

# ABSTRACTS

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

### PROPERTIES

#### Anomalous Stage I Recovery of Deformed Platinum

M. L. SWANSON, *Scripta Metall.*, 1969, 3, (9), 635-639

The stage I isochronal recovery from 1-2% extensions of 99.999% 0.0075 cm Pt wire below 60K showed certain anomalies possibly due to either dislocation motion, migration of point defects, or to unknown impurities in the wire. Other samples from the same spool behaved normally, i.e. <3% at 15K and <15% below 50K.

#### Acceleration of Sublimation of Platinum, Palladium and Platinum-Rhodium Alloy in Air during Deformation under the Action of Tensile Stress

I. I. NOVIKOV, E. I. RYTVIN and L. P. ULYBYSHEVA, *Dokl. Akad. Nauk SSSR*, 1969, 189, (1), 112-114

Tests on strips of Pt, Pd and 7% Rh-Pt at 1400°C showed that the rate of sublimation varied with the conditions of stress. The rate of sublimation is two orders of magnitude greater for samples under tension due to gravity than under compression. Samples deflected transversely have an intermediate rate of sublimation. Increase of tension by a large amount only increased the rate of sublimation by one order of magnitude. The mechanism of these phenomena is discussed.

#### g Factor and Magnetisation Measurements of Nickel-Platinum Alloys

G. FISCHER and M. J. BESNUS, *Solid State Commun.*, 1969, 7, (21), 1527-1530

Measurements on Ni-Pt of saturation magnetisation and of ferromagnetic resonance show initial linear dependence on total and spin mean magnetic moment. By extrapolation Pt has total moment 0.29 $\mu_B$ , hence  $g$  (Pt) = 1.65. As for Ni-Pd, ferromagnetism seems to disappear as a whole rather than by depolarisation.

#### On the Thermal Expansion Coefficient and the Temperature Coefficient of Young's Modulus of Nickel-Palladium and Nickel-Platinum Alloys

H. MASUMOTO and S. SAWAYA, *J. Japan Inst. Metals*, 1969, 33, (12), 1414-1417

Measurements of these coefficients and of the density of these alloys at high temperatures showed that the temperature at which the Elinvar property of Ni appears decreases as more Pd and Pt are added. A minimum linear coefficient of thermal expansion which represents

the Invar property is observed near a composition in which the Elinvar property occurs.

#### Resistance Minimum Phenomenon in Dilute Pt-Cr Alloys

H. NAGASAWA, *J. phys. Soc. Japan*, 1969, 27, (3), 787

The anomalous scattering of conduction electrons by localised magnetic moments was studied in Pt-Cr alloys. The solute resistivity  $\Delta R(T)/C$  was determined as a function of temperature, and the Kondo temperature, Weiss temperature and magnetic moment were calculated to be 200K,  $55 \pm 10$ K and  $1.2 \pm 0.1 \mu_B$  respectively.

#### Thermal Conductivity of Metals at High Temperatures by the Jain and Krishnan Method. IV. Palladium

S. C. JAIN, V. SINHA and B. K. REDDY, *Br. J. appl. Phys.*, *J. Phys. D*, 1969, 2, (9), 1283-1289

Thermal conductivity of Pd, measured at 1150-1420K, increases with temperature, the rate of increase being greater at the lower end of the range. Lattice conductivity is negative up to  $\approx 1250$ K. Electrical resistivity and total emissivity also increase with temperature over the range but the spectral emittance at 0.52-0.65 $\mu m$  decreases with temperature.

#### Determination of Optical Constants of Palladium and Silver from 2 to 90 eV from Energy Loss Measurements

J. DANIELS, *Z. Physik*, 1969, 227, (3), 234-253

The energy loss functions  $I_m(-1/\epsilon)$  of Ag and Pd were determined from energy loss experiments with 60 keV electrons. The influence of surface effects and multiple losses is discussed and the value of  $I_m(-1/\epsilon)$  is corrected for them. The optical constants  $\epsilon_1$  and  $\epsilon_2$  are calculated from these functions.

#### Hydrogen Diffusion in Palladium at Low Pressures

YU. A. BALOVNEV, *Zh. fiz. Khim.*, 1969, 43, (10), 2461-2464

Kinetic studies of the diffusion-catalytic evacuation of H<sub>2</sub> by Pd at low pressures showed that the limiting step is diffusion of H<sub>2</sub> in Pd.

#### Adsorption of Hydrogen on Palladium Films

YU. A. BALOVNEV, *Kinet. Kataliz.*, 1969, 10, (6), 1389-1390

Studies of the kinetics of absorption of H<sub>2</sub> by Pd films at 77K indicate that most of the difference between this and absorption at 293K is due to a

sharp increase in solubility at low temperatures. On this basis there is one mechanism of absorption at both 77 and 293K.

### Absorption of Hydrogen by Palladium and Electrical Resistivity up to Hydrogen-Palladium Atom Ratios of 0.97

D. A. OTTERSON and R. J. SMITH, *NASA tech. Note NASA-TN-D-5441*, 1969, 15 pp

The electrical resistivity of Pd-H was measured for H: Pd=0.97 at 4.2 and 273K. A model for the Pd-D systems was applied to Pd-H and is used to explain the resistivity peak at 50K and the values at 4.2K.

### The Electrical Resistance of Palladium and Palladium-Gold Alloy (50 wt.% Au and Pd) in Gaseous Hydrogen up to 24,000 atm at 25°C

R. BARANOWSKI and R. WISNIEWSKI, *Phys. Status Solidi*, 1969, 35, (2), 593-597

A double piston-cylinder system is described as a high pressure device for gaseous H<sub>2</sub>. The electrical resistance of Pd and 50 wt% Au-Pd foils was measured at  $2.5 \pm 0.1^\circ\text{C}$  up to 24,000 atm gaseous H<sub>2</sub>. The relative electrical resistance of Pd as a function of the at. ratio H : Pd is estimated.

