a Polar Group with Benzene

S. DANNO, I. MORITANI and Y. FUJIWARA, *Ibid.* 4819-4823

Phenylation of olefins containing a polar group, such as acrylonitrile, was carried out using Pd(OAc)<sub>2</sub> and AcOH as catalysts.

### Trichlorotris(4-biphenyl-1-naphthylphenylphosphine)rhodium(III), a New Homogeneous Hydrogenation Catalyst

R. E. HARMON, J. L. PARSONS, D. W. COOKE, S. K. GUPTA and J. SCHOOLENBERG, *Abstr. Papers, 158th Mtg, Am. Chem. Soc.*, 1969, (Sept.), INOR 202

This octahedral complex was synthesised from 4-biphenyl-1-naphthylphenylphosphine and RhCl<sub>3</sub>·H<sub>2</sub>O in stoichiometric amounts. It was used to reduce quantitatively internal and highly substituted double bonds in unsaturated carboxylic acids under mild conditions.

### Homogeneous Benzylic Oxidation Catalysed by Some Complexes of the Platinum Group

J. BLUM, J. Y. BECKER, H. ROSENMAN and E. D. BERGMANN, *J. Chem. Soc., B, phys. org.*, 1969, (8), 1000-1004

Studies of autoxidation of C<sub>6</sub>H<sub>5</sub>, C<sub>2</sub>H<sub>5</sub> and related compounds in the presence of various organic compounds of Ir, Pd, Pt, Rh, and Ru showed that RhCl(PPh<sub>3</sub>)<sub>3</sub> is the most effective catalyst but that use of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> is limited to oxidation of non-halogenated alkylarenes and needs a co-catalyst addition of polyhalogenoalkane.

## CHEMICAL TECHNOLOGY

### Corrosion Resistance of Ti-0.2 Pd Semi-finished Alloys Manufactured Industrially

N. D. TOMASHOV, F. A. ORLOVA, N. F. ANOSKIN, YA. V. MATLIS, E. I. OGINSKAYA and G. P. CHERNOVA, *Zashchita Metal.*, 1969, 5, (5), 491-495

0.2% Pd-Ti is shown to be a corrosion-resistant material for chemical engineering.

### Hydrogen Pick-up and Dissolution in Titanium and Titanium-Palladium Alloys

N. D. TOMASHOV, V. N. MODESTOVA, R. P. VASILEVA and N. I. STROGANOVA, *Ibid.*, 496-502

Small additions of Pd reduce pick-up of H<sub>2</sub> by Ti.

Corrosion of Pd-Ti causes Pd to accumulate on the surface of the alloy which reduces the potential so that H pick-up decreases. H<sub>2</sub> diffuses deep into Ti when anodic dissolution occurs at the unalloyed metal.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Platinum-doped Silicon Diodes with Negative Resistance

A. A. LEBEDEV and N. A. SULTANOV, *Fiz. Tekh. Poluprov.*, 1969, 3, (4), 622-623

Pt-doped Si diodes with normal V-A characteristics at room temperature, with a small voltage drop in the forward direction, had negative differential resistance at 77K. V<sub>max</sub> reaches 120V and V<sub>max</sub>/V<sub>min</sub> is 2-5.5. V<sub>max</sub> decreases as temperature rises and the negative resistance disappears at 150K. Diodes prepared from over-compensated Si where, after diffusion of Pt the p-Si is converted to n-Si, have some negative differential resistance at room temperature.

### A Thick-film Resistor Glaze of Precision Properties

P. R. VAN LOAN, *Proc. 1969 electron. compon. Conf.*, 1969, 285-288

Tl and Ru oxides dispersed in a Pb borosilicate glass matrix form thick-film glaze resistors with good electrical properties, especially stability. Pastes can be fired at 625-675°C to produce films with sheet resistivity 100 ohm/sq-1 kohm/sq, TCR values of ±50 p.p.m., noise < -25 db/decade, stability ≥ 1% ΔR in a wide range of environments.

## TEMPERATURE MEASUREMENT

### Determination of Temperatures below 14K with Platinum Thermometers

R. MUIJLWIJK, *Physica*, 1969, 43, (3), 419-423

By using the results of measurements of the resistances of eight Pt thermometers between 1.3 and 14K it is shown that temperature can be deduced from measurements with Pt thermometers between 2 and 14K with an accuracy of 0.02 deg K if the constants W<sub>0</sub>, A, B, and γ in the equation W=W<sub>0</sub>+AT<sup>2</sup>+BTγ are known from calibrations between 1.3 and 5K and between 10 and 14K. W is the resistance ratio R(T)/R(0°C).

### On the Definition of an International Practical Temperature Scale. The Interpolation of Differences in the Resistance Ratios of Platinum Thermometers between 91K and 14K

R. MUIJLWIJK, M. DURIEUX and H. VAN DIJK, *Ibid.*, (4), 615-621

The IPTS is defined by using the relation

between temperature and resistance ratio  $W(T) = R(T)/R(0^\circ\text{C})$  of Pt. In this study three methods for interpolation of  $\Delta W$  have been applied to experimental data. Between the boiling and triple points of  $\text{O}_2$  the accuracy is within 1 mK; between the boiling points of  $\text{O}_2$  and of  $\text{H}_2$  and also between the boiling and triple points of  $\text{H}_2$  accuracies within 2 mK are possible.

