

# ABSTRACTS

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

### PROPERTIES

#### **Electron Density and Electronic Properties in Noble-Metal Transition Elements**

M. A. JENSEN, B. T. MATTHIAS and K. ANDRES, *Science*, 1965, **150**, (3702), 1448-1450

It is shown empirically that, for the Pt group metals and their alloys, the superconducting transition temperature, the magnetic susceptibility and the electronic specific heat are adequately described as universal functions of the valence electron density.

#### **Surface Energy and the Secondary Recrystallisation of Platinum Sheet**

M. MCLEAN and H. MYKURA, *Acta Met.*, 1965, **13**, (12), 1291-1297

When growth rates of secondary crystals in thin Pt sheet at 1500°C were measured, only crystals with orientations close to {111} were observed to grow. They grew through the polycrystalline matrix at rates dependent on the specimen thickness and their own orientation. Impurities may cause the reduced grain boundary mobility. Contributions to driving pressure for 0.01 cm Pt sheet are: surface, 59%; grain boundary, 62%; impurity drag, -21%. No secondary recrystallisation is predicted for Pt sheet thicker than 0.027 cm. More possible orientations occur with thinner specimens.

#### **The Wetting of Gold and Platinum by Water**

K. W. BEWIG and W. A. ZISMAN, *J. Phys. Chem.*, 1965, **69**, (12), 4238-4242

A sessile drop of pure H<sub>2</sub>O placed on pure, polished Au or Pt spreads spontaneously over the clean surface with zero contact angle but if the surfaces have been contaminated by hydrophobic traces then white heat in a stream of high-purity gas is required previously. Similar traces in the gas may be adsorbed and keep the surfaces non-wetting but, if they are removed in an adsorbent cold trap, the Au and Pt specimens can be wetted completely.

#### **The Pressure Dependency in the Oxidation of Platinum Explained by a Boundary-layer Diffusion Mechanism**

G. C. FRYBURG, *Trans. Met. Soc. A.I.M.E.*, 1965, **233**, (11), 1986-1989

Evidence indicates a boundary-layer diffusion mechanism for Pt oxidation above 800°C except at the lowest pressures. The oxidation rate depends on the rate of diffusion of oxide through the boundary-layer away from the Pt, whereas for

W and Mo oxidation the rate is controlled by O<sub>2</sub> diffusion through the boundary-layer towards the metal. This difference results from the much lower oxidation rate of Pt.

#### **Thermal Diffusivity of Platinum**

J. J. MARTIN, P. H. SIDLES and G. C. DANIELSON, *U.S.A.E.C. Rept. IS-1261*, 1965, (Oct.), 11 pp

Values for the thermal conductivity of Pt were calculated from diffusivity measurements. They agree with other studies at room temperature but not at high temperature and the use of Pt as a conductivity standard will need additional measurements by absolute methods. Four Pt samples with resistivity ratios of 34, 100, 900 and 5000 were studied at 300-1200°K. Thermal diffusivity values were insensitive to small amounts of impurities.

#### **Magnetic Moments in the Ordered Fe<sub>2.8</sub>Pt<sub>1.2</sub> Alloy**

E. KRÉN and P. SZABÓ, *Solid State Commun.*, 1965, **3**, (11), 371-372

Neutron diffraction measurements on Fe<sub>2.8</sub>Pt<sub>1.2</sub>, which has Cu<sub>3</sub>Au-type structure, give  $\mu_{Fe} = 3.3 \pm 0.2 \mu_B$  and  $\mu_{Pt} = 1.5 \pm 0.2 \mu_B$ .

#### **Investigation of the Recovery of Atomic Defects in Palladium and Copper-Palladium Alloys**

W. KÖSTER and H.-P. KEHRER, *Z. Metallkunde*, 1965, **56**, (11), 760-767

Studies of the recovery of cold-worked and quenched Pd and Cu-Pd alloys by resistivity measurements at -40 to 300°C showed that Pd recovers in stages III and IV with activation energies of  $1.03 \pm 0.02$  eV (stage III after cold working only), due to recovery of interstitial atoms, and  $1.50 \pm 0.07$  eV (stage IV after quenching), due to annihilation of vacancies. Activation energies of the alloys increased with Pd content.

#### **On the Change in the Thermoelectric Power and the Electrical Resistance of Alloys of the Palladium-Silver System in a Transverse Magnetic Field**

T. RICKER and R. LUCK, *Ibid.*, 799-802

Studies were made on Pd-Ag, Pd-Rh and Ag-Cd alloys. A cryomagnet for the measurement of galvanomagnetic properties at low temperatures is described. The changes depend on both the magnetic induction and resistivity according to the second power although this is not strictly true in pure metals and in stronger fields.

### The Temperature Dependence of the Resistance and Other Electrical Properties of Palladium-Silver and Palladium-Rhodium Alloys

T. RICKER and E. PFLÜGER, *Ibid.*, 1966, 57, (1) 39-45

Results for the temperature dependence of the resistance of Pd-Ag and Pd-Rh alloys at 80-1100°K, for the Hall effect in Pd-Ag alloys at 80-400°K and for the Nernst effect in Pd-Ag, Pd-Rh and Pd-Mo alloys at room temperature agree well with an extended model of quasi-free electrons combined with Mott's picture of electron structure of transition metals. Ag-rich alloys show effects due to change of Debye temperature. The model enables temperature dependence of resistance, thermoelectric power and Nernst effect to be derived from the same density of states function. The concentration dependence of these effects is due essentially to scattering of electrons into the incompletely filled d-band.

