

# ABSTRACTS

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

### PROPERTIES

#### Effect of the Addition of Palladium on the Properties of Platinum-Cobalt Permanent Magnetic Alloys

K. WATAI, S. SHIMIZU and Y. TSUJI, *J. Japan Inst. Metals*, 1964, **28**, (11), 745-749

Pt-Co equiatomic alloys were prepared by powder metallurgy with Pd substituted for some Pt. This depressed the lattice transition temperature and raised the magnetic transition temperature. As Pd was added the axial ratio of the superlattice approached unity. Alloys with >10 at.% Pd formed no superlattice. Pd delayed the rate of lattice transition so that higher temperature and longer heat-treatment were needed for the best permanent magnets with improved high temperature stability. Alloys with 2 to 5 at.% Pd had energy product  $>10^7$  G.Oe with improved reproducibility.

#### Calculation of Thermoelectric Power of Pd-Ag and Pd-Rh Alloys

H. KIMURA and M. SHIMIZU, *J. Phys. Soc. Japan*, 1964, **19**, (9), 1632-1637

Assuming that only s-electrons are current carriers, calculations of thermoelectric powers of Pd-rich Pd-Ag and Pd-Rh alloys from the Mott model for s-d scattering and from the density of electronic states derived from low temperature specific heat data agreed qualitatively with experiments at room but not at low temperature. The role of d-holes is discussed. Experimental results can be assigned to a function of composition and temperature by assuming that phonon drag affects the thermoelectric power of Pd at low temperature.

#### Yield-strength Variation in Polycrystalline Silver-Palladium Alloys

P. RODRIGUEZ and K. K. RAO, *J. Inst. Metals*, 1964, **93**, (3), 96

Curves of yield strength and ultimate tensile strength against composition for Ag-Pd alloys were derived from true stress/true strain curves for each alloy tested. Specimens were polycrystalline 0.01 in. wires. Maximum yield strength occurred at 25 at.% Ag-Pd.

#### Thermodynamic Properties of Solid Palladium-Silver Alloys

K. M. MYLES, *Acta Metallurgica*, 1965, **13**, (2), 109-113

Chemical activities of Ag and of nine Ag-Pd alloys, and their free energies, entropies, and enthalpies of formation at 1200°K, were com-

puted from vapour pressure measurements by the torsion-effusion method at 1100 to 1300°K. Ag activities show large negative deviations from ideal behaviour over the whole range, while Pd activities deviate positively in Pd-rich and negatively in Ag-rich alloys. Thermodynamic properties are compared to earlier data. Excess entropies and enthalpies are both negative.

#### [Thermal Coefficient of Expansion of Palau Alloy]

P. L. SPEDDING, *J. Less-Common Metals*, 1964, **7**, (5), 395-396

The linear expansion coefficient of 80% Au-Pd was measured up to 1000°C using a precision micrometer type instrument. It varied from  $13.20 \times 10^{-6}$  cm/cm °C at 100°C to  $15.40 \times 10^{-6}$  cm/cm °C at 1000°C. Results are tabulated together with the slightly higher calculated values.

#### Effect of Temperature on the Lattice Parameter of a 58.98 at.% Gold-41.02 at.% Palladium Alloy

U. DEVI, C. N. RAO and K. K. RAO, *Acta Metallurgica*, 1965, **13**, (1), 44-45

Lattice parameters were proportional to temperature in the range 0-600°C. The alloy exhibited short-range order.

#### Lattice Spacings of Gold-Palladium Alloys

A. MAELAND and T. B. FLANAGAN, *Canad. J. Phys.*, 1964, **42**, (11), 2364-2366

Lattice parameters of alloys in the Au-Pd system were determined by X-ray diffraction and are tabulated. Small negative deviations from linear dependence of parameters on composition, predicted by Vegard's Law, which occur in the Au-Pd and Ag-Pd systems, are discussed. Greater deviations in the Ag-Pd system may be due to the compressibility of Ag being larger than that of Au.

#### Unit-cell Dimensions of Ni-Pd Alloys at 25 and 900°C

L. R. BIDWELL and R. SPEISER, *Acta Cryst.*, 1964, **17**, (11), 1473-1474

Lattice parameters from crystal studies of a complete range of Ni-Pd alloy compositions were tabulated to a precision estimated as  $\pm 1$  part in 10,000 at 25°C and  $\pm 3$  parts in 10,000 at 900°C.