### Effect of Various Additional Elements on the Properties of Non-magnetic Elinvar-type Alloys "Pallagold" in the Palladium-Gold System

H. MASUMOTO and S. SAWAYA, *J. Japan Inst. Metals*, 1969, 33, (12), 1410-1413

The temperature coefficient of Young's modulus of 50% Au-Pd, Pallagold, heated at 360°C for 15h after H<sub>2</sub>O quenching or cold working is  $+2.8 \times 10^{-5}$ . Tests on 45, 50 and 55% Au-Pd alloys with additions of Pt, Ir, In, Ta, Ag, Fe, Ni, Co, Mn, Cu, V, Mo, W, Sb, Sn, Zn, Cr, Al, Ti, Si, Cd, Be, Zr, and Nb show that generally the Young's modulus and hardness of the binary alloys are greater than those of the ternary alloys and that the temperature coefficient of Young's modulus is increasingly negative with addition elements.

### Mössbauer Effect Study of Palladium Gold Iron Alloys

G. LONGWORTH, *Phys. Lett. A*, 1969, 30A, (3), 180-181

Measurements of <sup>57</sup>Fe isomer shift and line width as a function of Au concentration were used to detect when the Pd *d* orbital became full.

### On the Structure and Properties of Some Alloys of the Au-Pd-W System

N. L. PRAVOVEROV and I. S. BEGETOVA, *Izv. Akad. Nauk SSSR, Metall.*, 1969, (6), 177-180

Studies of the Au-Pd-W system indicated a range of homogeneous ternary solid solutions at near

ambient temperature. Alloying of Au-Pd with W leads to increased strength.

### Thermodynamic Properties of Silver-Palladium Alloys

J. P. CHAN and R. HULTGREN, *J. chem. Thermodyn.*, 1969, 1, (1), 45-50

Measurements by liquid Sn solution calorimetry show that the minimum enthalpy of formation of Ag-Pd solid solutions is -1350 cal/mole at 1200K for 0.40 mole fraction of Pd. Alloys are diamagnetic below 0.40 mole fraction of Pd and paramagnetic above it.

### Specific Electrical Resistance of the Liquid Alloys Pd-Ni, Pd-Co, Pd-Cu, Pd-Fe, Pd-Mn, Pd-Al

E. L. DUBININ, O. A. ESIN and N. A. VATOLIN, *Zh. fiz. Khim.*, 1969, 43, (10), 2611-2613

The relation of alloy composition to specific electrical resistance  $\rho$  of these alloys was studied at 1300-1700°C.  $\rho$  has different values for each compound in the Pd-Mn and Pd-Al systems at the same temperatures.  $\rho$  varies with composition for Pd-Fe, Pd-Co and Pd-Ni.

### Calorimetric and Galvanic Cell Studies of the Thermodynamic Properties of Palladium-Tin Alloys

A. W. BRYANT, W. G. BUGDEN and J. N. PRATT, *Acta Metall.*, 1970, 18, (1), 101-107

Studies of the thermodynamic properties of the Pd-Sn system using reversible galvanic cells with ThO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> solid electrolyte and a Ni-NiO reference electrode at 900-1200K for 0-55 at.% Sn and using similar molten salt electrolyte cells on more Sn-rich liquid alloys gave the free energies of the system at 1050K. Heats of formation were measured at 320K on  $\alpha$ -solid solutions and on the phases Pd<sub>3</sub>Sn, Pd<sub>2</sub>Sn, Pd<sub>3</sub>Sn<sub>2</sub>, PdSn, PdSn<sub>2</sub>, PdSn<sub>3</sub> and PdSn<sub>4</sub>.

### Activated Sintering of Rhenium with Additions of Palladium

O. V. DUSHINA and L. V. NEVSKAYA, *Poroshkovaya Metall.*, 1969, (8), 50-52

Pd additions sharply activated the sintering of Re. Optimum addition was  $\approx 0.2-0.4$  wt% Pd. Density of the Pd-Re material rose with sintering temperature up to 2000°C. Standard Re powder sintered with Pd additions at 1900-2000°C reached a density 92% of the theoretical value; pure Re reached only 80%. The additive is not harmful to articles made of Re with the Pd.

### Thermoelectric Properties of Alloys of Palladium with Uranium

M. V. VEDERNIKOV, G. I. TEREKHOV, S. I. SINYAKOVA and O. S. IVANOV, *Izv. Akad. Nauk SSSR, Metall.*, 1969, (4), 191-199

Studies of 0-17.5 at.% U-Pd alloys at 20-1200°C confirmed the existence of UPd<sub>3</sub>, which was

transformed above 800°C to a disordered solid solution. UPd<sub>8</sub> possesses the high reported thermo-e.m.f. and is sufficiently plastic to be made into wire. It can be used as a branch of a thermocouple where a high thermo-e.m.f. is required (above 700°C).

#### Composition Diagrams of the Systems of Rhodium and Iridium with Carbon

B. P. BURYLEV, *Izv. vysshikh ucheb. Zaved., tsvet. Metall.*, 1969, (5), 112-116

Composition diagrams for the Rh-C and Ir-C systems are derived from work with other metals of Groups VI, VII, and VIII. The solubility of C in Rh and Ir is insignificant.

#### Tips for Fountain Pens - a Case History on the Adaptability of the Powder Metallurgy Process

M. R. PICKUS, *Internat. J. powder Metall.*, 1969, 5, (3), 7-15

2.5 wt% Pt-Ru alloy fabricated by powder metallurgy into spheres for pen tips is superior to Os alloys fabricated by other methods.

#### The Solubility and Adsorption of the Metals Au, Pt, Pd and Ru with regard to the Gases H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, A and Water Vapour

D. KORSCH, *Z. angew. Phys.*, 1969, 28, (2), 43-50

Determinations were made of the weights of H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O vapour adsorbed by evaporated films of Au, Pt, Pd and Ru. Adsorption isotherms of H<sub>2</sub>O at room temperature and up to 5 mm Hg vapour pressure and also solubility curves for the systems Pd-H<sub>2</sub>, Ru-H<sub>2</sub> and Ru-O<sub>2</sub> were plotted. Results showed that H<sub>2</sub> dissolved in Pd is replaced by O<sub>2</sub>, whereas O<sub>2</sub> dissolved in Ru is replaced by H<sub>2</sub>.

