

# ABSTRACTS

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

### PROPERTIES

#### Surface Structures on the Clean Platinum (100) Surface

S. HAGSTROM, H. B. LYON and G. A. SOMORJAI, *Phys. Rev. Letters*, 1965, **15**, (11), 491-493

Surface structures different from those of the substrate were found on clean Pt by X-ray diffraction. They are believed to be characteristic of the clean surface. One form is stable at  $\sim 350$  to  $550^\circ\text{C}$ ; the other is stable from  $\sim 750$  to  $1769^\circ\text{C}$  (melting point).

#### Enhanced Oxidation of Platinum in Activated Oxygen. III. Kinetics and Mechanism

G. C. FRYBURG, *J. Phys. Chem.*, 1965, **69**, (10), 3660-3662

The overall rate of Oxidation of Pt is expressed by  $w_1 = (k_1 + k_2 p_0)t$ , where  $w_1$  is the weight of Pt oxidised from a specimen,  $k_1$  is the temperature-dependent linear rate constant for oxidation due to  $\text{O}_2$  molecules at 0.5 Torr,  $k_2$  is the same for O atoms,  $p_0$  is the partial pressure of O atoms and  $t$  is the time. Tests were carried out at  $900$ - $1150^\circ\text{C}$ . O atoms are  $\sim 300$  times more reactive than  $\text{O}_2$  molecules at  $900^\circ\text{C}$  but about equally reactive at  $1500^\circ\text{C}$ . A mechanism is proposed.

#### Lattice Parameters and Structures of Pd-Pt Solid Solutions

A. KIDRON, *A.S.M. Trans. Q.*, 1965, **58**, (3), 432-434

X-ray studies on Pd-Pt alloys previously annealed at  $600^\circ\text{C}$  gave results lying on the curve  $a = 0.0257 X^2 - 0.0584 X + 3.9236$ , where  $a$  is the lattice parameter and  $X$  is Pd content in at.%, after correction to standard  $25^\circ\text{C}$ .

#### Some Thermoelectrical Characteristics of Alloys of Platinum with Rhodium

N. N. ERGARDT, *Teplofiz. Vysokikh Temp.*, 1965, **3**, (5), 691-694

Thermal e.m.f.s of Rh-Pt alloys against Pt at 100, 500 and  $900^\circ\text{C}$  are given for 6, 10, 13, 20, 30 and 40% Rh-Pt alloys and also the resistance of each alloy from 0 to  $1200^\circ\text{C}$ . A formula is derived for thermal e.m.f.s at  $800^\circ\text{C}$  for different Rh contents.

#### Activity Measurements in Pt-Ni, Pd-Ni and Pd-Co Alloys at 1000 and $1200^\circ\text{C}$

K. SCHWERDTFFGER and A. MUAN, *Acta Met.*, 1965, **13**, (5), 509-515

Activities of Pt and Pd in these alloys was derived

by a Gibbs-Duhem integration from activity data for Ni and Co in the alloys, determined from e.m.f. measurements at 1000 and  $1200^\circ\text{C}$  and from equilibrations with pure NiO and CoO and gas of known  $p_{\text{O}_2}$  at  $1200^\circ\text{C}$ .

#### Thermodynamics of Copper-Platinum Alloys

K. M. MYLES, *J. Metals*, 1965, **17**, (9), 1050, abs. 5  
Relative thermodynamic properties of solid Cu-Pt alloys at  $1350^\circ\text{K}$  were computed from equilibrium vapour pressures of Cu over the alloys. Integral free energies of formation vary smoothly with composition; the minimum is  $4300$  cal/mole at 55 at.% Cu. Integral enthalpies are negative. Integral excess entropies are nearly zero.

#### The Heats of Formation of Gold-Palladium Alloys

J. B. DARBY, *Ibid.*, abs. 4

Heats of formation were calculated from heats of solution data for Au, Pd and their alloys at  $425^\circ\text{C}$ . Negative deviation from ideality over the entire composition range reaches a maximum at  $\sim 40$  at.% Pd and resembles the behaviour of Cu-Pd and Ag-Pd systems. Absolute values of heats of formation increase in the order Ag-Pd < Au-Pd < Cu-Pd.

#### X-ray and Thermodynamic Studies of the Absorption of Hydrogen by Gold-Palladium Alloys

A. MAELAND and T. B. FLANAGAN, *J. Phys. Chem.*, 1965, **69**, (10), 3575-3581

At  $25^\circ\text{C}$ , Au-Pd alloys with <17 at % Au form two phases upon  $\text{H}_2$  absorption. In this region, enthalpy and free energy of adsorption become more negative in direct proportion to Au content. Lattice parameters were determined for various  $\text{H}_2$  contents. Their rate of increase with  $\text{H}_2$  content is independent of the Au content. Equilibrium solubilities of  $\text{H}_2$  at  $25^\circ\text{C}$ , 740 mm Hg were determined as a function of Au content.

#### Magnetic Properties of Palladium-Ruthenium Alloys

E. VOGT and E. OEHLER, *Ann. Physik*, 1965, **15**, (7-8), 357-362

Susceptibility measurements at  $90$ - $800^\circ\text{K}$  on Pd-Ru alloys with up to 10 at.% Ru indicated that the rigid-band model for Ag-Pd and Pd-Rh alloys can probably be extended to Pd-Ru alloys if exchange coupling of  $d$ -electrons through Ru is very greatly reduced.