#### The Relative Thermodynamic Properties of Solid Nickel-Palladium Alloys

*Ibid.*, *Acta Metallurgica*, 1965, **13**, (2), 61-70

Measurements at 700-1200°C using a solid electrolyte galvanic cell showed that the relative partial molar free energies of Ni were linear with

respect to temperature, that Ni-rich solutions have endothermic enthalpies of mixing and positive deviations from Raoult's Law for the solvent and negative for the solute and that Pd-rich solutions have exothermic enthalpies with negative deviations for solvent and solute. All excess entropies of mixing are positive. Ni-Pd alloys, especially when Pd-rich, have short-range order.

### The System Palladium-Molybdenum

E. M. SAVITSKIĬ, M. A. TYLKINA and O. KH. KHAMIDOV, *Zh. Neorg. Khim.*, 1964, 9, (12), 2738-2742

Microscopic and X-ray tests established the Pd-Mo constitution diagram as of peritectic type with two solid solutions and one intermetallic compound. The  $\alpha$ -solid solution contains up to 33 wt.% Mo. Electrical resistivity and the elastic limit rise with greater Mo content but the temperature coefficient of resistance decreases. The  $\beta$ -solid solution contains up to 17 wt.% Pd near the melting point but only 12 wt.% Pd at 1400°C. It has b.c.c. structure. The  $\epsilon$ -phase compound has h.c.p. structure with  $a=2.761$ ,  $c=4.476$  Å,  $c/a=1.62$  and is formed peritectically at  $1750 \pm 25^\circ\text{C}$  from the melt and the  $\beta$ -phase. It decomposes at  $1425 \pm 25^\circ\text{C}$  into the  $\alpha$ - and  $\beta$ -solid solutions.

### Ferromagnetism in Dilute Solutions of Gadolinium in Palladium

J. CRANGLE, *Phys. Rev. Letters*, 1964, 13, (19), 569-570

Magnetisation of Pd-Gd alloys containing up to 9.7 at.% Gd was plotted against magnetic field at temperatures between 1.5 and 81°K. Ferromagnetism persisted down to alloys with < 1 at.% Gd. Curie temperatures were lower than for Pd-Fe and Pd-Co alloys.

### Superconducting Tubes and Filaments

G. ARRHENIUS, R. FITZGERALD, D. C. HAMILTON, B. A. HOLM, B. T. MATTHIAS, E. CORENZWIT, T. H. GEBALLE and G. W. HULL, *J. Appl. Phys.*, 1964, 35, (12), 3487-3490

A regular prismatic honeycomb of a superconducting compound was observed when  $\geq 0.5$  at.% La was quenched with Rh in an arc furnace. For < 0.5 at.% La the network was not observed, indicating lowering and broadening of the superconducting transition region. At these concentrations superconducting tunnelling occurs through the elemental Rh phase. This points to the superconductivity of Rh at lower temperatures.

### Magnetic Susceptibility and Electronic Specific Heat of Transition Metals and Alloys. VIII. Zr and Rh Metals

M. SHIMIZU and A. KATSUKI, *J. Phys. Soc. Japan*, 1964, 19, (10), 1856-1861

Temperature variations for electronic specific heat of Rh are explained by calculated results but calculated values for spin paramagnetic susceptibility are lower than observed values.

## The Niobium-Rhodium Binary System. Part I. The Constitution Diagram

D. L. RITTER, B. C. GIESSEN and N. J. GRANT, *Trans. Met. Soc. A.I.M.E.*, 1964, 230, (6), 1250-1259

The complex constitution diagram of this system was determined from X-ray, metallographic, solubility limit, and transformation and solidus temperature tests and indicated nine intermediate phases with two eutectic, five peritectic, two eutectoid, and three peritectoid reactions.

## Part II. Crystal Structure Relationships

*Ibid.*, 1259-1267

The crystal structures of the nine intermediate phases are:  $\alpha$ -Nb<sub>3</sub>Rh, Cr<sub>3</sub>O-type;  $\sigma$ ,  $\sigma_{\text{FeCr}}$  type;  $\alpha$ , H.T. phase of unknown structure;  $\alpha_2$ , AuCu-type;  $\alpha_3$ , orthorhombic analogous to  $\alpha_1$  of the Ta-Rh system;  $\alpha_4$ , AuCd-type;  $\alpha_5$ , monoclinic related to Sm-type;  $\alpha_6$ , VCo<sub>3</sub>-type;  $\alpha$ -NbRh<sub>3</sub>, AuCu<sub>3</sub>-type. The last six are close-packed structures which are compared with Nb-Ir, Ta-Rh and Ta-Ir systems.