## CHEMICAL COMPOUNDS

#### The Crystal Structure of beta-Platinum Dioxide

S. SIEGEL, H. R. HOEKSTRA and B. S. TANI, *J. inorg. nucl. Chem.*, 1969, 31, (12), 3803-3807

β-PtO<sub>2</sub> crystallises as the orthorhombic CaCl<sub>2</sub>-type structure with a=4.488, b=4.533, c=3.138 Å. The O<sub>2</sub> coordinates are x=0.281, y=0.348. This leads to two long Pt-O bonds of 2.02 Å, four short bonds of 1.98 Å and a minimum O-O approach of 2.40 Å. Pt(IV) radius is 0.63 Å.

#### Information on Platinum(IV) Iodide

K. BRODERSEN, G. THIELE and B. HOLLE, *Z. anorg. allgem. Chem.*, 1969, 369, (3-6), 154-160

PtI<sub>4</sub> exists in two forms; the orthorhombic α form, space group Pbcu with a=12.90, b=15.64, c=9.90 Å. PtI<sub>6</sub> octahedra were found to be linked on two common sides to form zigzag chains,  $\infty$  [PtI<sub>4</sub>]<sub>2</sub>I<sub>2</sub>, with the two non-bridging I atoms in the cis position.

#### 4-Methylpent-4-en-2-one (Isomesityl Oxide) Complex of Platinum(II)

R. D. GILLARD, B. T. HEATON and M. F. PILBROW, *J. Chem. Soc., A, inorg. phys. theor.*, 1970, (2), 353-355

The reactions of mesityl and isomesityl oxide with Na chloroplatinate(II) and of dry acetone with PtCl<sub>4</sub> all give cis-[PtCl<sub>2</sub>(MeC(:O).CH<sub>2</sub>.CMe:CH<sub>2</sub>)]<sub>2</sub>, which reacts with phosphines to give 4-methylpent-4-en-2-one in high purity and yield, i.e., a convenient two-stage synthesis from acetone.

#### Potassium Hexachloropalladate and Potassium Hexachloroplatinate: a Comparative Study Using Nuclear Quadrupole Resonance

R. L. ARMSTRONG and D. F. COOKE, *Can. J. Phys.*, 1969, 47, (20), 2165-2169

Details are given of measurements of the temperature dependence of the NQR frequency  $\nu_Q$  and spin lattice relaxation time T<sub>1</sub> of <sup>35</sup>Cl nuclei in powdered K<sub>2</sub>PdCl<sub>6</sub>. Results are compared with those for K<sub>2</sub>PdCl<sub>6</sub> and the parameters characterising the NQR behaviour are tabulated. Temperature dependence of both  $\nu_Q$  and T<sub>1</sub> are dominated by the rotary lattice mode of frequency  $\approx 41$  cm<sup>-1</sup>.

#### Palladium Salts and Palladium Complexes in Organic Chemistry. II

R. HÜTTEL, *Brennstoff-Chem.*, 1969, 50, 331-334

Reactions of Pd compounds with organic reactants are studied: reactions with olefins, including allyl oxidation, dehydrogenation, hydrogenation, isomerisation, alkylation, arylation, and carbonylation; reactions with acetylenes; reactions of Pd(II) with non-olefinic organic compounds; reactions of [Ph<sub>3</sub>P]<sub>4</sub>Pd(O).

#### Thermal Expansion of Iridium Dioxide

K. V. K. RAO and L. IYENGAR, *Curr. Sci.*, 1969, 38, (13), 304-305

Measurements of the thermal expansion of IrO<sub>2</sub> at 28-702°C gave coefficients of expansion  $\alpha_{||} = 1.266 \times 10^{-6} + 8.823 \times 10^{-9}t - 6.870 \times 10^{-12}t^2$  and  $\alpha_{\perp} = 3.532 \times 10^{-6} + 7.963 \times 10^{-9}t - 3.825 \times 10^{-12}t^2$  at temperature t, i.e. IrO<sub>2</sub> has negative thermal expansion anisotropy.

## ELECTROCHEMISTRY

#### Development of an Electrochemical Acid Generator

L. H. SHAFFER and R. A. KNIGHT, *J. electrochem. Soc.*, 1969, 116, (11), 1595-1600

A catalytic membrane electrode, prepared by bonding a platinised 10% Rh-Pt gauze to a cation permeable membrane precoated with a slurry of Pt black, is the kernel of a system to acidify the feed stream to a desalination plant. The acid generator requires only inputs of electricity and the desalination plant feed stream.

It combines fuel cell and electro dialysis technology to produce an acidified sea water stream as product, a partially desalted stream and an alkaline stream.

### Electrochemical Exchange Current of Palladium and Platinum Alloy Electrodes as a Function of their Hydrogen Contents

G. L. HOLLECK and T. B. FLANAGAN, *Trans. Faraday Soc.*, 1969, **65**, (11), 3064-3073

Electrochemical exchange currents  $i_0$  have been measured on Pd/H and 18 wt% Au-Pd/H electrodes as a function of their  $H_2$  content. It was found that  $i_0$  is markedly dependent upon  $H_2$  content of the electrodes. The results are interpreted in terms of the expected dependence of  $i_0$  on the equilibrium  $H_2$  pressure which is equivalent to the  $H_2$  content of the electrodes.

### Electrochemical Behaviour of Rhodium in 1N $H_2SO_4$ Solution

T. OKAMURA, *Denki Kagaku*, 1969, **37**, (12), 831-835

Studies of the polarisation curves of Rh in 1N  $H_2SO_4$  by the potential sweep method and of the transformation of its oxide layer showed oxidation current peaks for  $H_2 \rightarrow 2H^+$  and  $Rh \rightarrow (Rh_2O) \rightarrow Rh_2O_3$  and reduction current peaks for  $O_2 \rightarrow 4OH^-$  and  $Rh_2O_3 \rightarrow (Rh_2O) \rightarrow Rh$  but  $Rh_2O$  and  $Rh_2O_3$  were not separated. 0.5V potential hysteresis was observed for both oxidation and reduction.  $Rh_2O_3 \rightleftharpoons RhO_2$  was not observed clearly because of  $O_2$  evolution.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Electroless Palladium Deposition

F. PEARLSTEIN and R. F. WEIGHTMAN, *Plating*, 1969, **56**, (10), 1158-1161

$NaH_2PO_2 \cdot H_2O$  was used as the reducing agent for electroless deposition of Pd from  $PdCl_2$  at 30-70°C. Deposits contained  $\approx 1.5\%$  P and had Vickers hardness  $\approx 165$  kg/mm<sup>2</sup>. Alloys containing Pd with 6% Ni, 10% Co or 36% Zn were deposited similarly.