### Amorphous Phase in Palladium-Silicon Alloys

P. DUWEZ, R. H. WILLENS and R. C. CREWDSON, *J. Appl. Phys.*, 1965, **36**, (7), 2267-2269

An amorphous phase in 15-23 at.% Si-Pd alloys did not crystallise after one month at 250°C but, when heated at >20°C/min, rapidly crystallised at 400°C with ~1000 cal/mol heat release. 17 at.% Si-Pd in the amorphous state has 2.6 times the electrical resistivity of the crystalline form.

### Metastable Amorphous Ferromagnetic Phases in Palladium-base Alloys

C. C. TSUEI and P. DUWEZ, *U.S.A.E.C. Rept. CALT-221-10*, 1965, (May), 3 pp

Fe, Co and Ni, which form complete series of solid solutions with Pd, were substituted for some of the Pd in 20 at.% alloys and the amorphous structure obtained by rapid quenching from the liquid state, which occurs in 16-22 at.% Si-Pd alloys, was retained. The ternary alloys studied were 5% Fe-20% Si-Pd, 12% Co-20% Si-Pd and 15% Ni-20% Si-Pd.

### The Crystal Structure of Pd<sub>2</sub>Hg<sub>5</sub>

P. ETTMAYER, *Monatsh. Chem.*, 1965, **96**, (3), 884-888

Tetragonal Pd<sub>2</sub>Hg<sub>5</sub> has lattice parameters a=9.46<sub>3</sub> Å, c=3.03<sub>1</sub> Å, c/a=0.320<sub>3</sub> and is somewhat similar to Mn<sub>2</sub>Hg<sub>5</sub>.

### The Lattice Spacings of Palladium-Nickel-Copper Ternary Alloys

K. K. RAO, *J. Less-Common Metals*, 1965, **9**, (1), 70-73

Lattice parameters of alloys in this system are tabulated from X-ray data. A triangular graph of lattice parameter against composition indicates that some deviation from random solid solution occurs and that 39.6% Cu-40% Ni-Pd and 38.4% Cu-10.89% Ni-Pd exhibit ordering.

### Rare-earth Intermediate Phases. II. Phases Formed with Palladium

I. R. HARRIS and G. V. RAYNOR, *Ibid.*, (4), 263-269  
Lattice spacings were measured at room temperature for 13 R.E.Pd<sub>3</sub>-type, intermediate phases with f.c.c. structure. Ce atoms in CePd<sub>3</sub> appeared to adopt a valency state similar to that of γ-Ce with effective valency state 3.1. Eu in EuPd<sub>3</sub> and Yb in YbPd<sub>3</sub> appear to behave as 3-valent elements. Hardnesses were measured.

### The Electron Beam Zone Refining of Ruthenium

J. T. SCHRIEMPF, *Ibid.*, (1), 35-39

Ru single crystals about 0.5 cm diameter, <8 cm long were prepared by electron beam zone melting at 10<sup>-5</sup> Torr. Their purity profiles from measuring the ratio of their electrical resistance at room temperature to that at 4.2°K for both

99.9 and 99.999% pure starting materials are shown. A ratio of 1100 is shown for a crystal grown from the purer material.

### Phase Transformations in Iron-Ruthenium Alloys under High Pressure

L. D. BLACKBURN, L. KAUFMAN and M. COHEN, *Acta Met.*, 1965, **13**, (5), 533-541

Fe-Ru alloys with <12 at.% Ru show a diffusionless α (b.c.c.) ⇌ γ (f.c.c.) transformation on heating and cooling at atm. pressure. Alloys with 12-36 at.% Ru show a diffusionless ε (h.c.p.) ⇌ γ (f.c.c.) transformation. High pressure moves α⇌γ to lower temperatures; ε⇌γ to higher temperatures. Pressure also causes α⇌ε at room temperature in alloys which contain α at atm. pressure. The triple point pressure at which α, γ and ε coexist is less as Ru content rises. Fe also exhibits a triple point.

### Lattice Parameters of Tantalum-Osmium Alloys

P. S. RUDMAN, *J. Less-Common Metals*, 1965, **9**, (1), 77-79

Lattice parameters and structures of Ta-Os alloys at 10 at.% Os intervals were obtained from X-ray diffraction films of samples at room temperature after rapid cooling from 1600°C. Results are tabulated. Lattice parameter behaviour is quite like that of the W-Os system.

### The Constitution Diagram of the Tungsten-Molybdenum-Osmium System

A. TAYLOR and N. J. DOYLE, *Ibid.*, (3), 190-205

Tentative constitution diagrams at 1600, 2000 and 2375°C for the W-Mo-Os system drawn from thermal, micrographic and X-ray data revealed no ternary phases of a structure different from those of the constituent binary systems.

### Redetermined Crystal Structures of PdAs<sub>2</sub>, PdSb<sub>2</sub>, PtP<sub>2</sub>, PtAs<sub>2</sub>, PtSb<sub>2</sub>, α-PtBi<sub>2</sub> and AuSb<sub>2</sub>

S. FURUSETH, K. SELTE and A. KJEKSHUS, *Acta Chem. Scand.*, 1965, **19**, (3), 735-741

X-ray powder studies of these pyrite-type crystals gave redetermined values of their lattice constants and parameters, which are tabulated.

## CHEMICAL COMPOUNDS

### Osmium and its Compounds

W. P. GRIFFITH, *Q. Rev. (Chem. Soc.)*, 1965, **19**, (3), 254-273

A general review of the occurrence, extraction, and physical and chemical properties of Os, which, as the most reactive Pt group metal, oxidises even in air at room temperature. Compounds and complexes for all nine oxidation states from VIII to 0 are considered in detail. OsO<sub>4</sub> is extremely toxic and its physiological effects and their treatment are described. (111 refs.)