### Ordered Alloys of Gold-Palladium System. I. Electron Diffraction Study of Evaporated Au<sub>3</sub>Pd Films

A. NAGASAWA, Y. MATSUO and J. KAKINOKI, *J. Phys. Soc. Japan*, 1965, 20, (10), 1881-1885

Electron diffraction study of evaporated single crystal films of 10-60 at.% Pd-Au alloys revealed an ordered phase with Cu<sub>3</sub>Au-type structure at 25 at.% Pd-Au with an order-disorder transformation which occurs at 850°C.

### Plastic Deformation of Pd-H Alloys

S. TAKAGI and T. SUGENO, *Japan J. Appl. Phys.*, 1965, 4, (10), 772-777

Tensile tests on Pd-H alloys were carried out at various temperatures and strain rates. Hardening of Pd due to H-charging was more pronounced in  $\alpha$ - than in  $\beta$ -phase. In polycrystalline d-alloys the temperature and concentration dependence of yield stress were measured at -80 to +130°C and indicated that hardening was dominated by the chemical interaction. Low H<sub>2</sub>-concentration specimens at liquid H<sub>2</sub> temperatures had serrated stress-strain curves (the Portevin-Le Chatelier effect) but why is not known.

### Absorption Isotherms of Hydrogen in the $\alpha$ -Phase of the Hydrogen-Palladium System

J. W. SIMONS and T. B. FLANAGAN, *J. Phys. Chem.*, 1965, 69, (11), 3773-3781

Absorption isotherms were determined at 0-90°C from variations in the electrode potential and electrical resistivity of Pd wires during slow absorption of H<sub>2</sub> from dilute HCl solutions, and represent equilibrium data. Average isosteric heat of absorption is  $4780 \pm 100$  cal/mole of H<sub>2</sub> from H-Pd=0.002 to 0.014. Statistical analysis of the isotherms is based on interacting absorbed protons.

### The Plastic Deformation of Iridium Single Crystals

R. HAASEN, H. HIEBER and B. L. MORDIKE, *Z. Metallkunde*, 1965, 56, (12), 832-841

The critical shear stress of zone-refined Ir single crystals has temperature dependence similar to that of impure Cu and Ag. Activation energy is 1.2 eV and initial activation volume is  $2.5 \cdot 10^{-19}$  cm<sup>3</sup>. Stacking fault energy is estimated to be  $\gamma = 296 \pm 59$  erg/cm<sup>2</sup>, i.e. more than other noble metals and comparable to that of Ni, i.e. dislocations are practically undissociated. Elastic and plastic parameters of Ir show quantitative agreement of mechanical properties with other f.c.c. metals if the characteristic deformation stresses are related to shear modulus, which for Ir is very high and limits its range of plasticity. The influence of impurities is still apparent and yet more so in polycrystalline Ir.

### Establishment of Two New Compounds IrBi<sub>3</sub> and IrBi<sub>2</sub> in the System Bismuth-Iridium

N. N. ZHURAVLEV and E. M. SMIRNOVA, *Kristallografiya*, 1965, 10, (6), 828-832

IrBi<sub>3</sub> has rhombic crystals isomorphous with NiBi<sub>3</sub>. IrBi<sub>2</sub> has monocyclic crystals isomorphous with  $\alpha$ -RhBi<sub>2</sub> and possesses arsenopyrite structure.

### The Reaction of Niobium with Ruthenium

L. A. PANTALEIMONOV, O. P. NESTEROVA, Z. A. GUTS, K. G. AKHMETZIANOV and I. G. SOKOLOVA, *Vest. Moskov. Univ., Ser. II, Khim.*, 1965, (6), 57-62

NbRu melts at 1900°C, the eutectic point occurs at 1760°C, 66 at.% Ru and there is a minimum in the solidus curve at 1800°C, 40 at.% Ru. This minimum and that of the isotherm of electrical resistivity and of the temperature coefficient of resistance, the maximum of the hardness curve and the b.c.c. lattice to tetragonal lattice transition all occur at ~40% Ru.

### The Reaction of Ruthenium with Tantalum

L. A. PANTALEIMONOV, O. P. NESTEROVA, K. G. AKHMETZIANOV and I. G. SOKOLOVA, *Ibid.*, 63-68

The Ru-Ta system has a eutectic point at 1950°C, 70 at.% Ru, a minimum in the solidus curve at 1970°C, 44-45 at.% Ru and RuTa melts at 2050°C. The maximum in the hardness curve and the b.c.c. to tetragonal lattice transition also occur at 44-45 at.% Ru.

### On the Occurrence of Some U<sub>2</sub>X Compounds of Uranium with Transition Metals

A. F. BERNDT and A. E. DWIGHT, *Trans. Met. Soc. A.I.M.E.*, 1965, 233, (12), 2075-2078

The stoichiometrically prepared compounds U<sub>2</sub>Tc, U<sub>2</sub>Rh, U<sub>2</sub>Os and U<sub>2</sub>Ir, formed by peritectic or peritectoid reactions, are isostructural with U<sub>2</sub>Ru. Lattice parameters and miscibility relationships are listed.

## New $T_3B_7$ Compounds

F. HULLIGER, *Nature*, 1966, **209**, (5022), 500-501  
New compounds synthesised include  $Ir_3Ga_4Ge_3$ ,  $Ir_3In_4Sn_3$ ,  $Ir_3Ga_3Ge_4$ ,  $Ir_3Ga_3Sn_4$ ,  $Ir_3In_3Ge_4$ ,  $Ir_3In_3Sn_4$ ,  $Mo_3Sb_7$ ,  $OsIr_2Sn_7$ ,  $Tc_3As_7$ ,  $Re_3As_7$ .