### Investigation of Internal Stresses in Electrolytic Palladium-Cobalt Alloys

S. N. VINOGRADOV and N. T. KUDRYAVTSEV, *Zashchita Metal.*, 1969, **5**, (6), 686-687

Studies of the effects of some organic substances and of asymmetric a.c. on the internal stress of Pd-Co alloys showed that the least internal stress is produced when 0.5 g/l saccharin is added to the electrolyte but that asymmetric a.c. has little effect.

### Electrodeposition of Ruthenium

G. S. REDDY and P. TAIMSALU, *Trans. Inst. Metal Finish.*, 1969, **47**, (5), 187-193

An electrolyte based on the anionic complex of

Ru with formula  $(NH_4)_3[Ru_2NCl_8(H_2O)_2]$  gave Ru deposits which are bright at cathode current efficiencies up to 100%. The bath is stable and has a useful working life (i.e., total deposit weight per litre of electrolyte), of  $>50$ g/l Ru.

## HETEROGENEOUS CATALYSIS

### Chemisorption and Catalytic Reactions of Hydrogen at Metal Surfaces

G. C. BOND, *Surface Sci.*, 1969, **18**, (1), 11-27

A study of the correlation of catalytic activity and solid state properties of a number of base and noble metals including Pt group metals, Au and Ag. Existing information on the activities of the transition metals for reactions involving  $H_2$  is reviewed and the calculation of  $H_2$ -metal bond strengths is described. Metallic bonding is discussed in terms of molecular orbitals and its importance is stressed in connection with the understanding of surface processes.

### Chlorinated Platinum-Alumina Low Temperature Isomerisation Catalysts

J. P. GIANNETTI and R. T. SEBULSKY, *Ind. engng Chem., prod. Res. Dev.*, 1969, **8**, (4), 356-361

Low temperature paraffin isomerisation catalysts can be prepared by the reaction of  $Pt/Al_2O_3$  at elevated temperatures with various chlorinating agents, e.g.,  $Cl_2SO$ ,  $SO_2Cl_2$ ,  $S_2Cl_2$ , or a mixture of  $SO_2$  and  $Cl_2$ . Increased catalytic activity is obtained if  $Pt/Al_2O_3$  is treated with HCl prior to chlorination.

### The Problem of the Nature of the "Soluble" Form of Platinum in Platinum/Alumina Catalysts

S. I. ERMAKOVA and N. M. ZAIDMAN, *Kinet. Kataliz.*, 1969, **10**, (6), 1395-1397

In the absence of  $O_2$  the content of "soluble" Pt is negligible and unrelated to the concentration of Pt or to the temperature of roasting of the samples in a stream of  $H_2$ . The content of "soluble" Pt rises sharply after contact with atmospheric  $O_2$  at room temperature and is chiefly related to the previous roasting temperature. It is suggested that the content of "soluble" Pt after contact with atmospheric  $O_2$  depends on the stage of crystallisation of Pt grains.

### Investigation of the Mechanism of Liquid-phase Oxidation of *n*-Propanol on Platinum

V. V. SHALYA, B. I. KOLOTUSHA, F. A. YAMPOL'SKAYA and YA. B. GOROKHOVATSKII, *Ibid.*, (5), 1090-1096

Studies of the liquid-phase oxidation of  $C_3H_7OH$  over Pt/fine sand at 65-85°C using the inhibitor diphenylamine showed that 70% of the process occurs by the heterogeneous-homogeneous radical bonding mechanism and 30% by the heterogeneous mechanism. Pt plays a part in the generation and breaking of the bonds.

### Mixed Metal Catalysts in Catalytic Hydrogenation

G. C. BOND and D. E. WEBSTER, *Ann. N.Y. Acad. Sci.*, 1969, **158**, (2), 540-549

Hydrogenations of various unsaturated organic groups showed that the maximum activity of each of a number of Ru-Pt mixed oxides exceeded that of reduced PtO<sub>2</sub> and that the composition giving the maximum activity varied between the reactions. RuO<sub>2</sub> had zero activity. Studies were also undertaken with Ir-Pt, Rh-Pt, Ru-Rh, Ru-Pd, and Rh-Pd mixed oxides. Maximum activity of the Ru-Pt catalyst is connected with the optimum number of *d*-electron holes per atom.

### Catalysis of the Reduction of Supported Nickel Oxide

E. J. NOWAK, *J. phys. Chem.*, 1969, **73**, (11), 3790-3794

Most evidence favours reduction by surface-diffusing H atoms as the mechanism for H activation of NiO/Al<sub>2</sub>O<sub>3</sub> by Pt and Pd. Au and Ag, which do not readily absorb H atoms, do not enhance catalyst activation. Hydrogenolysis, isomerisation and aromatisation of *n*-heptane with H<sub>2</sub> were reactions in a pulse-flow reactor which demonstrated that Pt or Pd atom ratios to NiO as low as  $5 \times 10^{-3}$  were enough to cause large increases in conversion over Ni but that Au and Ag in similar ratios up to  $1 \times 10^{-1}$  caused no enhancement.

### Some Topics in Electrocatalysis

J. N. BUTLER, J. GINER and J. M. PARRY, *Surface Sci.*, 1969, **18**, (1), 140-158

This investigation of the mechanism of electrocatalysis embraces: fundamental studies of the H<sup>+</sup> ion discharge reaction on liquid metal electrodes including amalgams of Pt, Pd, In, and Ga with Hg and Ga-In alloys; the preparation and activity of Pt black electrocatalysts; a survey of possible electrocatalysts.

### On the Interconnection of Pt and Pd with the Surface of Clay Supports

D. V. SOKOL'SKII, N. K. NADIROV and I. V. SHLOTGAUER, *Zh. fiz. Khim.*, 1969, **43**, (11), 2954-2956

Pt and Pd catalysts of various contents were studied for surface area and metal dispersion. The conductivity at a given pH gave the energy of bonding of metal to clay support. The distribution of the active metals increased with decrease of metal concentration of the surface.