## New Simple and Complex Fluorides of the Noble Metals

N. BARTLETT, P. R. RAO and N. K. IHA, *Abs. Sci. Papers, I.U.P.A.C. XXth Internat. Congress, Moscow, 1965*, D1.

The synthesis and properties of Pd(IV) fluoride, PdF<sub>3</sub> as Pd<sup>2+</sup>[PdF<sub>6</sub>]<sup>2-</sup>, the salts Pd<sup>2+</sup>[GeF<sub>6</sub>]<sup>2-</sup>, Pd<sup>2+</sup>[PtF<sub>6</sub>]<sup>2-</sup> and Pd<sup>2+</sup>[SnF<sub>6</sub>]<sup>2-</sup> isomorphous with Pd<sup>2+</sup>[PdF<sub>6</sub>]<sup>2-</sup>, XePtF<sub>6</sub><sup>+</sup>, Xe(PtF<sub>6</sub>)<sub>2</sub>, and new fluorides of Rh and Au. Magnetic susceptibility of all Pd<sup>2+</sup>[MF<sub>6</sub>]<sup>2-</sup> salts obeys the Curie Weiss law with  $\mu_{\text{EFF}} = 2.83$  BM for Pd<sup>2+</sup>. The new formula for PdF<sub>3</sub> eliminates the Pd<sup>3+</sup> ion, which was incompatible with the regular octahedral coordination of the Pd atom.

## Ruthenium Compounds and the Periodic Table

J. M. FLETCHER, G. TOPPING and J. L. WOODHEAD, *Ibid.*, D41

The preparation and properties of oxide hydrates, chlorides and oxide chlorides of Ru show that different types of bridges exist between Ru atoms. Differences between Ru compounds and those of neighbouring elements in the periodic table are discussed.

## The Crystal Structure of $\beta$ -Iridium(III) Chloride

D. BABEL and P. DEIGNER, *Z. anorg. allgem. Chem.*, 1965, **339**, (1-2), 57-66

Lattice parameters of orthorhombic  $\beta$ -IrCl<sub>3</sub> are a=6.95, b=9.81, c=20.8<sub>2</sub> Å. The anion arrangement is similar to that of  $\alpha$ -IrCl<sub>3</sub> but the Ir atoms are distributed differently on the octahedral holes of the structures.

## The Crystal Structures of Osmium Tetroxide

T. UEKI, A. ZALKIN and D. H. TEMPLETON, *Acta Cryst.*, 1965, **19**, (2), 157-160

Monoclinic OsO<sub>4</sub> crystals have space group C<sub>2/c</sub>, four molecules in the cell, and lattice parameters a=9.379, b=4.515, c=8.632 Å,  $\beta = 116.6^\circ$ .

## ELECTROCHEMISTRY

### Oxygen Overvoltage Measurements on Bright Platinum in Acid Solutions. III. Nitric Acid-passivated Bright Platinum

J. P. HOARE, *J. Electrochem. Soc.*, 1965, **112**, (8), 849-853

O<sub>2</sub> overvoltage measurements on Pt electrodes passivated in HNO<sub>3</sub> showed that the reversible O<sub>2</sub> electrode can be obtained. The HNO<sub>3</sub> treatment appeared to change the Pt surface, possibly by its conversion to a Pt-O alloy. This is better peroxide decomposition catalyst than Pt and it speeds up O<sub>2</sub> adsorption and the electron transfer step. The O<sub>2</sub>-reduction rate increases by two orders of magnitude. The overvoltage drops by at least 200mV.

### The Preparation and Thermodynamic Properties of a Palladium-Hydrogen Electrode

M. J. VASILE and C. G. ENKE, *Ibid.*, 865-870

Studies of the potential of a Pd-H electrode, prepared electrolytically, as a function of electrode composition, temperature and pH led to the preparation of a Pd-H reference electrode for use in H<sub>2</sub>-free solutions. Potential is a function of electrode composition in each of the  $\alpha$  and  $\beta$  phases but is independent of composition in the  $\alpha + \beta$  phase.

### A New Assemblage for Hydrogen Electrodes

G. BIANCHI, A. BAROSI, G. FAITA and T. MUSSINI, *Ibid.*, (9), 921-923

The assembly consists of a porous graphite support, activated with Pt black, which requires no continuous H<sub>2</sub> flow. Tests in various environments at 25°C show an exchange current of 11-30 mA/cm<sup>2</sup> and a bias potential of 0.03 mV with stability better than 0.01 mV after some days ageing. This electrode is convenient for precision measurements and often avoids difficulties arising from liquid junction potentials which occur with many commonly used reference electrodes.

### Reactivity and Surface Composition. Anodic Methanol Oxidation on Platinum-Gold Alloys

M. W. BREITER, *J. Phys. Chem.*, 1965, **69**, (10), 3377-3383

Voltammetry and periodic potentiostatic current-potential curves for heterogeneous Pt-Au alloys showed that the rate of CH<sub>3</sub>OH oxidation is approximately proportional to the surface area of Pt-rich phase, the only place where it occurs. Results on inhibition of CH<sub>3</sub>OH oxidation by O<sub>2</sub> layers agree with this. No direct correlation exists between reactivity and d-band character in these alloys. Various mechanisms are discussed.