## The Niobium-Iridium Constitution Diagram

B. C. GIESSEN, R. KOCH and N. J. GRANT, *Ibid.*, 1268-1273

X-ray, metallographic, solubility limit and solidus tests of the Nb-Ir system showed the five intermediate phases:  $\alpha$ -Nb<sub>3</sub>Ir, cubic Cr<sub>3</sub>O-type;  $\sigma$ , tetragonal  $\sigma_{\text{Fe-Cr}}$  type;  $\alpha$ , tetragonal AuCu-type;  $\alpha_2$ , orthorhombic isostructural with  $\alpha$ , in the Ta-Rh system;  $\alpha$ -NbIr<sub>3</sub>, cubic AuCu<sub>3</sub>-type.  $\alpha$ -Nb<sub>3</sub>Ir and  $\alpha$ -NbIr<sub>3</sub> melt congruently. There are three eutectic and three peritectic reactions.

## Phase Diagram of the System Chromium-Ruthenium

A. K. SHURIN and G. P. DIMITRIEVA, *Sb. Nauchn. Rabot Inst. Metallofiz., Akad. Nauk Ukr. S.S.R.*, 1964, (18), 170-174

X-ray and micrographic studies of 18 homogeneous and repeatedly annealed Ru-Cr alloys with 3.8-73 wt.% Ru revealed that 20 wt.% Ru-Cr melted at 1780-90°C and that a eutectic formed at 37.5 at.% Ru,  $1610 \pm 10^\circ\text{C}$ . In cooling from liquid,  $\beta$ -phase Cr in Ru solid solution crystallised at 1665°C, the eutectic at 1600°C, and  $\alpha$ -phase Ru in Cr, which was homogeneous over 35.5-37.5 at.% Ru, at 1580°C. Ru in Cr was 34 at.% soluble at 1600°C to 19 at.% at 800°C; Cr in Ru 52.5 at.% at 1600°C to 46 at.% at 900°C. Cubic  $\beta$ -W-type RuCr<sub>3</sub> decomposed at 780°C. Structure and decomposition temperature of RuCr<sub>4</sub> could not be determined.

## Transformations in Iron-Ruthenium Alloys under High Pressure

L. D. BLACKBURN, L. KAUFMAN and M. COHEN, *U.S. Rept. AD 437,579*, 1964, 37 pp.

A diffusionless  $\alpha$  (b.c.c.)  $\rightleftharpoons$   $\gamma$  (f.c.c.) transformation occurs on heating and cooling < 12 at.% Ru-Fe alloys at atm. pressure and 12-36 at.% Ru-Fe

alloys show a diffusionless  $\epsilon$  (h.c.p.)  $\rightleftharpoons$   $\gamma$  (f.c.c.) transformation. High pressure depresses the  $\alpha$ - $\gamma$  reaction temperature but elevates that of the  $\epsilon$ - $\gamma$  reaction. Pressure also causes an  $\alpha$ - $\epsilon$  transformation at room temperature in alloys which contain  $\alpha$  at atm. pressure. Pressure-temperature diagrams at constant composition have triple points involving  $\alpha$ ,  $\gamma$ ,  $\epsilon$ . Triple-point pressure decreases continuously as Ru content increases.

## CHEMICAL COMPOUNDS

### Thermal Dissociation of Platinum Iodides

S. A. SHCHUKAREV, T. A. TOLMACHEVA and G. M. SLAVUTSKAYA, *Zh. Neorg. Khim.*, 1964, **9**, (11), 2501-2506

Thermal stability studies on  $PtI_4$  and  $PtI_3$  showed that dissociation pressure varied continuously during their oxidation. Enthalpy of dissociation was:  $PtI_3$ ,  $\sim 4$  kcal/mol;  $PtI_3$ ,  $\sim 12$  kcal/mol. Dissociation pressure was 1 atm for  $PtI_4$  at 246°C; for  $PtI_3$  at 277°C.