### Reactions of Benzylic and Allylic Alcohols Catalysed by Metallic Palladium

H. OKADA, Y. INOUE and H. HASHIMOTO, *Kogyo Kagaku Zasshi*, 1969, **72**, (9), 2018-2023, A113

An investigation of the reactions of benzylic- and allyl-type alcohols with metallic Pd to give

respectively reduced (hydrocarbon) and oxidised (aldehyde) products. Results are interpreted in terms of hydride transfer reactions assisted by Pd complexes and possible mechanisms for these reactions are discussed.

### Investigation of the Properties of Palladium Catalysts Modified by Cadmium Cations

G. D. ZAKUMBAEVA, D. KH. CHURINA, D. V. SOKOL'SKII and N. A. ZAKHARINA, *Kinet. Kataliz.*, 1969, **10**, (5), 1079-1085

Modification of Pd black by Cd<sup>2+</sup> from CdSO<sub>4</sub> leads to absolute selectivity of hydrogenation of acetylenic to vinylic alcohols. Tests were carried out using propargyl alcohol, butyn-1-ol-3, butyn-2-diol-1,4 and tetramethylbutyndiol. The charging curve method showed that a  $\beta \rightarrow \alpha$  transition occurred with consequent decrease of sorption of H<sub>2</sub> on Pd. Heats of H<sub>2</sub> sorption and desorption were calculated in this range and the thermodynamics of the processes were compared.

### Investigation of the Poisoning of Platinum Group Catalysts by Thermal Desorption. Part 2. Mercury Poisoning of Benzene Hydrogenation on Palladium

S. AFFROSSMAN, J. PATON and W. MCFALL, *Trans. Faraday Soc.*, 1969, **65**, (12), 3341-3348

The poisoning by Hg of a Pd catalyst for C<sub>6</sub>H<sub>6</sub> hydrogenation was investigated by thermal desorption. Adsorption of Hg leads to alloy formation before the catalyst is poisoned completely. The mechanism is consistent with a homogeneous catalyst surface which is blocked geometrically by the poison. Initially the blocking is random, then patches of alloy are formed at high coverages of poison, and the poisoning becomes less efficient.

### Dehydrocyclisation of *n*-Hexane in the Presence of Palladium/Alumina Catalyst

V. S. FADEEV, I. V. GOSTUNSKAYA and B. A. KAZANSKII, *Dokl. Akad. Nauk SSSR*, 1969, **189**, (4), 788-790

Tests on 0.6 wt. % Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> showed the effect of duration of contact on the conversion of *n*-C<sub>6</sub>H<sub>14</sub> at 500°C, the effect of temperature on this conversion at a rate of H<sub>2</sub> feed of 25 ml/min, the products of dehydrocyclisation of *n*-C<sub>6</sub>H<sub>14</sub> and selectivity of Pd/Al<sub>2</sub>O<sub>3</sub> (compared to Pt/Al<sub>2</sub>O<sub>3</sub>), and the products of conversion of methylcyclopentane and 3-methylpentane at H<sub>2</sub> feed rate 25 ml/min.

### Hydrogenation of Olefins: Part 6 - Reaction of *n*-Butenes with Hydrogen and with Deuterium over Alumina-supported Palladium

G. C. BOND and J. M. WINTERBOTTOM, *Trans. Faraday Soc.*, 1969, **65**, (10), 2779-2793

Reactions of each of the three *n*-C<sub>4</sub>H<sub>8</sub> isomers with H<sub>2</sub> and D<sub>2</sub> over a Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst was studied from 0 to 70°C. The hydrocarbon

products were analysed, the components were separated by gas-liquid chromatography and were examined by mass spectrometry. Kinetics of hydrogenation and of olefin isomerisation are reported and the reaction mechanism is discussed.

### Hydrocracking of *n*-Hexane and Cyclohexane over Zeolites

A. VOORHIES and W. J. HATCHER, *Ind. engng Chem., prod. Res. Dev.*, 1969, 8, (4), 361-366

The hydrocracking of *n*-C<sub>6</sub>H<sub>14</sub> and of cyclohexane was investigated using two crystalline Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts, which were both very active.

### Hexane Isomerisation over a Zeolite Catalyst

R. BEECHER and A. VOORHIES, *Ibid.*, 366-371

A synthetic H-mordenite catalyst, with or without dispersed Pd, had the same very high C<sub>6</sub>H<sub>14</sub> isomerisation activity. This unique crystalline zeolite without metal was investigated using the five isomeric hexanes to develop a kinetic model. The activity of the metal-containing and non-metal catalysts was compared. For *n*-C<sub>6</sub>H<sub>14</sub> the calculated reaction rate constant fitted an Arrhenius function of temperature with an apparent activation energy of 24.4 kcal/mole.

### Effect of the Conditions of Treatment of Pd/Zeolite Catalysts on their Activity and Selectivity in the Isomerisation of *n*-Hexane

KH. M. MINACHEV, V. I. GARANIN, V. V. KHARLAMOV, L. I. PIGUZOVA and A. S. VITUKHINA, *Neftekhimiya*, 1969, 9, (6), 808-811

The activity of 0.5% Pd/CaY for isomerisation of *n*-C<sub>6</sub>H<sub>14</sub> passes through a maximum as the temperature of reduction is raised from 150 to 550°C. The activity is increased by treatment with air or N<sub>2</sub> before reduction. Optimum activation conditions are air treatment at 380°C for 5h and reduction of the catalyst by H<sub>2</sub> at 250-400°C for 10h.

### Catalytic Properties of Iridium Supported on Alumina. II. Study of Chemisorbed Hydrogen by Temperature Programmed Desorption

J. P. CONTOUR and G. PANNETIER, *Bull. Soc. chim. Fr.*, 1969, (8), 2658-2662

The nature of chemisorbed H<sub>2</sub> and the quantity of gas adsorbed by Ir were studied by temperature programmed desorption. The molecules may be bound strongly or weakly, the existence of lower energy sites probably being due to a metal-support interaction.