### The Electrolytic Formation and Dissolution of the Oxide Layer on Rhodium in an Acid Solution

S. SHIBATA, *Bull. Chem. Soc. Japan.*, 1965, **38**, (8), 1330-1337

Oxidation of a smooth Rh surface consists of three stages; OH adsorption, formation of an oxide, Rh-O, and formation of the higher oxide Rh<sub>2</sub>O<sub>3</sub>. This oxide is reduced cathodically step by step in two potential regions. These mechanisms were derived from charging curves, corrosion data during a.c. electrolysis, and electrode capacity variation during electrolysis.

### Electrosynthesis of Dimethyl Ethers of Some Dicarboxylic Acids in Methanol and Ethylene Glycol

YU. M. TYURIN, E. P. KOVSMAN and E. A. KARAVAEVA, *Zh. Prikladnoi Khim.*, 1965, **38**, (8), 1818-1824

Diether yield and anodic decomposition rate depend on the anode material, the solvent and

the molecular weight of the monoether starting material. Best yield occurs in  $\text{CH}_3\text{OH}$  on Pt anodes but electrodes of  $\text{MnO}_2$ ,  $\text{PbO}_2$ ,  $\text{Fe}_2\text{O}_4$ , Ti and Ta are ineffective. The mechanism of anodic disintegration is discussed.

### Oxidation of Organic Substances through a Palladium Membrane

A. G. POLYAK, YU. B. VASIL'EV and V. S. BAGOTSKII, *Elektrokhimiya*, 1965, 1, (8), 968-971

The side of the Pd membrane in contact with organic substances in solution ( $\text{HCOOH}$  and  $\text{HCHO}$ ) gains potential  $0.06 \pm 0.015\text{V}$  compared to the side not in contact with them.  $\text{H}_2$  diffuses through the membrane as the organic substances are dehydrogenated during adsorption.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Electrodeposition of Rhodium and Ruthenium for Slip-ring Surfaces

H. C. ANGUS, *Trans. Inst. Met. Finishing*, 1965, 43, (4), 135-142

Mechanical wear of Rh and Ru electrodeposits operating as slip-ring surfaces with Ag-Pd brushes is a function of electrolyte composition, plating conditions and coating thickness. Deposits work well and are wear-resistant;  $40 \times 10^{-6}\text{in}$  is sufficient for most applications with Ru providing a more suitable surface than Rh. Types of roughness to be avoided, their measurement and control are discussed.

### The Electrodeposition of Iridium

C. J. TYRRELL, *Ibid.*, 161-168

Of the aqueous electrolytes proposed for Ir electrodeposition, only that prepared by dissolution of hydrated  $\text{IrO}_3$  in boiling  $\text{HBr}$  appeared to have outstanding merit and has been developed to give a useful thickness of Ir deposit. The bath is stable with bright adherent deposits of hardness 900 DPN. Deposits are somewhat porous and are subject to cracking when thicker than  $1 \mu$ .  $10 \mu$  deposits are obtained on Cu, brass, Ni, mild steel, Mo and Ti; acid Au undercoat is required for the first four of these. Cathode efficiency at  $75^\circ\text{C}$ ,  $5\text{g/l}$ ,  $0.15\text{A/dm}^2$  is 65% on most base metals, 45% on Ti.

### Deposition of Platinum-Rhodium Alloys from *cis*-Dinitrodiamino Electrolytes

G. V. KOZLOVA and G. T. BAKHLOVA, *Zashchita Met.*, 1965, 1, (4), 370-373

Rh-Pt alloys of satisfactory quality are deposited on Cu, Ni, steel, and bronze from an electrolyte containing  $[\text{Pt}(\text{NH}_3)_4](\text{NO}_2)_2$ ,  $[\text{Rh}(\text{NH}_3)_6](\text{NO}_2)_2$ ,  $\text{NaNO}_2$  and  $\text{NH}_3$ . Rh content of the alloy rises with increased Rh concentration in the electrolyte and with higher current density, decreases with increased pH and electrolyte temperature, and is unaffected by  $\text{NaNO}_2$

concentration. Alloy yield rises at pH 7-7.5 but falls with pH increase to 10-11.

### Electrodeposition of Platinum-Rhodium Alloys from Hydrochloric Acid Electrolyte

*Ibid.*, (5), 511-514

Rh-Pt alloys with 45-75% Rh adhere satisfactorily to substrates when deposited from an HCl electrolyte. The alloys' Rh content rises with increases of Rh concentration, temperature and mixing of the electrolyte but increases of Rh content in the electrolyte, current density and chloride content decrease the amount of alloy deposited. The composition of the immersed cathode can regulate the ratio of Rh and Pt in the electrolyte.

### The Platinising of Titanium and Tantalum Electrodes in Aminonitrite Electrolyte

L. V. KUDRYAVTSEVA, K. N. KHARLAMOVA and M. I. MORKHOV, *Ibid.*, 500-504

The recommended electrolyte is Pt (as  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) -  $10\text{g/l}$ ,  $\text{NaNO}_2$  -  $100-280\text{g/l}$ ,  $\text{NH}_4\text{OH}$  (as 5% solution) -  $1-2\text{g/l}$ . Conditions for platinising are  $60-70^\circ\text{C}$ , and current density  $2-10\text{A/dm}^2$  for Ti,  $2-3\text{A/dm}^2$  for Ta.

### Study of Cathodic Processes in Alkaline Electrolytes for Palladising

YA. L. MORGENSHTERN and R. M. VISHOMIRSKIS, *Ibid.*, 505-510

Effects of the concentration and composition of the kinetics of Pd electrodeposition from solutions containing KOH were studied. The process is faster with higher Pd concentration but is retarded by increased alkalinity.