## The Occurrence of Superconductivity in Sulphides, Selenides, Tellurides of Pt-group Metals

C. J. RAUB, V. B. COMPTON, T. H. GEBALLE, B. T. MATTHIAS, J. P. MAITA and G. W. HULL, *J. Phys. Chem. Solids*, 1965, **26**, (12), 2051-2057

Superconductivity occurs in Pd-Se and Pd-Te compounds, in  $IrTe_3$  and in PtTe. 85-87 at.% Pd-Se alloys have  $T_c = 0.66^\circ K$ , which is unusually high for its valence-electron concentration. Homogeneity ranges exist for hexagonal B8-type PdTe and for trigonal C6-type  $PdTe_2$ . Low temperature heat capacity measurements for PdTe and  $PdTe_{1.04}$  show that large changes of  $T_c$  with composition are accompanied by large changes in linear heat capacity coefficient  $\gamma$ .

## CHEMICAL COMPOUNDS

### Platinum Carbonyls Substituted by Tertiary Phosphines

G. BOOTH, J. CHATT and P. CHINI, *Chem. Commun.*, 1965, (24), 639-640

A series of quite stable trinuclear Pt carbonyl derivatives was produced by substitution of tertiary phosphines and also a less well-defined polymeric dicarbonyl  $[Pt_n(CO_2)_n]$ . Ease of preparation fell when methyl groups replaced phenyl groups. Structures, melting points and some other properties are tabulated. Those derivatives which contain triangles of Pt atoms are the first to be reported.

### Rhodium Sulphate Complexes

S. I. GINSBURG and N. N. CHALISOVA, *Zh. Neorg. Khim.*, 1965, **10**, (11), 2411-2417

Thermogravimetric, polarographic and potentiometric studies of the synthesis of Rh sulphates show that the mononuclear aquohydroxysulphate is formed at room temperature with single bonds which readily split in aqueous solution. At 100-125°C the sulphate is more complex with double bonds and  $Rh:SO_4 = 2:3$ . At 250-325°C the stable trisulphate is formed with triple bonds and  $Rh:SO_4 = 1:3$ .

### Chemical and Structural Characterisation of Some $\pi$ -Allylic Derivatives of Rhodium(III)

G. PAIARO, A. MUSCO and G. DIANA, *J. Organomet. Chem.*, 1965, **4**, (6), 466-474

$RhCl_3 \cdot 3H_2O$  and *trans,trans,trans*-1,5,9-cyclododecatriene react in boiling  $C_2H_5OH$  to form insoluble red diamagnetic dichloro(cyclodeca-1,5-dienyl)rhodium(III), which is polymeric through Cl bridges and which reacts with Lewis bases to give octahedral derivatives such as

$C_{12}H_{19}RhCl_2B_2$  where B is monodentate basic ligand.

### Ionisation and Dissociation of Ruthenium and Osmium Tetroxides

J. G. DILLARD and R. W. KISER, *J. Phys. Chem.*, 1965, **69**, (11), 3893-3897

Principal ions from ionisation and dissociation of  $RuO_4$  and  $OsO_4$  by electron impact were determined by mass spectrometry and their heats of formation were obtained.  $MO_2^-$  is formed by dissociative electron attachment;  $MO^-$  and  $MO_3^-$  are produced by ion-pair formation processes.  $I(RuO_4) = 12.33 \pm 0.23 eV$ ,  $I(OsO_4) = 12.97 \pm 0.12 eV$ ,  $D(O-RuO_2) = 104$  kcal/mole and  $D(O-OsO_3) = 108$  kcal/mole.

## ELECTROCHEMISTRY

### Nature of the Surface of a Platinum-Rhodium Alloy in Electrocatalysis

A. DAMJANOVIC, A. DEY and J. O'M. BOCKRIS, *J. Catalysis*, 1965, **4**, (6), 721-724

Steady state potential-log rate relationships for the electrochemical oxidation of  $H_2O$  to  $O_2$  and for the cathodic reduction of  $O_2$  to  $H_2O$  in 1 N  $HClO_4$  and in 1 N  $KOH$ , plotted for Rh, Pt and 40% Rh-Pt, show that the reactions on the alloy follow the kinetic characteristics of whichever pure metal has the faster rate at a given electrode potential, indicating the possibility that the homogeneous alloy substrate has become a heterogeneous mixture of the metal oxides and therefore a type of polyelectrode.

### Anodic Corrosion of Rhodium in Hydrochloric Acid Solutions

J. LLOPIS, I. M. TORDESILLAS and M. MUÑIZ, *Electrochim. Acta*, 1965, **10**, (11), 1045-1055

Anodic corrosion of Rh in  $HCl$  by action of dc occurs with high overpotential and Rh(III) complex formation (yellow solutions) and it is enhanced by increasing temperature and  $HCl$  concentration. Superimposed ac increases the attack and at low overpotentials raspberry-red Rh(III) solutions are obtained; ac effect increases as frequency decreases. For a given dc value no apparent corrosion occurs until a threshold  $i_{ac} \gg i_{dc}$  is reached. Order of corrosion resistance is  $Rh < Pt \ll Ir$ .

### Oxygen Overvoltage on Bright Palladium in Acid Solutions

J. P. HOARE, *J. Electrochem. Soc.*, 1965, **112**, (11), 1129-1133

Galvanostatic and potentiostatic overvoltage measurements of anodic evolution and cathodic reduction of  $O_2$  on bright Pd electrodes in  $O_2$ -saturated 2 N  $H_2SO_4$  gave generally similar kinetic results. Pd catalysed peroxide decomposition less well than Pt. Adsorbed PdO film was a poor electronic conductor.  $O_2$  was evolved anodically on a Pd anode by decomposition of

PdO<sub>2</sub> to PdO and O<sub>2</sub>. O<sub>2</sub> was reduced from adsorbed O<sub>2</sub> molecules on a Pd cathode.