### Hydrogenolysis of Ethane and of Propane over a Commercial Ruthenium Catalyst

D. G. TAJBL, *Ind. engng Chem., proc. Des. Dev.*, 1969, 8, (3), 364-370

The kinetics of C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> hydrogenolysis were studied over a commercial 0.5% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. The rate dependence of the

reactions was calculated; the energies of activation were 42 kcal/mole and 35.8 kcal/mole for C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> respectively.

### Methanation of Low-concentration Carbon Monoxide Feeds over Ruthenium

S. S. RANDHAVA, A. REHMAT and E. H. CAMARA, *Ibid.*, (4), 482-486

The methanation of CO at p.p.m. levels was studied over a 0.5% Ru/Al<sub>2</sub>O<sub>3</sub> catalyst in a fixed-bed reactor. Gas mixtures of 3450, 1090 and 505 p.p.m. CO in H<sub>2</sub> were used. The rate of reaction of CO follows simple pseudo first-order kinetics and the rate constant follows the Arrhenius temperature dependence at low temperatures.

### Activity of Pt, Pd and Rh Catalysts in the Nascent State

A. N. MAL'TSEV, N. I. KOBOZEV and L. V. VORONOVA, *Zh. fiz. Khim.*, 1969, 43, (11), 2814-2817

Nascent Pt, Pd and Rh catalysts prepared from solutions of their salts possess much more activity than their blacks. Pt and Pd have increases of 50-130 times the activity and this is more than increased surface area might indicate. Specific activity falls with growth of solution concentration.

### Deuterium as a Tracer in Reactions of Hydrocarbons on Metallic Catalysts

R. L. BURWELL, *Accounts chem. Res.*, 1969, 2, (10), 289-296

Isotopic exchange of D and H in hydrocarbons was studied over a variety of catalysts including Pd/Al<sub>2</sub>O<sub>3</sub>, Pt/Al<sub>2</sub>O<sub>3</sub> and Rh. The mechanism of exchange is discussed and the different catalysts are compared. Topics include isotopic exchange, racemisation, epimerisation, steric aspects of sites, and reactions with olefins. (29 references.)

### Mechanism of the Electrocatalytic Acceleration of Hydrogenation Processes on Mixed Powdered Platinum Metals

G. A. BOGDANOVSKII, G. I. SHCHEREV and G. P. KHOMCHENKO, *Kinet. Kataliz*, 1969, 10, (5), 1169-1172

A series of organic substances were hydrogenated on Pd black and powdered Ir, Os, and Ru, or on their mixtures, in H<sub>2</sub>SO<sub>4</sub>, thus establishing that mixing of powders leads to an activity greater than the sum of the activities of the components.

### On the Distribution of Hydrogen Adsorbed from Solution on the Surface of Some Hydrogenation Catalysts. II. The Effect of Temperature on the Form of the Differential Isotherms of Hydrogen Adsorption on Platinum Metals

YU. A. PODVYAZKIN, O. R. SERGUTKINA and G. P. GRECHUSHKINA, *Ibid.*, (6), 1385-1387

Values are given for H<sub>2</sub> adsorption on the surface

of Pt, Pd, Ir, Rh, Os, and Ru blacks in  $H_2SO_4$  solutions at 0–50°C.

## HOMOGENEOUS CATALYSIS

### The Hydrogenation Catalyst Made from Chloroplatinic Acid and Triethylsilane

C. EABORN, E. C. PANT, E. R. A. PEELING and S. C. TAYLOR, *J. Chem. Soc., C, org.*, 1969, (19), 2823–2830

An active hydrogenation catalyst is made as a suspension by warming  $H_2PtCl_6$  with  $(Et)_3SiH$  in 95%  $C_2H_5OH$ . The activity, which is associated with suspended solid particles, is retained on prolonged storage. The catalyst is compared with the Adams' catalyst for a variety of hydrogenation and hydrogenolysis reactions and in many cases it is the more efficient.

### Investigation of the Kinetics of Hydrogenation of Ethylene on Homogeneous Pt(II)–Sn(II) Chloride Catalyst

A. P. KHRUSHCH, N. F. SHVETSOVA and A. E. SHILOV, *Kinet. Kataliz.*, 1970, 10, (6), 1226–1229

Studies in mild conditions and in solvents  $CH_3OH$ ,  $C_2H_5OH$ ,  $CH_3O.CH_3$  and tetrahydrofuran showed that the reaction rate at  $p_{H_2} > 200$  mm Hg is given by  $-d[C_2H_4]/dt = k_{eff}[Pt].[C_2H_4]$ , and that the activation energies are almost equal and are 14–16 kcal/mole. A proposed mechanism for  $C_2H_4$  hydrogenation includes the introduction of  $C_2H_4$  at the Pt–H bond and hydrolytic decomposition of ethylplatinum derivatives.

### Oxidations of Olefins with Alcoholic Palladium(II) Salts

W. G. LLOYD and B. J. LUBEROFF, *J. org. Chem.*, 1969, 34, (12), 3949–3952

Simple olefins, including most mono- and 1, 2-disubstituted ethylenes, are readily oxidised by alcoholic solutions of Pd(II) salts, e.g.,  $PdCl_2$ , to yield the corresponding acetals or ketals. When a little  $H_2O$  is present the free carbonyl compounds are obtained. Oxidations proceed readily with little or no  $H_2O$ ; they are retarded by more  $H_2O$ . If  $O_2$  and a reoxidant, e.g.,  $CuCl_2$  with  $PdCl_2$ , are present the reactions are selectively homogeneous catalytic.

### Aromatic Substitution of Olefins. IV. Arylation of Olefins with Palladium(II) Acetate

Y. FUJIWARA, I. MORITANI, S. DANNO, R. ASANO and S. TERANISHI, *J. Am. Chem. Soc.*, 1969, 91, (25), 7166–7169

Olefins react with  $C_6H_6$  derivatives to produce aryl-substituted olefins by direct substitution of the aromatic compound for H on the olefin double bond in the presence of Pd salts and reduced Pd metal. The reaction is made catalytic by using Cu or Ag acetates, and air, as reoxidants.