## LABORATORY APPARATUS AND TECHNIQUE

### Apparatus for Electrochemical Determinations of Hydrogen in Inert Gas Mixtures

G. BIANCHI, G. FAITA and T. MUSSINI, *J. Sci. Instrum.*, 1965, 42, (9), 693-695

This potentiometric method uses a cell with porous graphite electrodes activated by a thin layer of Pt black catalyst and similar to high-performance fuel cell electrodes. Equilibrium is rapidly reached and is maintained. Accuracy is better than  $\pm 0.2\%$ . The method is applicable to continuous  $\text{H}_2$  determinations from 100 to  $0.1\%$  in inert gas mixtures.

### Apparatus for High Pressure, High Temperature Studies of Oxide Materials

H. J. VAN HOOK, *Rev. Sci. Instrum.*, 1965, 36, (8), 1119-1120

The pressure vessel contains a furnace with a central hot zone 2.5 cm diameter, 5 cm long within an alumina tube wound with  $1.52\text{mm}$  20% Rh-Pt resistance wire as element. Samples are suspended

within it by Pt wires from an alumina rod. Temperature is measured by a 5% Rh-Pt: 20% Rh-Pt thermocouple. Phase equilibria of oxides have been measured at 1200–1700°C and O<sub>2</sub> pressures up to 100 atm. Small samples are quenched under pressure with few pressure seals to be broken to introduce and remove them.

### Resistance Strain Gauges for the Measurement of Steady Strains at Temperatures above 650°C

R. BERTODO, *J. Strain Anal.*, 1965, **1**, (1), 11–19  
Following a review of 46 metal and alloy systems for use in strain gauges at 0–1000°C, and particularly above 650°C, tests on laboratory specimens and on turbojet components showed that Pt/W-Pt dual elements yield steady strain data to  $\pm 6\%$  in the presence of moderate temperature gradients along the longitudinal axis of the element providing that the mean temperature is known. Accuracy declined where significant temperature gradients existed and the gauge was unusable with components too large for controlled temperature-cycling.

### Enrichment of Tritium by Diffusion through Palladium

S. CHARALAMBUS and K. GOEBEL, *Z. Naturforschung*, 1965, **20a**, (8), 1085–1087

Electrolytic enrichment is preferable for large quantities of T<sub>2</sub> but for small quantities, where it becomes complicated, enrichment of T by diffusion through or adsorption on Pd is simpler. Such occurs in reasonable amounts below  $\sim 150^\circ\text{C}$  where the different diffusion velocities of H<sub>2</sub> and T<sub>2</sub> are significant. Towards 400°C the diffusion velocity of T<sub>2</sub> approaches that of H<sub>2</sub> and only above 300°C are they completely separated from other gases.

## CATALYSIS

### On the Oxidation of Hydrogen on Platinum

V. I. POPOV and S. Z. ROGINSKII, *Kinetika i Kataliz*, 1965, **6**, (4), 695–703

Measurements of the kinetic isotope effect and of the kinetics in static conditions at  $\sim 10^{-1}$  mm Hg for H<sub>2</sub> oxidation on Pt showed that reaction rate at 20°C was  $\propto \sqrt{(\text{O}_2 \text{ concentration})}$  and unrelated to H<sub>2</sub> concentration. Reaction rates were the same for H<sub>2</sub> and D<sub>2</sub> showing that H<sub>2</sub> was not involved in those stages determining the overall rate of the process. The O<sub>2</sub> concentration affected those stages and about half of the reaction by O<sub>2</sub> occurred by the dissociation of O<sub>2</sub> adsorbed on Pt.

### Methane-Deuterium Exchange over Platinum-Rhodium Alloys

D. W. MCKEE and F. J. NORTON, *J. Catalysis*, 1965, **4**, (4), 510–517

The rate of CH<sub>4</sub>-D<sub>2</sub> exchange was studied on

unsupported Rh-Pt alloys at 80–150°C. At lower temperatures the most important mechanism was stepwise exchange to form deuteromethanes successively. Initial rates of formation of CHD<sub>3</sub> and CD<sub>4</sub> during multiple exchange increased with rising temperature. Maximum specific activity occurred with 70 wt.% Rh-Pt, corresponding to one unpaired *d* electron per metal atom.

### Kinetics of Methane-Deuterium Exchange over Noble Metal Alloys. The Palladium-Ruthenium System

D. W. MCKEE, *Trans. Faraday Soc.*, 1965, **61**, (10) 2273–2283

Kinetics of CH<sub>4</sub>-D<sub>2</sub> exchange were studied over Pd-Ru alloys, (powders up to 21 wt.% Ru), at 90–170°C. Ru tended to promote multiple exchange more than Pd. Stepwise exchange was most important at lower temperatures. Maximum specific activity and minimum activation energy occurred with 40 wt.% Ru-Pd. A marked kinetic isotope effect was observed for CD<sub>4</sub>-H<sub>2</sub> exchange. Results suggest an electron-pair bond of CH<sub>3</sub>:M type for stepwise exchange and a higher impaired electron concentration leading to more strongly bonded CH<sub>2</sub>=M species for multiple exchange.

### Results from the Development of Reforming Catalyst 8813

H. BLUME, E.-R. STRICH, C. KURPJUN, H. BARWALD, W. NAUNDORF and W. THIELEBEULE, *Chem. Tech.*, 1965, **17**, (8), 453–459

VEB Leuna-Werke "Walter Ulbricht" has developed a new Pt reforming catalyst, number 8813, with higher activity for isomerisation, dehydrocyclisation and dehydrogenation than numbers 8801 and 8811 previously used. Improvements stem from a new halogen-promoted active Al<sub>2</sub>O<sub>3</sub>, a new forming process and better impregnation of Al<sub>2</sub>O<sub>3</sub> by H<sub>2</sub>PtCl<sub>6</sub>. Results from full scale use at VEB Kombinat "Otto Grotewohl", Bohlen, show that it corresponds to internationally known reforming catalysts.