### New Fluorides of Palladium: Palladium(II) Hexafluoropalladate(IV) and Related Compounds and Palladium Tetrafluoride

N. BARTLETT and P. R. RAO, *Proc. Chem. Soc.*, 1964, (Dec.), 393-394

The "trifluoride" of Pd is  $Pd^{2+}[PdF_6]^{2-}$ . It was obtained by adding  $BrF_3$  to  $PdBr_2$ . Other compounds of general formula  $Pd^{2+}[MF_6]^{2-}$  were prepared by adding  $BrF_3$  to  $Pd(II)Br_2$  and the appropriate acid former, e.g.  $GeO_2$  for  $PdGeF_6$ . Fluorination of these salts at 150-300°C yields  $PdF_4$  in the case of  $Pd^{2+}[PdF_6]^{2-}$  and mixed tetrafluorides in the other cases.  $PdF_4$  has tetragonal unit cell with  $a=6.585 \pm 0.0005$  Å,  $c=5.835 \pm 0.005$  Å,  $V=253$  Å<sup>3</sup>,  $Z=4$ .

### Molecular Structure of $\pi$ -Allyl-palladium Acetate

M. R. CHURCHILL and R. MASON, *Nature*, 1964, **204**, (4960), 777

Results of a three-dimensional X-ray analysis of  $\pi$ -allyl palladium acetate are illustrated and discussed.

### Complexes of Ruthenium, Rhodium, Iridium, and Platinum with Tin(II) Chloride

J. F. YOUNG, R. D. GILLARD and G. WILKINSON, *J. Chem. Soc.*, 1964, (Dec.), 5176-5189

Pt metal salts reacted with Sn(II) chloride to form the anions  $[RuCl_2(SnCl_3)_2]^{2-}$ ,  $[Rh_2Cl_2(SnCl_3)_4]^{4-}$ ,  $[Ir_2Cl_6(SnCl_3)_4]^{4-}$ , and *cis*- and *trans*- $[PtCl_2(SnCl_3)_2]^{2-}$ , where the trichlorostannate (II) has a donor anionic ligand as strong as chloride ion. Neutral Rh, Ir, and Pt complexes were prepared with an  $SnCl_3$  group bound to the metal together with ligands such as di-olefins, triphenylphosphine and -arsine, e.g.  $(C_7H_8)_3RhSnCl_3$  and  $(Ph_3P)_2PtCl(SnCl_3)$ .

## Transition Metal-Carbon Bonds. Part II. $\pi$ -Allylic and Related Complexes from Some Cyclic 1,3-Dienes

S. D. ROBINSON and B. L. SHAW, *J. Chem. Soc.*, 1964, (Dec.), 5002-5008

Preparations are described of chloro-bridged methoxy  $\pi$ -allylic Pd(II) complexes from several cyclic 1,3-dienes, of cyclohepta- and cyclo-octadienyl Pd(II) complexes, and of a methoxyloctatrienyl Pd(II) complex.

## The Action of Reducing Agents on Pyridine Complexes of Rhodium(III)

B. N. FIGGIS, R. D. GILLARD, R. S. NYHOLM and G. WILKINSON, *Ibid.*, 5189-5193

A series of pyridine complexes containing Rh(II) is now shown to contain Rh(III).

## Thermodynamic Properties and Stability of Ruthenium and Osmium Oxides

A. B. NIKOL'SKII and A. N. RYABOV, *Zh. Neorg. Khim.*, 1965, **10**, (1), 3-9

A review of data for enthalpy of formation, entropy, and free energy of formation of Ru and Os and their oxides. (32 refs.)

## Defining the Heat of Sublimation of Ruthenium Tetroxide

A. B. NIKOL'SKII, *Ibid.*, 290-292

$\Delta H_{\text{subl.}} RuO_4$  is  $13.2 \pm 0.2$  kcal/mole.

## New Complex Compounds of Phthalocyanine with Ruthenium and Iridium

B. D. BEREZIN and G. V. SENNIKOVA, *Dokl. Akad. Nauk. S.S.S.R.*, 1964, **159**, (1), 117-120

The acidic-basic properties, absorption spectra, and kinetics of stability were determined for  $H_2SO_4IrPc$  and  $H_2SO_4RuPc$ , which are compared with Pt metal and Ni and Co phthalocyanines.