### Catalytic Conversion of Benzoic Anhydrides into Fluorenones

J. BLUM and Z. LIPSHES, *J. org. Chem.*, 1969, 34, (10), 3076–3080

$RhCl(PPh_3)_3$  catalyses transformation of benzoic anhydride to fluorenone and of substituted benzoic anhydrides to fluorenone derivatives. Benzoic anhydride and  $RhCl(PPh_3)_3$  react at 140°C to form a divalent Rh complex. A mechanism of this new catalytic reaction and a general route to formation of fluorenones are suggested.

### Homogeneous Catalytic Hydrogenation of Unsaturated Organic Compounds

R. E. HARMON, J. L. PARSONS, D. W. COOKE, S. K. GUPTA and J. SCHOOLENBERG, *Ibid.*, (11), 3684–3685

The general applicability and usefulness of  $RhCl(PPh_3)_3$  in organic syntheses was shown by selective hydrogenations of a wide variety of  $\alpha, \beta$ -unsaturated carboxylic acids, esters, aldehydes, ketones, nitriles, and nitro compounds.

### Hydroformylation Catalysis by Arylphosphine Complexes of Rhodium

J. H. CRADDOCK, A. HERSHMAN, F. E. PAULIK and J. F. ROTH, *Ind. engng Chem., prod. Res. Dev.*, 1969, 8, (3), 291–297

Olefins can react catalytically with  $H_2$  and CO using  $Rh(PPh_3)_2(CO)Cl$  as a homogeneous liquid phase catalyst to produce selectively aldehydes (>99 mole%). No hydrogenation side reactions occur. When  $\alpha$ -olefin feedstocks are used, isomerisation reactions can be controlled effectively to yield aldehydes having a linear content of 75–80%.

### Continuous Propylene Hydroformylation in a Gas-sparged Reactor

A. HERSHMAN, K. K. ROBINSON, J. H. CRADDOCK and J. F. ROTH, *Ibid.*, (4), 372–375

The complex  $Rh(PPh_3)(CO)Cl$  is a very reactive, stable and selective hydroformylation catalyst, and is used effectively in a gas-sparged reactor, e.g., gaseous  $C_3H_6, H_2$  and  $CO_2$  were sparged through the catalyst solution and the butyraldehyde product was removed continuously. No noticeable deactivation of the catalyst occurred in >80h running time.

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

R. E. HARMON, J. L. PARSONS and S. K. GUPTA, *J. Chem. Soc., D. chem. Commun.*, 1969, (23), 1365–1366

This new saturated Rh(III) complex is as effective as  $RhCl(PPh_3)_3$  for the hydrogenation of  $\alpha, \beta$ -unsaturated carboxylic acids under identical conditions (50°C,  $p_{H_2} = 80$  lb/in<sup>2</sup>, 8h time of reaction).

## Kinetics and Mechanism of the Reduction of Cerium(IV) by Mercury(I) Nitrate Catalysed by Iridium

K. B. YATSMIRSKII, L. P. TIKHONOVA and I. P. SVARKOVSKAYA, *Zh. neorg. Khim.*, 1969, **14**, (11), 2982-2986

A mechanism is proposed for the reduction of Ce(IV) by  $\text{Hg}_2(\text{NO}_3)_2$ , catalysed by solutions of  $\text{Na}_3\text{IrCl}_6$  and  $\text{Na}_2\text{IrCl}_6$ , which includes three successive stages. Stability constants were calculated for formation of intermediate complexes. The rates of their decomposition and the activation energies for the reduction with and without catalyst were determined also.

## Preparation and Properties of Hydrido-carboxylatotris(triphenylphosphine)-ruthenium(II) Complexes, Including Homogeneous Catalytic Hydrogenation of Alk-1-enes

D. ROSE, J. D. GILBERT, R. P. RICHARDSON and G. WILKINSON, *J. Chem. Soc., A, inorg. phys. theor.*, 1969, (17), 2610-2615

$\text{RuH}(\text{OCOR})(\text{PPh}_3)_3$  complexes, obtained by reacting  $\text{RuCl}_2(\text{PPh}_3)_3$  with the Na salt of the carboxylic acid  $\text{RCO}_2\text{H}$  in  $\text{CH}_3\text{OH}$  solution under  $\text{H}_2$  atmosphere, were characterised by analysis and spectroscopy. They efficiently catalyse selective hydrogenation of alk-1-enes. The rate of hydrogenation of hex-1-ene with  $\text{RuH}(\text{OCOCF}_3)(\text{PPh}_3)_3$  was studied. Selectivity for alk-1-ene reduction is due to steric factors caused by  $\text{PPh}_3$  groups.

## FUEL CELLS

### The Oxidation of Water-soluble Organic Fuels Using Platinum-Tin Catalysts

K. J. CATHRO, *J. electrochem. Soc.*, 1969, **116**, (11), 1608-1611

Electrodeposits of Pt and Sn mixtures from  $\text{H}_2\text{PtCl}_6$  and  $\text{Sn}_2\text{Cl}_2$  have greater activity than Pt black for oxidation of  $\text{CH}_4$ ,  $\text{HCHO}$  and  $\text{HCOOH}$ , especially with  $\text{HCHO}$  where anode polarisation is decreased by 0.4V at 100 mA/cm<sup>2</sup>.

## CHEMICAL TECHNOLOGY

### Loss of Platinum from Platinised Titanium in Hypochlorite Cells at Low Electrolyte Temperatures

C. MARSHALL and J. P. MILLINGTON, *J. appl. Chem.*, 1969, **19**, (10), 298-301

Loss of Pt from Pt/Ti anodes during NaOCl production by electrolysis of brine is explained by a potential-dependent change in surface structure. Loss can be avoided by control of anode potential. The conditions of loss were studied in a cell similar to those operated commercially.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Thick Films or Thin?

R. E. THUN, *IEEE Spectrum*, 1969, **6**, (10), 73-79

A comparison of the relative merits of thick and thin film technologies in the fabrication of hybrid integrated circuits, i.e., ceramic substrates with deposited passive components and attached active devices. In the case of thick films, including Ru, the deposited pattern of circuit elements is applied by screen-printing and firing, while thin films are applied by vacuum deposition or by cathode sputtering.