### On the Adsorption Properties of Rhodium and Ruthenium Electrodes in Relation to Electrolytes

G. P. KHOMCHENKO, A. F. LUNEV and K. N. BOGDANOVSKAYA, *Elektrokhimiya*, 1965, 1, (11) 1352-1355

Adsorption properties of Rh and Ru electrodes depend on the electrolytes in relation to the potential. Comparison of their properties of gas adsorption and retention demonstrates the roles of the ionic double layer and of the potential drop at the metal-solution grain boundary. Just as the Pt surface is fully degasified in the double layer potential region so on Rh is an insignificant amount of gas present, whose atoms have dipole bonding with the metals.

### New Method of Dissolving Ruthenium

A. A. GORYUNOV and A. N. RYABOV, *Zh. Neorg. Khim.*, 1965, 10, (12), 2596-2601

The anodic dissolution of Ru powder in an alkaline medium to obtain a concentrated solution of ruthenates and perruthenates of the alkaline metals, free from extraneous salts, occurs efficiently and relatively quickly in a described cell.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Investigation of Electrolytic Mixed Deposits of Platinum and Palladium with Ruthenium

O. A. PETRII and V. E. KAZARINOV, *Elektrokhimiya*, 1965, 1, (11), 1389-1391

Ru-Pt and Ru-Pd deposits on Pt from 1% [xH<sub>2</sub>PtCl<sub>6</sub>+yK<sub>2</sub>RuNOCl<sub>6</sub>] and 1% [xPdCl<sub>2</sub>+yK<sub>2</sub>RuNOCl<sub>6</sub>] solutions were checked for thickness and composition by radioactive labelling of K<sub>2</sub>RuNOCl<sub>6</sub>. The amount of Ru is proportional to the amount in solution until secondary factors cause its value to pass through a maximum. Mixed electrolytic deposits containing 5-80% Ru have high chemical stability and are more active for catalytic and electrochemical processes than the metallic alloys.

## LABORATORY APPARATUS AND TECHNIQUE

### Diffusion-Sorption Pumping

P. L. READ and H. H. GLASCOCK, *J. Vacuum Sci. Technol.*, 1965, 2, (6), 307-308

Pressure in a small system was reduced from 760 Torr to  $1 \times 10^{-8}$  Torr by using H<sub>2</sub> diffusion through a 25% Ag-Pd foil combined with the sorption of gas on liquid-N<sub>2</sub>-chilled synthetic zeolite. This is a useful technique for a forepump in getter-ion-pumped ultra-high vacuum systems. Ag-Pd alloy is used because pure Pd might crack during thermal cycling.

### Hydrocarbon-leak-detector Tool Contributes to Cleaner Air

*Oil Gas J.*, 1965, 63, (48), 65

Esso Research and Engineering Co have developed a leak detector for hydrocarbons with a sensing head containing shielded and unshielded Pt wires. When gaseous fumes reach the less-shielded wire the Pt catalytically raises the burning of the gases and also changes the circuit resistance to alert the operators. Use of the device at Humble's Bayway Refinery, Linden, N.J., has reduced hydrocarbon leakage to the sewers, and air and water pollution.

## CATALYSIS

### Platinum-based Reforming Catalysts

J. TOMASIK and J. WRZYSZCZ, *Chem. Stosowana*, 1965, 9, (2A), 205-216

Tests on catalysts containing 0.1-1.0 at.% Pt for both low and high pressure reforming show that the amount of Pt does not affect the isomerisation activity but that it affects the degree of conversion and the aromatisation. These data can be used in optimising Pt content of industrial contact catalysts.

### Changes of the Aromatisation Property of Platinum-Alumina Catalyst in Relation to the Content in it of Platinum and Sodium

N. R. BURSIAK, S. B. KOGAN and Z. A. DAVYDOVA, *Kinetika i Kataliz.*, 1965, 6, (6), 1046-1051

The aromatisation of N-hexane at 545°, atm. pressure over Pt/Al<sub>2</sub>O<sub>3</sub> catalysts with 0.01-1.2 wt.% Pt and 0.02-1.6 wt.% Na and the conversion of N-hexene-1 over Al<sub>2</sub>O<sub>3</sub> were studied in the same conditions. Possible mechanisms for alkylaromatic hydrocarbon formation were examined. A scheme for conversion of N-hexane over Pt/Al<sub>2</sub>O<sub>3</sub> with parallel formation of aromatic hydrocarbons on Pt and acid centres is proposed. Optimum Na concentration depended on the Pt content of the catalyst.

### Development of a Mathematical Description of Platforming for Optimisation of the Process. I.

YU. M. KHOROV, G. M. PANCHENKOV, S. P. ZEL'TSER and YU. A. TIRAK'YAN, *Ibid.*, 1092-1097

This mathematical model of platforming takes account of the catalyst and of the composition of the input material and its fractions. Determinations of the reaction parameters show good agreement between calculation and experiment.

### The Production of High Octane Petrol by Catalytic Reforming

G. N. MASLYANSKII, R. F. PANNIKOVA and G. D. KAMUSHER, *Khim. i Tekhnol., Topliv i Masel*, 1965, (12), 1-6

Catalytic reforming of a wide range of petroleum fractions can be carried out at 20 atm without

regeneration of the catalyst for many months. The use of Pt catalysts with high selectivity increases the yields of high-octane petrol and of  $H_2$ . Fractions evaporating in the ranges 85–140, 85–180, 105–140 and 105–180°C, which contain 60% paraffins can be reformed to 95 octane petrol with a yield between 78.7% and 85.7% compared to the original composition.  $H_2$  yield is 1.5–1.8%.