### The Effect of Sodium on the Properties of Platinum-on-Alumina Catalysts

N. R. BURSIAK, S. B. KOGAN and Z. A. DAVYDOVA, *Kinetika i Kataliz*, 1965, **6**, (4), 744–746

Tests on 0.02–2.5 wt.% Na in Pt/Al<sub>2</sub>O<sub>3</sub> and in Al<sub>2</sub>O<sub>3</sub> show that Na is a catalyst poison for Pt/Al<sub>2</sub>O<sub>3</sub> during the hydrogenation of C<sub>6</sub>H<sub>6</sub> and the isomerisation of *n*-C<sub>6</sub>H<sub>12</sub> but that Na (<0.8 wt.%) promotes Pt/Al<sub>2</sub>O<sub>3</sub> during the dehydrogenation of cyclohexane. Na in Al<sub>2</sub>O<sub>3</sub> prevents dehydration of isopropyl alcohol but promotes its dehydrogenation.

### Dehydrogenation of Methylcyclohexane over a Platinum Alumina Catalyst

A. W. RITCHIE and A. C. NIXON, *Abs. Papers, 150th Meeting, Am. Chem. Soc.*, 1965, 4U–11

Studies of this reaction, as a possible endothermic

heat sink reaction for high-speed aircraft and use of toluene and  $H_2$  produced in it as aviation fuel, showed that the total heat sink at complete conversion would be  $\sim 2000$  Btu/lb fuel, about half of this from the reaction, which proceeds at  $700^\circ\text{--}1100^\circ\text{F}$ , a space velocity of 100 with  $>95\%$  conversion and a selectivity to toluene of  $\sim 99\%$ .  $H_2$  addition to maintain catalyst activity is unnecessary if the conversion gives  $p_{H_2} \sim 10$  p.s.i.a.; which at 10 atm total pressure, requires 3% conversion. Reaction rate decreases at total pressure  $>10$  atm. Specific first-order rate constant at  $820^\circ\text{F}$ , 10 atm is  $1 \text{ sec}^{-1}$  and activation energy is  $\sim 12 \text{ kcal.mole}^{-1}$ .

#### Effect of the Loss of Activity of Platinum-on-Silica Gel Thin Layer Hydrogenation Catalysts

ZH. V. STREL'NIKOVA and V. P. LEBEDEV, *Vest. Moskov. Univ., Ser. II, Khim.*, 1965, (4), 7-9  
Pt/SiO<sub>2</sub> catalysts were prepared from "monomeric" Pt amine and from a "dimeric" salt with two Pt atoms per molecule. Layers prepared from the former, with  $\alpha = 0.0005\text{--}0.007$ , were deactivated completely but Pt layers prepared from the latter remained active because the larger molecules did not clog the pores of the support and reduce the area of active surface.

#### Chemisorption and Catalysis on Platinised Silica Gel. II. Specific Catalytic Activity

O. M. POLTORAK and V. S. BORONIN, *Zh. Fiz. Khim.*, 1965, 39, (10), 2491-2498

Specific catalytic activity of Pt/SiO<sub>2</sub> depends on the position of the active centres in the crystal lattice. Tests of H<sub>2</sub>O<sub>2</sub> decomposition, hydrogenation of hexene-1 and H<sub>2</sub>-D<sub>2</sub> exchange show that the most active catalyst has Pt concentrated evenly rather than these with crystal or surface variations.

#### The Hydrogenation of Terminal Acetylenes - a New Convenient Procedure for the Selective Hydrogenation of Mono-substituted Acetylenes

C. A. BROWN, *Abs. Papers, 150th Meeting, Am. Chem. Soc.*, 1965, 31S-66

Precipitates formed by NaBH<sub>4</sub> and Group VIII metal salts catalyse the hydrogenation of terminal acetylenes but the reaction proceeds less readily than for the olefin analogues. The order of activity is colloidal Ni  $>$  granular Ni  $>$  Pd  $>$  Pt  $\gg$  Ru  $\approx$  Rh, with Rh almost totally poisoned by acetylenes. Only Pd/C has appreciable selectivity, with olefin formed 50 times as fast as paraffin. Amine additions to the hydrogenation mixture increase the rate of hydrogenation of the acetylenes, decrease it for the corresponding olefins, especially with Rh, and suppress hydrogenolysis of propargylic functions. Various terminal acetylenes

may be hydrated selectively to olefins with 85-95% yields, 92-98% purities.

#### Platinum-catalysed Reactions of Silacyclobutanes and 1,3-Disilacyclobutanes

D. R. WEYENBERG and L. E. NELSON, *J. Org. Chem.*, 1965, 30, (8), 2618-2621

Pt catalysed the ring-opening polymerisation of silacyclobutanes and of 1, 1, 3, 3-tetramethyl-1,3-disilacyclobutane to form polymers  $[R_2Si(CH_2)_2]_x$  and  $[Me_2SiCH_2]_x$ . Pt also catalysed the interaction of Si hydrides ( $R'_3SiH$ ) with them to form telomers  $R'_3Si[(CH_2)_2SiR'_2]_xH$  and  $R'_3Si[CH_2SiMe_2]_{2x}H$ . The latter reaction involves exchange of the Si-H bond of the hydride and the ring Si-C bond of the silacyclobutanes and is the first example of Pt catalysing the exchange of alkyl and H on Si.