## ELECTROCHEMISTRY

### The Transmission of Electrolytically Deposited Hydrogen through a Palladium Membrane Electrode. I. The Rate Equations

G. W. CASTELLAN, *J. Electrochem. Soc.*, 1964, **111**, (11), 1273-1276

### II. Experimental. Oxidising Agents and Hydrogen Gas on the Exit Side

R. A. LA PIETRA and G. W. CASTELLAN, *Ibid.*, 1276-1279

### III. Pressure and Temperature Dependence

P. L. DAMOUR and G. W. CASTELLAN, *Ibid.*, 1280-1283

A mechanism is postulated for transport of  $H_2$  through a Pd membrane which relates the amount of  $H_2$  transmitted to a current density,  $-j$ , and the rate of deposition of  $H_2$  per  $cm^2$  to a polarisation current density,  $-i$ . In general, for

equilibrium on both sides of the membrane, 50% of the  $H_2$  deposited is transmitted. Transmission rate reaches a limiting value,  $-j_m$ , when  $-i$  is high and for thin membranes of thickness  $L$ ,  $L \propto i/(-j_m)$ . The slope of this relation depends on the diffusion coefficient of  $H_2$  in Pd, is independent of surface reaction rates, but may depend on the equilibrium coverage by H atoms. The mechanism was tested and gave a low diffusion coefficient  $D$ , which just below room temperature has  $D = 0.0260 \exp(-6800/RT) \text{ cm}^2/\text{sec}$ . From 0.329 to 1 atm. the penetration-exit reaction  $H_{(\text{ads})} = H_{(\text{bulk})}$  is the slowest surface reaction but is fast enough to have an exchange current density of 0.8 A/cm<sup>2</sup> at 1 atm.

#### Preparation and Surface Area Measurements of Platinised-Platinum Electrodes

M. J. JONCICH and N. HACKERMAN, *Ibid.*, 1286-1289  
Surface areas of platinised Pt electrodes measured by two methods were in good agreement. Specific surface areas of the Pt deposits were functions of the geometry of the plating system, the composition of the plating solution, the time of plating, and the current density. Deposits from the first stages of plating tended to have higher specific surface areas. Additions such as Pb acetate assist adherence of deposits but decrease reproducibility.

#### Passivation of Rhodium in Hydrochloric Acid Solutions

J. LLOPIS and M. VÁZQUEZ, *Electrochim. Acta*, 1964, 9, (12), 1655-1663

Anodic and cathodic charging curves for a Rh plate electrode show that passivation occurs by electrochemical surface oxidation, in  $HClO_4$  electrolyte by the formation of monomolecular films of  $Rh_2O_3$  or  $RhO_2$ , depending on the potential, and in  $HCl$  electrolyte by the formation of  $Rh_2O_3$  only and the absorption of Cl atoms.

## ELECTRODEPOSITION AND SURFACE COATINGS

#### Development of a Process for the Deposition of Noble Metal Resistors in Microcircuits

E. E. WRIGHT and W. W. WEICK, *Electrochem. Technol.*, 1964, 2, (9-10), 262-267

Pt and Pd-Au resin films were applied to glass and ceramic substrata by dipping or spinning and were decomposed thermally to produce resistive films of 30-100 ohm/cm<sup>2</sup> and 10-30 ohm/cm<sup>2</sup> respectively. Microcircuits for a five-bit computer adder were made in this way. Life tests indicated high resistor stability. Resistors seem well suited for high temperature service.

#### Metallising Non-conductors

E. B. SAUBESTRE, L. J. DURNEY and E. B. WASHBURN, *Metal Finishing*, 1964, 62, (11), 52-59

New methods of metallising A.B.S. plastics use

chemical conditioning in place of roughening followed by etching and cleaning. The metallising steps of sensitising, activation with dilute  $PdCl_2$  solution, and electroless Cu plating are unaltered. The Cu electroplating step has been improved and final plating is now easier.

## LABORATORY APPARATUS AND TECHNIQUE

#### The Preparation of Calcium Tungstate Crystals by a Modified Floating Zone Recrystallisation Technique

D. B. GASSON, *J. Sci. Instrum.*, 1965, 42, (2), 114-115

Precise control over the shape of the growth front of the  $CaWO_4:Nd^{3+}$  single crystal is maintained by having a small area of an Ir strip heater immersed in the melt itself. Ir is the only metal which leaves the crystal free of metal or oxide particles. Uniform growth is ensured by rotation of the growing crystal at 60 rev min<sup>-1</sup>. Two holes in the Ir strip ensure that only the periphery of the growth front is affected. The afterheater furnace which anneals the crystal is wound with Pt wire.