#### Catalytic Oxidation of Ammonia on Platinum

E. J. NOWAK, *Chem. Engng. Sci.*, 1966, **21**, (1), 19–27

The kinetics and mechanism of  $NH_3$  oxidation on Pt or Pt alloy screens and gauzes are discussed with respect to new data on heat and mass transport compared with those for a single infinite circular cylinder. The adequacy of mass transport for a solely heterogeneous mechanism is indicated. Effects of catalyst shape and roughness together with analysis of earlier data suggest that catalyst losses during commercial oxidation are due to oxidative volatilisation of Pt.

#### The Mechanisms of Hydrogenolysis and Isomerisation of Hydrocarbons on Metals. I. Hydrogenolysis of Cyclic Hydrocarbons

G. MAIRE, G. PLOUDY, J. C. PRUDHOMME and F. G. GAULT, *J. Catalysis*, 1965, **4**, (5), 556–559

Product distribution for hydrogenolysis of methylcyclobutane and of various substituted cyclobutanes and cyclopentanes on metal films depends on the metal, on the temperature and on  $p_{H_2}$ ; on the corresponding metal/ $Al_2O_3$  it depends on metal concentration. At high temperatures on Pt and Pd films and on low content Pt/ $Al_2O_3$  and Pd/ $Al_2O_3$  it is typical, denoting equal chances of breaking the cyclic bonds;  $\pi$ -allylic triadsorbed species are involved in the inferred mechanisms. On 10% Pt/ $Al_2O_3$  or Pt film, or on Ni, only disubstituted  $CH_2-CH_2$  cyclic bonds of cyclobutanes and cyclopentanes are broken;  $\alpha, \alpha, \beta, \beta$ -tetrasorbed species are involved in the suggested mechanism. Distributions from methylcyclopentane on Pt/ $Al_2O_3$  and the  $p_{H_2}$  dependency of methylcyclobutane hydrogenolysis on Pt films point to another mechanism. Similar distributions on films to those on supported catalysts indicate no catalytic effect by the carrier.

#### The Effect of Deformation on Catalytic Activity of Platinum in the Decomposition of Hydrogen Peroxide

K. B. KEATING, A. G. ROZNER and J. L. YOUNGBLOOD, *Ibid.*, 608–619

The decomposition of 0.3%  $H_2O_2$  on annealed and cold-worked Pt foils is first order. The rate constant increases with cold working. The catalytic activity of Pt and its deformation are related directly. Increased activity seems due directly to deformation since possible effects of preferred orientation and of increased surface were proved negligible.

#### Catalytic Conversions of 1,4-Endomethylene-spiro-(5,5)-undecane on Platinum Catalyst

N. V. ELAGINA, A. K. MIRZAEVA, KH. E. STERIN, A. V. BOBROV and B. A. KAZANSKII, *Neftekhimiya*, 1965, **5**, (5), 671–675

Final products (wt.%) of the catalytic conversion with Pt/C at 320°C are 2,3-benzbicyclo-[1,2,3]-octane and 2,3-benzbicyclo-[0,3,3]-octane, (50); 1-methyl-3-phenylcyclopentane, (11); benzylcyclopentane, (9); monoalkylbenzenes, (7).

#### Hydrogenation of 2-Methyl-5-acetylfuran on Platinised Carbon in a Flow System under Pressure

N. I. SHUIKIN, G. K. VASILEVSKAYA and I. F. BEL'SKII, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1965, (11), 2029–2032

The reaction was studied at 200–220°C. Changing  $p_{H_2}$  from 1 to 50 atm. did not affect the reduction of the carbonyl group nor hydrogenolysis of the furan ring but increased the degree of hydrogenation of the hydrogenolysis products.

#### Kinetic Regularity of the Isomerisation Reaction of *n*-Pentane on Platinum Catalysts

N. R. BURSIAK and N. K. VOLNUKHINA, *Zh. Prikladnoi Khim.*, 1965, **38**, (10), 2273–2278

The rate of  $n-C_5H_{12}$  isomerisation is directly proportional to  $p_{C_5H_{12}}$  up to 10 atm when  $p_{H_2}$  is 30 atm from 15 to 75 atm. The rate is inversely proportional to  $p_{H_2}$  from 15 to 75 atm when  $p_{C_5H_{12}}$  is 1 atm, and from 60 to 90 atm when  $p_{C_5H_{12}}$  is 10 atm. Changes of working pressures between 15 and 100 atm do not affect the rate of  $n-C_5H_{12}$  isomerisation if  $p_{C_5H_{12}}$  does not exceed 10 atm. Studies establish that adequate activity and stability of the Pt/ $SiO_2-Al_2O_3$  catalyst for the industrial process occur at: working pressure, 35–40 atm;  $p_{C_5H_{12}}$ , 10 atm;  $p_{H_2}$ , 25–30 atm, which are the optimum conditions.

#### The Conversion of *cis*-8-Methylhydrindane in the Presence of Platinised Carbon

E. S. BALENKOVA, N. A. KHAFIZOVA and S. I. KHROMOV, *Neftekhimiya*, 1965, **5**, (6), 797–800

Pt/C catalysed the conversion at 300°C of *cis*-8-methylhydrindane with the formation of *o*-xylene, *o*-methylethylbenzene, *o*-methylpropylbenzene, indane, and 1- and 4-methylindane. This shows that some methyl groups were split off during aromatisation and that methyl radicals also exchanged positions with neighbouring C atoms.