#### Catalytic Conversions of Diethylamine on Platinum and Palladium Catalysts

O. V. BRAGIN, G. K. GUR'YANOVA and A. L. LIBERMAN, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1965, (7), 1242-1248

Two main conversions of diethylamine which occur at  $200\text{--}310^\circ\text{C}$  on Pt/C and Pd/C are decomposition to form acetonitrile, and cyclisation to pyrrolidine with partial conversion of the remainder to butyronitrile. Pt/C is more likely to support decomposition and is a stronger dehydrogenation catalyst than Pd/C. Pyrrole is identifiable in the catalysate. The reaction mechanisms are discussed.

#### On the Mechanism of the Hydrogenation of Dienes with Isolated Double Bonds

L. KH. FREIDLIN, E. F. LITVIN and L. M. KRYLOVA, *Neftekhimiya*, 1965, 5, (4), 468-472

Liquid-phase hydrogenation of pentadiene-1,4 takes place with high selectivity in the presence of Pd black but with lower selectivity on Raney Ni. Saturated hydrocarbons are formed immediately over Pt- and Rh-black. Pentene-2 forms on the surface of the Pd catalyst directly from pentadiene-1,4 but not from pentene-1. Dienes with more than one double bond (piperylene) are not formed from pentadiene-1,4, unlike the hydrogenation of hexadiene-2,5.

#### Radiation Catalytic Oxidation of Formic Acid in the Presence of Pd-Charcoal Catalysts

D. BERTRAM, *Abs. Sci. Papers, I. U.P.A.C. XXth Internat. Congress, Moscow*, 1965, B64

Oxidation of aqueous HCOOH solutions by O<sub>2</sub> over Pd/C is accelerated by 200 kV X-rays. Oxidation rate  $V = b.C_k + a$ , where  $C_k$  is catalyst concentration,  $a$  is constant of radiolytic H<sub>2</sub>O<sub>2</sub> formation and  $b$  is effective radiation constant. Tests with 0.01 - 0.5 M HCOOH, 0.25 - 1.5 mg/ml Pd/C, at  $38\text{--}48^\circ\text{C}$ , 760 rad/min show these effects.

### Acetaldehyde via the Direct Oxidation of Ethylene

R. JIRA, *Eur. Chem. News Large Plants Supp.*, 1965, (Sept. 10), 58-64

The Aldehyd GmbH process is based on work by Consortium für Elektrochemische Industrie G.m.b.H. and by Farbwerke Hoechst A.G. The aqueous catalyst solution contains  $\text{PdCl}_2$  and  $\text{CuCl}_2$ . Pd formed in the reaction is oxidised to  $\text{PdCl}_2$  by  $\text{CuCl}_2$  so that the formation of  $\text{CH}_3\text{CHO}$  is catalytic with respect to Pd and very little Pd is needed initially. One- and two-stage processes are described and assessed.

### Organic Syntheses by means of Noble Metal Compounds. X. Carbonylation Reaction of Cyclopropane Catalysed by Palladium Chloride

J. TSUJI, M. MORIKAWA and J. KIJI, *Tetrahedron Letters*, 1965, (13), 817-819

Cyclopropane can be carbonylated easily in the presence of  $\text{PdCl}_2$  in  $\text{C}_6\text{H}_6$  to form  $\alpha$ -,  $\beta$ - and  $\gamma$ -chlorobutyl chlorides and also *n*-propylbenzene. This is the first reported cyclopropane carbonylation catalysed by a transition metal.

### XII. Reaction of the Cyclooctadiene - Palladium Chloride Complex with Ethyl Malonate

J. TSUJI and H. TAKAHASHI, *J. Am. Chem. Soc.*, 1965, 87, (14), 3275-3276

1,5-Cyclooctadiene-palladium chloride reacted with ethyl malonate in the presence of  $\text{Na}_2\text{CO}_3$  at room temperature to form  $\mu$ ,  $\mu$ -dichlorobis-(8-dicarboxymethyl-4-cyclooctenyl) dipalladium. The reaction with ethyl acetoacetate was similar. Both showed facile nucleophilic attack of carbanions on the  $\text{PdCl}_2$  complex.

### XIII. Carbonylation of Butadiene- and Isoprene-Palladium Chloride Complexes

J. TSUJI and S. HOSAKA, *Ibid.*, (18), 4075-4079

Two sites of CO attack on the complexes produced different unsaturated carboxylic acid derivatives depending on reaction conditions.

### On the Catalytic Hydrocondensation of Carbon Monoxide with Olefins and their Hydropolymerisation in the Reaction of Carbon Monoxide and Hydrogen. Part 39. Activity of Rhodium Catalysts

YA. T. EIDUS, B. K. NEFEDOV, M.A. BECROZVANNYI and YU. V. PAVLOV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1965, (7), 1160-1169

Hydrocondensation of CO with  $\text{C}_2\text{H}_4$  over Rh/clay occurs with 70% maximum yield at 150°C, 30 atm. Polymerisation does not occur at 150-250°C, 1-30 atm. Liquid products of hydrocondensation of  $\text{C}_2\text{H}_4$  with CO and  $\text{H}_2\text{O}$  contain chiefly aldehydes, (propionaldehyde and 2-methylpenten-2-al-1), and alcohols (propanol-1). At 250-300°C, 1-50 atm. hydrogenation of CO by  $\text{H}_2$  over Rh catalyst gives mainly  $\text{CH}_4$ , while Pt and Pd catalysts are inactive.