## CATALYSIS

#### Catalytic Activity of Reduced Platinum-Ruthenium Oxides

G. C. BOND and D. E. WEBSTER, *Proc. Chem. Soc.*, 1964, (Dec.), 398

Pt-Ru oxides, prepared by a modified Adams method, on reduction have high activity in certain hydrogenations performed by shaking 10-50 mg catalyst with 20 ml alcohol solution of reactant at 30°C. Compared to  $PtO_2$ , the rate was enhanced four times for nitrobenzene, twice for *o*-nitroaniline. Indirect evidence that the Pt and Ru are alloyed in the catalyst is presented.

#### Homogeneous Isomerisation of Pent-1-ene Catalysed by a Platinum-Tin Chloride Complex

G. C. BOND and M. HELLIER, *Chem. & Ind.*, 1965, (1), 35-36

The complex isomerised pent-1-ene to *cis*- and *trans*-pent-2-ene when shaken in  $CH_3OH$  under  $H_2$  at 25°C. The *trans* : *cis* ratio at equilibrium after 1.5 h was about 81 : 17.5. A mechanism is proposed to explain this ratio by means of a complex ion of Pt and Sn chlorides reacting with  $H_2$ .

#### The Importance of $\pi$ -Bonded Intermediates in Hydrocarbon Reactions on Transition Metal Catalysts

J. J. ROONEY and G. WEBB, *J. Catalysis*, 1964, 3, (6), 488-501

Mechanisms involving  $\pi$ -bonded intermediates for exchange of paraffins, olefins and aromatics

with D<sub>2</sub> for hydrogenation, dehydrogenation and isomerisation reactions on transition metal catalysts are reviewed, affording a rational explanation of many unrelated phenomena. Metal surface atoms have properties resembling those of free atoms and ions. Heats of chemisorption of  $\pi$ -bonded intermediates, and catalytic activity and selectivity should be functions of the metals' positions in the periodic table.

#### On the Problem of the Kinetics of Dehydrocyclisation of *n*-Heptane and *n*-Octane on Alumina-Platinum Catalysts

YU. N. USOV, N. I. KUBSHINOVA and L. S. SHESTOVA, *Neftekhimiya*, 1964, 4, (5), 700-707

Conversions of *n*-heptane and *n*-octane were studied at 380-420°C, atm. pressure, over Pt/Al<sub>2</sub>O<sub>3</sub>. Product ratios of alkanes, alkenes and arenes are tabulated and the reaction kinetics are discussed.

#### Kinetic Equations for the Reaction of *n*-Heptane under Catalytic Reforming Conditions

F. A. FEIZKHANOV, G. M. PANCHENKOV and I. M. KOLESNIKOV, *Ibid.*, 722-726

Isomerisation, hydrocracking and dehydrocyclisation of *n*-heptane were studied on platforming catalysts. Kinetic equations were derived as functions of the adsorption coefficient, the reaction rate and the activation energy of the reactions.

#### Organic Synthesis by means of Noble Metal Compounds. VIII. Catalytic Carbonylation of Allylic Compounds with Palladium Chlorides

J. TSUJI, J. KIJU, S. IMAMURA and M. MORIKAWA, *J. Am. Chem. Soc.*, 1964, 86, (20), 4350-4353

Allyl chloride and allyl alcohol reacted with CO at 100 kg/cm<sup>2</sup> in C<sub>6</sub>H<sub>5</sub>OH in the presence of PdCl<sub>2</sub> to form ethyl 3-butenate. Other allylic compounds reacted similarly. In C<sub>6</sub>H<sub>6</sub> solution allyl acetate formed 3-butenic acetic anhydride and allyl ether yielded 3-butenic anhydride by CO addition to the allylic carbon.

#### IX. Preparation of a New Type of $\pi$ -Allylic Palladium Chloride Complex and its Carbonylation

J. TSUJI, S. IMAMURA and J. KIJU, *Ibid.*, 4491

New complexes were formed from  $\alpha$ ,  $\beta$ - and  $\beta$ , $\gamma$ -unsaturated carboxylic esters by heating the latter in the presence of PdCl<sub>2</sub>, by addition of the esters to an alcoholic solution of Na chloropalladate, or by their addition to C<sub>6</sub>H<sub>6</sub> solution of bisbenzotriledichloropalladium. Physical properties of the complexes are tabulated and their carbonylation is being studied.