#### Activation Energy of Crystalline Catalysts

LI VEN'-CHZHOU, A. N. MAL'TSEV and N. I. KOBOZEV, *Zh. Fiz. Khim.*, 1965, **39**, (11), 2704–2707

Pt black is 140 times more active than thin Pt layers for the strongly exothermic oxidation of  $C_2H_5OH$  to  $CH_3COOH$  ( $Q_p = 117$  kcal/mol). Moderately exothermic reactions exhibit less activation of Pt atoms in the lattice. Results con-

firm that the Pt crystals account for the energy of the reaction by the way in which catalyst atoms act as acceptors of energy when the reaction occurs at active centres.

#### Effect of Exposure on the Catalytic Activity of Platinum during Hydrogenation

I. V. KRYLOVA, A. P. FILONENKO and N. I. KOBOZEV, *Ibid.*, 2742-2744

Exposure of Pt catalysts to light from mercury-quartz lamps caused increased activity for hydrogenation of cyclohexene but preliminary illumination decreased activity for reduction of nitro groups (e.g. in nitrophenol) and for  $H_2O_2$  decomposition. Tested were Pt/SiO<sub>2</sub> and Pt black.

#### The Oxidative Coupling of Aromatic Compounds with Palladium Salts

R. VAN HELDEN and G. VERBERG, *Rec. Trav. Chim.*, 1965, 84, (9-10), 1263-1273

$C_6H_6$ , PdCl<sub>2</sub> and CH<sub>3</sub>COONa react in CH<sub>3</sub>COOH to produce biphenyl in high yield but no reaction occurs in the absence of CH<sub>3</sub>COONa. A mixture of isomeric biphenyls is obtained from mono-substituted benzenes. Steric effects affect the reaction with disubstituted benzenes, e.g. 3,4,3',4'- and 2,3,3',4'-tetramethylbiphenyl were obtained from *o*-xylene in ratio 2.7:1. The assumed mechanism involves complex formation between the aromatic compound and PdCl<sub>2</sub>, then  $\pi$ -cyclohexadienyl-PdCl<sub>2</sub> formation by reaction between the complex and acetate ions, and decomposition to biphenyl and Pd metal.

#### The Oxidation of Propylene by Palladium Chloride in Acetic Acid

A. P. BELOV, G. YU. PEK and I. I. MOISEEV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1965, (12), 2204-2206

$C_3H_6$  oxidised by PdCl<sub>2</sub> in glacial CH<sub>3</sub>COOH forms *iso*-, *cis-n*- and *trans-n*-propenylacetates, the respective alkylidenediacetates and small amounts of allylacetate.

#### Organic Syntheses by means of Noble Metal Compounds. XI. Copolymerisation of Carbon Monoxide and Norbornadiene

J. TSUJI and S. HOSAKA, *J. Polymer Sci., Part B, Polymer Letters*, 1965, 3, (9), 703-707

Norbornadiene and CO react in  $C_6H_6$  to form a 1:1 copolymer in the presence of a catalytic amount of PdCl<sub>2</sub>, which is the first copolymerisation of CO and olefins catalysed by a transition metal compound to be reported.

#### XVI. Carbonylation of Allene-Palladium Chloride Complexes

J. TSUJI and T. SUSUKI, *Tetrahedron Letters*, 1965, (34), 3027-3031

Structures of substances prepared by carbonylation of allene-PdCl<sub>2</sub> were identified and the mechanisms are discussed.

#### XVII. Reaction of $\pi$ -Allylpalladium Chloride with Nucleophiles

J. TSUJI, H. TAKAHASHI and M. MORIKAWA, *Ibid.*, (49), 4387-4388

$\pi$ -Allylpalladium chloride reacts smoothly with ethyl malonate and acetoacetate to form ethyl allylmalonate and ethyl diallylmalonate. Enamines react similarly with the complex. Thus carbanions can attack the C atom of the Pd complex to give allyl derivatives in high yield. Acetate and alcoholate anions react with the complex to give allyl acetate and ether in low yield.

#### XX. Decarbonylation of Acyl Chloride and Aldehyde Catalysed by Palladium and its Relationship with the Rosenmund Reduction

J. TSUJI, K. OHNO and T. KAJIMOTO, *Ibid.*, (50), 4565-4568

Olefin was formed from acyl chloride with evolution of CO and HCl in the presence of metallic Pd from PdCl<sub>2</sub> decomposed by heating, e.g. decanoyl chloride treated thus formed nonene isomers. Thus Pd catalyses both carbonylation of olefin to acyl halide and decarbonylation of acyl halide to olefin. Decarbonylation of aliphatic aldehyde to form a mixture of olefin and the corresponding paraffin also occurred, e.g. decanal to nonane and nonene. A mechanism for the olefin-CO reaction in the presence of Pd is proposed; connection with the Rosenmund reduction (acyl halide into aldehyde) is established.

#### XXI. Decarbonylation of Aldehyde Using Rhodium Complex

J. TSUJI and K. OHNO, *Ibid.*, (44), 3969-3971

Chlorotris(triphenylphosphine)rhodium was converted into chlorocarbonylbis(triphenylphosphine)rhodium by reaction with aldehydes even at room temperature and thus aldehydes were decarbonylated smoothly into corresponding paraffins.

#### The Transannular Addition of Carbon Monoxide to Cyclo-octa-1,5-diene

S. BREWIS and P. R. HUGHES, *Chem. Commun.*, 1966, (1), 6-7

Pd complexes catalyse this reaction, e.g. cyclo-octa-1,5-diene in tetrahydrofuran reacted with CO at 150°C, 1000 atm in the presence of 1% diiodobis(tributylphosphine)palladium(II) to give 40-45% yield after 8 h of bicyclo-[3,3,1]-non-2-en-9-one. Some 45-50% cyclo-octa-1,3-diene was obtained.