### Thick-film Integrated Circuits

P. J. HOLMES and J. R. CORKHILL, *Electron. Components*, 1969, **10**, (10), 1171-1175; (11), 1331-1333

A review of current manufacturing techniques used for screen-printed thick-film circuits on ceramic substrates. Discussed are resistor inks based on Pd and Ag, conductor inks based on Pt, Pd, Rh, and Au, and conductor terminations of Pd-Ag and Pd-Au. The electrical characteristics of components made in this way are outlined, and problems associated with the addition of active circuit elements and packaging are highlighted.

## TEMPERATURE MEASUREMENT

### Extensions of Callendar's Equations for Platinum Resistance Thermometry

J. M. DIAMOND, *Rev. sci. Instrum.*, 1969, **40**, (11), 1477-1481

Callendar's equations have been generalised to permit interpolation between arbitrary fixed points appropriate to the temperature region under study. Greater accuracy is expected, especially where Pt thermometer and means of measurement are not perfect. Callendar's definition of Pt temperature is generalised to mean temperature found by linear interpolation with a Pt thermometer between given fixed points using a given measurement method. True temperature can be found by recursion or by extension of Callendar's correction scheme. Correction  $C=f(\delta, P)$ , where P is the Pt temperature. Use of a general calibration interval alters  $\delta$  in a calculable way.

### New Two-point Calibration Method for Platinum Resistance Thermometers for the Range 75-400K

J. P. PRATT and D. C. AILION, *Ibid.*, (12), 1614-1616

Pt resistance thermometers have been calibrated to  $\pm 0.01$  deg C over the range 75-400K by measurements at only the liquid  $\text{N}_2$  and ice points.



## Thermoelectric Power of Binary Solid Solutions on a Palladium Base

T. F. TARASOVA, I. L. ROGEL'BERG and I. S. GIL'DENGORN, *Tr. Gos. Nauch.-Issled. Proekt. Inst. Splavov Obrab. Tsvet. Metal.*, 1969, (29), 5-23

Thermoelectric powers were measured at temperatures from 100 to 1200°C for alloys of Pd with Ag, Al, Au, Co, Cr, Fe, Ir, Mn, Mo, Nb, Ni, Pt, Re, Rh, Ru, V, and W. Most additions increase the thermoelectric power of Pd; Au, Ag, Cu, Al, and Mn decrease it.

## Thermocouples of Palladium-containing Alloys

T. F. TARASOVA, I. L. ROGEL'BERG and I. S. GIL'DENGORN, *Ibid.*, 140-150

Thermoelectric properties are described for Pallaplat (5% Rh-Pt : 2% Pt - 46% Pd - Au), TB 19-29 (10% Rh-Pt : 10% Pt - 30% Pd - Au), Baker 417 (10% Rh-Pt : 40% Pd-Au), Pallador I (10% Rh-Pt : 40% Pd-Au), Platinel I (3% Au-14%Pt-Pd : 35% Pd-Au), Platinel II (14% Au-31%Pt-Pd : 35% Pd-Au), PIP (15% Ir-Pt : Pd).

# NEW PATENTS

## METALS AND ALLOYS

### Palladium-Vanadium Resistance Alloys

JOHNSON MATTHEY & CO. LTD

*British Patent 1,171,674*

Pd-V alloys having high specific resistance and reduced temperature coefficient of resistance contain 74 to 98.5 wt.% Pd, 1 to 15 wt.% V and 0.5 to 11 wt.% in total of one or more of the elements Au, Mo or Al.

### Manufacture of Titanium Dioxide

LAPORTE TITANIUM LTD *British Patent 1,173,593*  
TiCl<sub>4</sub> may be preheated in a tube constructed of refractory material. This is preferably SiO<sub>2</sub> or a suitable metal e.g., Pt, a Pt alloy or Pt-lined Inconel.

### Constant Conductivity Alloys

TRW INC.

*British Patent 1,173,703 U.S. Patent 3,463,636*

The alloys consist of: 70-90 wt% Pt, Rh, Ir, Au or Ag, 7-23 wt% W, 2-8 wt% Re; e.g., 70 wt% Pt, 22.5 wt% W, 7.5 wt% Re.

### Sparking Plug Alloy

INTERNATIONAL NICKEL CO. INC.

*U.S. Patent 3,466,158*

A bonded compound article, e.g., a sparking plug, comprises a Ag component and a high melting point component of Ir, Ru or an Ir-rich or Ru-rich alloy. They are connected by a junction made of a Ag-Pd alloy.

### Platinum Metal Ball Bearings, Pivots, Etc.

INTERNATIONAL NICKEL CO. INC.

*U.S. Patent 3,466,165*

The difficulty of producing very small balls, pivots for instruments, porous metal filter raw materials from these metals and their alloys are overcome in a matrix system. Small spheres and spheroid-like articles which are predominantly

of Ru, Ir, Os or Rh are formed in a molten matrix of other metal and the matrix is then solidified and leached to recover spheres or spheroids. In the examples Pd and Ag form the matrix.

### Hydrogen-permeable Membrane

JAPAN GAS-CHEMICAL CO. INC.

*U.S. Patent 3,469,372*

A H<sub>2</sub> permeable membrane consists of a Pd or a Pd alloy, the surface of the membrane having a wavy configuration as a result of being stamped with the surface of a plain dutch weave wire netting of 20-200 meshes.

### Stabilised Group VIII Metal Alloys

JOHNSON MATTHEY & CO. LTD

*French Patent 1,570,312*

The high temperature properties of Group VIII noble metal alloys are stabilised by the presence of up to 20% of a lanthanide, Sc, Y, Ti, V, Zr, Nb, Hf and/or Ta.

### Bonding Two Different Metals

JOHNSON MATTHEY & CO. LTD

*German Patent 1,521,335*

In bonding metals, e.g., Pt or its alloys to stainless steels, interdiffusion is reduced by interposing a layer of a metal/ceramic mixture. The metal in the layer is insoluble in one of the metals being bonded but is virtually soluble in the other. Mo, W, Nb, Ta and Ti are suitable metals. This corresponds to *British Patent 1,093,136*.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Electrodeposition of Palladium

SEL-REX CORP.

*British Patent 1,171,734*

A plating bath consists of a solution of a urea complex of Pd, adjusted to a pH >8. It is claimed that this prevents porosity previously found in thin (2.5 to 5 μm) Pd coatings.