#### VII. Reactions of Olefin-Palladium Chloride Complexes with Carbon Monoxide

J. TSUJI, M. MORIKAWA and J. KIJU, *Ibid.*, (22), 4851-4853

Olefin-PdCl<sub>2</sub> complexes reacted under 40-100 kg/cm<sup>2</sup> pressure of CO to form  $\beta$ -chloroacyl

chlorides. Yields were moderate only. Carbonylation was followed by esterification. Similar reactions of some chlorinated olefins were also studied.

#### Isomerisation of *n*-Pentane over Platinum Alumina Catalysts of Different Activity

W. N. LISTER, J. L. HOBBS and H. W. PRENGLE, *Am. Inst. Chem. Eng. J.*, 1964, 10, (6), 907-912

Reaction of *n*-C<sub>5</sub>H<sub>12</sub> over 0.3 wt. % Pt/Al<sub>2</sub>O<sub>3</sub> took place at two distinct sites on the catalyst; the amount of hydrogenation-dehydrogenation depended on the Pt content and the isomerisation depended on the acidic content; 0.26 and 1.69 wt. % chloride contents were tested. Diffusion within the catalyst pores may have affected the rate of reaction. Kinetic factors are evaluated and discussed.

#### Study of Mixed Adsorption Catalysts for Dehydrogenation. III. Pd-Au/SiO<sub>2</sub> as a Catalyst for Cyclohexane Dehydrogenation

A. A. ALCHUDZHAN, M. A. MANTIKYAN and A. M. AIKAZYAN, *Izv. Akad. Nauk Armyan. S.S.R., Khim. Nauki*, 1964, 17, (4), 368-374

Catalysts with 1.0 or 0.2 wt. % Pd and Pd:Au ratios from 1:1 to 1:18 were tested. Au did not affect the activity of 1.0 wt. % Pd catalysts whatever the method of Pd and Au deposition on SiO<sub>2</sub>. 0.2 wt. % Pd catalysts prepared by joint deposition of Pd and Au showed increasing activity as the Au content rose. Activity then reached a maximum and decreased.

#### Hydrogenation of $\beta$ -Furylpropionic Acid on Catalysts Containing Certain Metals of Group VIII

N. I. SHUIKIN, V. V. AN, V. M. SHOSTAKOVSKII and I. F. BEL'SKII, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1964, (11), 2102-2103

Hydrogenolysis of the furan group of  $\beta$ -furylpropionic acid over 5% Rh/C at atmospheric pressure and 265°C in a flowing system yielded  $\gamma$ -ketoenantiic acid from which H<sub>2</sub>O was eliminated to give 60% yield of 5-propylbutyrolactone. Over 5% Pd/C the hydrogenation of double bonds in the furan group yielded 47%  $\beta$ -tetrahydrofurylpropionic acid at 250°C. 5% Pt/C, 10% RaneyPd and 30% Ni/ZnO were also studied.

#### Study of the Dual Nature of Selectivity and Stereospecificity in the Process of Hydrogenating *n*-Pentynes on Pd-, Pt- and Rh-Catalysts

L. KH. FREIDLIN and YU. YU. KAUP, *Ibid.*, (12), 2146-2151

Monoolefin formation by hydrogenation of *n*-pentynes on Pd-, Pt- and Rh-black and on Raney Ni catalysts is determined by the adsorption of the pentyne and desorption of the products at the catalytic surface. Graphs show the relative amounts of products formed using each catalyst.

## FUEL CELLS

### Fuel Cell Uses Methanol. Methanol is Source of Hydrogen for Hydrogen-Oxygen Fuel Cell that Generates 5 kw Electricity

*Chem. Eng. News*, 1964, 42, (52), 31

The Shell Research Ltd fuel cell generates up to 5 kw at 60°C by converting CH<sub>3</sub>OH to H<sub>2</sub> and reacting the latter with air. The H<sub>2</sub> is purified by diffusion through Ag-Pd alloy. Electrodes are microporous PVC sheets with a Ag layer over which is a Pt metal catalyst layer. Each electrode is 85% porous and about 1.3 ft<sup>2</sup>, 0.03 in. thick. The electrolyte is alkaline, 62 cells in each of two batteries form a truck-mounted unit.