#### Homogeneous Catalytic Hydrogenation of Ethylene and Acetylene with Four-Coordinated Iridium and Rhodium Complexes. Reversible Catalyst-Substrate Adducts

L. VASKA and R. E. RHODES, *J. Am. Chem. Soc.*, 1965, 87, (21), 4970-4971

The *trans*-[MX(CO)(Ph<sub>3</sub>P)<sub>2</sub>] complexes, where M=Ir, Rh and X=halogen, catalyse reactions of

$C_3H_4$ ,  $C_3H_6$  and  $C_2H_2$  with  $H_2$  in  $C_6H_6$  or  $C_6H_5CH_3$  solutions at subatmospheric pressure and 40–60°C. These systems combine the features of: catalyst complexes with known compositions, properties and structures; Ir complexes reacting reversibly with 1 mol. $H_2$ /complex; the  $H_2$  adducts  $[H_2IrX(CO)(Ph_3P)_2]$ , which have been isolated, characterised, and their molecular configurations established; Ir complexes reacting reversibly with  $C_2H_4$ ,  $C_2H_2$  etc. at ambient conditions.

### The Isomerisation of Cyclo-octadienes Catalysed by Rhodium, Iridium and Platinum Complexes

J. K. NICHOLSON and B. L. SHAW, *Tetrahedron Letters*, 1965, (39), 3533–3535

During the preparation of  $[RhCl(C_8H_{12})_2]$  from cycloocta-1,5-diene and  $RhCl_3$  all the uncomplexed olefin is converted to the 1,3-isomer and much of the 1,4-isomer is formed as an intermediate. In the reaction of chloroiridic acid with 1,5- $C_8H_{12}$  to give  $[IrHCl_2(C_8H_{12})_2]$  all the uncomplexed olefin is converted into 1,3- $C_8H_{12}$ . Tertiary phosphine complexes also isomerise 1,5- $C_8H_{12}$  to 1,3- $C_8H_{12}$ , e.g.  $[IrHCl_2(PEt_2Ph)_2]$  at 130°C gives 90% conversion after 120 min.  $[IrCl_2(PEt_2Ph)_3]$  is five times less effective. Diethylphenylphosphine inhibits the isomerisation.  $[RhCl_3(PEt_2Ph)_3]$  is also a good catalyst but *trans*- $[PtHCl(PEt_2)_2]$  and *trans*- $[PdI_2(PMe_2Ph)_3]$  are poor. A high yield of catalyst can be recovered from 1,3- $C_8H_{12}$ .

### The Isomerisation of Octenes Catalysed by Phosphine Complexes of Iridium(III)

R. S. COFFEY, *Ibid.*, (43), 3809–3811

Similar work to the preceding abstract has been carried out with Ir complexes on octene isomerisation.

### Polymerisation by the Derivatives of Transition Metals. III. Competitive Action of Different Ligands on the Stereospecific Polymerisation of Butadiene by Rhodium Salts in Aqueous Emulsion

P. TEYSSIE and R. DAUBY, *Bull. Soc. Chim. France.*, 1965, (10), 2842–2848

Rh salts catalyse the stereospecific polymerisation of butadiene in aqueous emulsion to give only the poly-*trans*-1,4 isomer. The reaction is co-ordinated polymerisation. Very active catalyst systems (Rh-cyclohexadiene) were discovered and the possibility of polymerising butadiene and piperylene simultaneously.

### Hydrogenation of Aromatic Amines on Ruthenium Catalysts

A. S. CHEGOLYA, N. S. SMIRNOVA, B. I. ZHIZDYUK, L. M. RYSHENKO, G. I. GOLUB and A. A. PONOMAREV, *Zh. Org. Khim.*, 1965, 1, (10), 1868–1871

The activity and stability of Ru catalysts were

studied during liquid phase hydrogenation of aromatic amines under pressure. Conditions for stereospecificity during the hydrogenation of 1,4-phenylenediamine to *trans*-1,4-diaminocyclohexane with high yield over  $RuO_2$  were established.

### Oxidation of Sugars with Ruthenium Dioxide-Sodium Periodate: A Simple Method for the Preparation of Substituted Keto Sugars

V. M. PARIKH and J. K. N. JONES, *Canad. J. Chem.*, 1965, 43, (12), 3452–3453

Substituted keto sugars as intermediates in the synthesis of antibiotic agents are prepared by combining the two steps of the previous method into one, whereby  $RuO_4$  oxidant is formed from  $RuO_2$  and then oxidises the alcohol to the sugar. Advantages include nearly quantitative sugar yields, use of only trace quantities of  $RuO_2$ , time-saving and destruction of impurities in the starting material.

### Homogeneous Hydrogenation and Hydroformylation Using Ruthenium Complexes

D. EVANS, J. A. OSBORN, F. H. JARDINE and G. WILKINSON, *Nature*, 1965, 208, (5016), 1203–1204

The Ru(II) complexes  $RuCl_2(PPh_3)_4$  and  $RuCl_2(PPh_3)_3$  dissociate in  $C_6H_6$  solutions. Olefines and acetylenes such as hept-1-ene and hex-1-yne are hydrogenated rapidly by the complexes at 25°C, 1 atm in  $C_6H_6/C_2H_5OH$  solution.  $Ru(CO)_3(PPh_3)_2$  in  $10^{-2}$  M  $C_6H_6$  at 100 atm of  $CO:H_2(1:1)$  gives 80% yield of hexaldehydes from pent-1-ene in 15 h, and is the first case of a Ru complex hydroformylation.