#### Comparison of Platinum Resistance Thermometers with the Hydrogen Vapour-pressure Thermometer

*Ibid.*, 622-632

Pt thermometers are compared with the 20.4K equilibrium  $\text{H}_2$  vapour pressure thermometer in three different apparatuses, using the CCT-64 scale for the Pt thermometers and the  $T_{1,60}$  scale for the vapour pressure thermometer. "Best

values" on the CCT-64 scale of the fixed points of the 1968 IPTS in the liquid  $\text{H}_2$  range are given.

#### The Behaviour of Pt/PtRh and Ni/NiMo Thermal Elements in the High Temperature Furnace in the Presence of Material Containing Chromium

E. LENZ, *Werkstoffe Korrosion*, 1969, (8), 651-658

Evaporation of Cr from alloy parts of the furnace during vacuum annealing at  $10^{-3}$  to  $10^{-4}$  Torr,  $>1200^\circ\text{C}$  leads to deposition of Cr on thermocouples, which suffer reduction of service life by formation of hard, brittle intermetallic compounds. Suggested cures include use of vacuum-tight sheaths for the thermocouples, introduction of some  $\text{N}_2$  to the vacuum above  $1000^\circ\text{C}$ , and replacement of Cr alloy components by ceramic materials or Mo alloys.

## NEW PATENTS

### METALS AND ALLOYS

#### Composite Metal Articles

INTERNATIONAL NICKEL LTD

*British Patent* 1,168,130

Articles for high temperature use in non-oxidising atmospheres consist of a core of Ir, Ru, W and Mo, a barrier layer and a coating of at least 95% Ir, Ru, W or Mo. The barrier layer between the core and coating consists of Au, Pd, Pd-Ag alloy or Pd-Cu alloy of specified composition.

#### Platinum-Iron Permanent Magnet Alloys

CITIZEN TOKAI K.K.

*U.S. Patent* 3,444,012

Pt-Fe alloys of the super-lattice type are treated to improve their magnetic characteristics by cold-working and thermal-ageing.

#### Dispersion Hardening of Platinum Metals and Alloys

DEUTSCHE GOLD- & SILBER-SCHNEIDANSTALT

*Dutch Patent* 69,00716

Materials comprising Pt group metal(s), Au or alloys thereof, together with an element having high  $\text{O}_2$ -affinity (preferably Zr) are dispersion hardened by internal oxidation by heating at  $800$ - $1200^\circ\text{C}$  in an  $\text{O}_2$ -containing atmosphere for more than 5 h and preferably more than 20 h.

#### Production of Metallic Oxides

JOHNSON MATTHEY & CO. LTD

*Swiss Patent* 478,063

Electrolytic production of oxides of Pt and/or Pd or oxides of Pt and/or Pd mixed with oxides of other metals not harmful to the catalytic properties of the Pt and/or Pd oxides by electrolysis of

appropriate Pt, Pd, Pt alloy or Pd alloy anode in a molten bath of alkali metal halide and nitrate. This corresponds to *British Patent* 1,106,814.

### CHEMICAL COMPOUNDS

#### Manufacture of Palladium Halides

FARBWERKE HOECHST A.G. *British Patent* 1,159,225

Metallic Pd is treated with  $\text{O}_3$  (or air) in the presence of a carboxylic acid solution of a halide of a metal of Group Ia, IIa or IIIb or an ammonium halide at  $10$ - $150^\circ\text{C}$ . The Pd used is Pd black. It becomes converted to Pd(II) halides.

#### Ruthenium Carbonyl

IMPERIAL CHEMICAL INDUSTRIES LTD

*British Patent* 1,160,765

$\text{Ru}_3(\text{CO})_{12}$  is prepared by reaction of  $\text{RuCl}_3$ , Na naphthenate or Na acetyl-acetonate and a  $\text{CO-H}_2$  mixture.

#### Production of Carbonyl Compounds

HERCULES INC.

*British Patent* 1,164,561

Carbonyl compounds are produced by reacting an organic Group VIII noble metal compound with CO to form a CO derivative of the organic group. The Group VIII reactant is formed *in situ*, e.g., from p-carboxy-phenyl mercuric chloride and  $\text{PdCl}_2$ . The reaction of this with CO gives terephthalic acid.

#### Hexaruthenium-octadecarbonyl

LONZA LTD

*British Patent* 1,167,691

This new carbonyl compound  $\text{Ru}_6(\text{CO})_{18}$  is produced by heating trimeric  $\text{Ru}(\text{CO})_4$  at  $150$ - $250^\circ\text{C}$  in a closed vessel.  $\text{O}_2$  is absent, and  $p_{\text{CO}}$  is 0.2-2 atm.