### Fuel Cells. I. Propane on Palladium Catalyst. II. Propane and Propylene on Adams' Platinum Catalyst. III. The Propylene Potential in Low Temperature Cells

M. FUKADA, C. L. RULFS and P. J. ELVING, *Electrochim. Acta*, 1964, 9, (12), 1551-1562, 1563-1580, 1581-1586

Low temperature cells using gaseous hydrocarbons as fuels were studied. First, negative electrode catalysts of Pd, reduced by C<sub>3</sub>H<sub>8</sub> at H<sub>2</sub>, supported on porous discs of Ni or C, in many cases waterproofed, were tested using gaseous C<sub>3</sub>H<sub>8</sub> fuel, 30% KOH electrolyte, carbon-black air electrode, at 50°C. Repeated small current

discharges gave steady high open-circuit potentials and electrodes with fairly good discharge rates. Fifteen discs of Adams' catalyst pressed with Ag powder were tested at 80°C in He, C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub>, and H<sub>2</sub>. The effect of the period of electrode reduction on the potential with C<sub>3</sub>H<sub>6</sub> was studied. Finally, from the reproducible C<sub>3</sub>H<sub>6</sub> potential at the Pt catalyst in 30% KOH, at 25°C a potential of 0.465 V (NHE) was calculated compared to 0.838V for the C<sub>3</sub>H<sub>6</sub>-O<sub>2</sub> cell. Possible reaction mechanisms in C<sub>3</sub>H<sub>6</sub> cells are discussed.

## ANODIC PROTECTION

### Anodic Protection of Stainless Steel by Galvanic Coupling with Platinum

G. BIANCHI, A. BAROSI and S. TRASATTI, *Electrochim. Acta*, 1965, 10, (1), 83-95

Stainless steel in H<sub>2</sub>SO<sub>4</sub> is passivated and does not corrode when coupled galvanically to Pt sheet with areas in suitable ratio; e.g. R=1 with 38% H<sub>2</sub>SO<sub>4</sub> at room temperature; R=100 with 52% H<sub>2</sub>SO<sub>4</sub> at 75°C. Tests with Pt, Pd and Au show that the efficiency of Pt for anodic protection of stainless steel is due to its dual effect on passivation, not shared by Pd and Au. Stainless steel first enters the zone of unstable passivity, since over-voltage of Pt for discharge of H<sup>+</sup> is low; then it enters the zone of stable passivity, since O<sub>2</sub> in solution is reduced more easily on Pt than on stainless steel.

## NEW PATENTS

### METALS AND ALLOYS

#### Spring Elements

THE INTERNATIONAL NICKEL CO. (MOND) LTD.  
*British Patent* 974,057

A spring for use at 500°C or above consists of an Ir alloy containing 0.5-7 wt.% W and incidental impurities.

#### Commutator Devices for Micromotors

HITACHI LTD. *British Patent* 975,299  
A commutator device for micromotors has commutator segments made of 80-60 wt.% Ag and 20-40 wt.% Pd alloy and holders carrying in sliding contact with the segments metallic brushes made of 95-70 wt.% Pt and 5-30 wt.% Ir alloy.

#### Improving the Ductility of Ruthenium

THE INTERNATIONAL NICKEL CO. (MOND) LTD.  
*British Patent* 981,535

The workability of Ru is improved by melting it under neutral conditions in contact with 0.05-5 wt.% of one or more of the elements: Zn, Cd, Bi, Ti, Ge, Ba, Hf, Ce, Er, Ga, Ho, La, Pr, Sm, Y or Yb and allowing it to solidify without changing the conditions.

#### Precious Metals and Alloys

THE INTERNATIONAL NICKEL CO. (MOND) LTD.  
*British Patent* 981,792

A sheet or strip of Pt group metals or their alloys is produced by forming a compact of flake powder with or without alloying ingredients, heating so that sintering occurs and working the sintered metal to give the desired sheet or strip.

#### Electrical Resistors

INTERNATIONAL RESISTANCE CO.  
*U.S. Patent* 3,154,503

An electrical resistor is produced by applying to a ceramic substrate and firing a vitreous enamel consisting of 99-50 wt.% glass frit including 1-24 wt.% Ag<sub>2</sub>O and 1-50 wt.% finely divided Pd, Pt or Rh.

#### Coating Glass or Refractory Oxides

DEUTSCHE GOLD- & SILBER-SCHNEIDANSTALT  
*French Patent* 1,366,570

The thermal resistance of refractory metal oxide bodies or mixtures of silicates is improved and their corrosion by other materials is prevented by coating them with a Pt alloy containing 2-10 wt.% Rh and 0.5-10 wt.% Pd.