## FUEL CELLS

### The Electrochemical Oxidation of Hydrocarbons on a Tantalum-supported Platinum Catalyst

R. THACKER, *Electrochem. Technol.*, 1965, 3, (11–12), 312–316

Teflon-bonded Pt/Ta cathodes with 9 mg Pt/cm<sup>2</sup> were used in the oxidation of  $C_2H_6$ ,  $C_3H_8$ ,  $C_2H_4$ ,  $C_6H_6$  and *n*- $C_4H_{10}$  gases, and *n*- $C_6H_{12}$  and  $CH_3OH$  vapours, with 14.6 M  $H_3PO_4$  electrolyte immobilised on an asbestos matrix, at 150°C. Cells with higher Pt content on the cathode had been preferred for oxidation of  $C_6H_6$ . Rest potential and polarisation behaviour is discussed.

### Electrochemical Energy Conversion in a Palladium Hydrogen Diffusion Electrode

H. J. CLEARY and N. D. GREENE, *Electrochim. Acta*, 1965, 10, (11), 1107–1115

Current densities of 165 mA/cm<sup>2</sup> were achieved at 30°C on Pd-H diffusion wall electrodes after pretreatment by abrading and oxidising in air at 800°C.  $H_2$  transport is governed by solid-state diffusion.  $H_2$  diffusion in  $\beta$ -Pd is expressed by  $D_{\beta} = 3.8 \times 10^{-4} \exp(-2930/RT)$ .

## CATHODIC PROTECTION

### Anode Design for Shipboard Cathodic Protection

R. L. BENEDICT, *Materials Protection*, 1965, 4, (12), 36-38

Effective protection depends on the shape and voltage of the anodes and on their area. They should be located where mechanical abrasion of paint is unlikely to occur. Platinised Ti, and Pb anodes with Pt micro-electrodes are most effective and should last the life of the ship.

## GLASS TECHNOLOGY

### A Wide Range (up to $10^{10}$ P) Rotating Cylinder Viscometer

A. NAPOLITANO, P. B. MACEDO and E. G. HAWKINS, *J. Res. N.B.S., Sect. A, Phys. Chem.*, 1965, 69A, (5), 449-455

Three techniques enable the range of this viscometer (described in *Platinum Metals Rev.*, 1963, 7, (2), 54-55) to be extended up to  $10^{10}$ P. At  $10^0 - 10^8$ P the outer Pt cylinder is rotated at constant speed and the torque measured on the inner Pt bob. From  $10^{4.5}$  to  $10^{7.5}$ P the bob is rotated through an angle and timed as it returns to its zero position. From  $10^{5.5}$  to  $10^{10}$ P the bob is driven through an angle at constant torque and is timed as it does so.

## NEW PATENTS

### METALS AND ALLOYS

#### Hydrogen Diffusion Tubes

JOHNSON, MATTHEY & CO LTD.  
*British Patent* 1,009,326

A closing plug for sealing the open end of Pd or Pd/Ag alloy  $H_2$  diffusion tube comprises a body formed of a material having approximately the same coefficient of thermal expansion and is dimensioned to give a tight fit and has a projecting, threaded spigot of smaller diameter than the tube and used to form a means for attachment of or for stabilising an internal support for the tube.

### ELECTROCHEMISTRY

#### Activated Platinum Electrodes

J. BISHOP & CO. *U.S. Patent* 3,202,594  
The overvoltage of electrodes coated with a Pt group metal, in particular Pt, is lowered by contacting the coating with an alkali metal amalgam, removing the alkali metal from the Hg film and heating the electrode so that Hg and Pt metal react and finally Hg is distilled off leaving an activated Pt group metal coating.

## TEMPERATURE MEASUREMENT

### Reference Tables for Platinum-40% Rhodium/Platinum-20% Rhodium Thermocouples

R. E. BEDFORD, *Rev. Sci. Instrum.*, 1965, 36, (11), 1571-1580

Tables in the range 0-1880°C are based on calibrations in air of ten thermocouples from four wire lots at the freezing points of Zn, Sb, Ag and Au; the melting points of Pd and Pt by the wire method, and from comparison with standard Pt:10%Rh-Pt and 5%Rh-Pt:20%Rh-Pt thermocouples at 0-1750°C. Test thermocouples are intercompared at 0-1850°C. A.P.H. Report No. 1292 gives more detailed tables.

### Measurement and Control of Gas Temperature in the FINGAL Process

M. N. ELLIOTT and J. R. GROVER, *Br. Chem. Engng.*, 1965, 10, (12), 846-849

The design of a bare wire Pt:13% Rh-Pt thermocouple is described for measurement of off-gas temperatures in the FINGAL process, developed at Harwell for the incorporation of highly radioactive fission product wastes in glass. A similar thermocouple is used with a suction-type pyrometer for gas temperatures in the process vessel.

### Silver Oxide-Palladium Electrode

GENERAL MOTORS CORP. *U.S. Patent* 3,212,934

An electrochemical secondary battery cell comprises a Zn cathode, an alkaline electrolyte and an Ag anode having 1-1.5 wt.% Pd alloyed with it.

### ELECTRODEPOSITION AND SURFACE COATINGS

#### Electrodeposition of Palladium

TECHNIC INC. *British Patent* 1,014,045  
Heavy, clean stress-free and bright electroplated Pd films are formed by using an aqueous electrolyte bath containing 2-10 g/l Pd as its chelate with N,N'-cycloalkane diamine tetraacetic acid and a buffer maintaining a pH 4-12.

#### Improved Method of Coating Graphite or Like Elements and Products Obtained by Such Method

STE. NATIONALE D'ETUDE ET DE CONSTRUCTION DE MOTEURS D'AVIATION

*British Patent* 1,016,309

C elements, e.g. graphite, are protected against thermal shock by applying on them a fixative