### Liquid-phase Hydrogenation of Some Mononuclear Aromatic Compounds in the Presence of Ruthenium Catalysts

A. A. PONOMAREV, A. S. CHEGOLYA and N. S. SMIRNOVA, *Dokl. Akad. Nauk S.S.S.R.*, 1965, 163, (2), 379-382

$\text{RuO}_2$ , 5% Ru/C and 5% Ru/SiO<sub>2</sub> show promise as industrial catalysts for hydrogenation of aromatic compounds in the liquid phase without loss of activity. Tests were carried out at 100 atm  $\text{H}_2$  pressure or more and at various temperatures. Hydrogenations included those of benzene and toluene to cyclohexane and methylcyclohexane; of phenol and cresols to cyclohexanol and its homologues; of aromatic acids, their salts and esters; of nitrobenzene to aniline at 70-90°C (85% yield) and cyclohexylamine at 100-130°C (76% yield); of aromatic amines to those of the cyclohexane series.

### Hydrogenations of Some Aromatic Acids and their Preparation on Ruthenium Catalysts

N. S. SMIRNOVA, A. S. CHEGOLYA and A. A. PONOMAREV, *Zh. Org. Khim.*, 1965, 1, (8), 1422-1425

$\text{RuO}_2$  and Ru/C catalysed hydrogenations of aromatic acids. Reaction conditions and results are tabulated.

### Hydrogenation of Carbon Monoxide and Carbon Dioxide on Supported Ruthenium Catalysts at Moderate Pressures

F. S. KARN, J. F. SHULTZ and R. B. ANDERSON, *Abstr. Papers, 150th Meeting, Am. Chem. Soc.*, 1965, 20U-53

During research on coal conversion, 0.5 wt.% Ru/ $\text{Al}_2\text{O}_3$  catalysed the hydrogenation of CO and  $\text{CO}_2$  at 21.4 atm, 220-240°C, hourly space velocity 300. Molecular weight of product decreased sharply as  $\text{H}_2$  content of the feed gas increased. There were large yields of hard wax from 1  $\text{H}_2$ +1 CO feed and of  $\text{CH}_4$  from 4  $\text{H}_2$ +1  $\text{CO}_2$ . Tests with 3  $\text{H}_2$ +1 CO showed that the rate increases with total pressure to the power 1.2. The empirical equation  $r = k p_{\text{H}_2}^{1.33} / p_{\text{CO}}^{0.13}$  defines the differential reaction rate. High CO concentrations in feed gas tended to poison the catalyst. The small amount of Ru in Ru/ $\text{Al}_2\text{O}_3$  may make it no more expensive than Raney Ni for  $\text{CH}_4$  production.

### A Novel Method of Making Metallic Catalysts

S. J. THOMSON and G. WEBB, *Chem. Commun.*, 1965, (20), 473-474

32 cm lengths of 0.008 in. diameter wires of Ni, Pd and Pt were exploded in ~200 mm Ar or  $\text{H}_2$  to form films on the walls of a Pyrex explosion chamber. Pd wires exploded in  $\text{H}_2$  produced catalysts more active than evaporated Pd films. Samples exploded in Ar were inactive. Tests on the chemisorption of  $\text{H}_2$  and  $\text{C}_2\text{H}_4$  by the exploded material were carried out.

## FUEL CELLS

### Paper Fuel Cell Electrodes

W. A. BARBER and N. T. WOODBERRY, *Electrochem. Technol.*, 1965, 3, (7-8), 194-198

Waterproofed and platinised acrylic paper forms large-area, uniform electrode sheets with performance in  $H_2-O_2$  fuel cells equal to Pt black on a metal screen.

## TEMPERATURE MEASUREMENT

### Differences between the Thermodynamic Scale and the International Practical Scale of Temperature from 0°C to -183°C

C. R. BARBER and A. HORSFORD, *Metrologia*, 1965, 1, (3), 75-80

The thermodynamic scale was realised at 0 to -183°C using an He constant volume gas thermometer, against which Pt resistance thermometers were calibrated to relate accurately the resistance of pure Pt and the thermodynamic temperature. The IPTS, as defined by the Pt resistance thermometer using the Callendar-Van Dusen equation, errs by  $-0.036^\circ$  at  $-80^\circ C$ ,

$+0.023^\circ$  at  $-150^\circ C$ , estimated limit of error on these differences  $\pm 0.006^\circ C$ .

### On the Accuracy of Temperature Measurement with the Platinum Resistance Thermometer

V. V. SYCHEV and N. I. GORBUNOVA, *Teplofiz. Vysokikh Temp.*, 1965, 3, (4), 632-637

Theoretical methods are developed which enable the limits of absolute error to be calculated in the range 0-600°C.

### High Voltage Cathode Temperature Measurement

R. L. FORGACS, B. A. PARAFIN, and E. EICHEN, *Rev. Sci. Instrum.*, 1965, 36, (8), 1198-1203

The temperature measurement and control system of the high voltage cathode of an emission microscope operating to 1300°C, 50 kV consists of a Pt:10% Rh-Pt thermocouple, a recorder, controller and power amplifier. The voltage is  $\sim 10^9$  greater than the permissible thermocouple voltage error but this has negligible effect on the indicated temperature. The thermocouple unit is enclosed in a shield at cathode potential. Accuracy is  $\pm 5^\circ C$ .

## NEW PATENTS

### METALS AND ALLOYS

#### Palladium-Silver Alloys

E. I. DU PONT DE NEMOURS & CO  
*British Patent* 1,004,652

Pd-Ag alloys in powder form are produced by preparing a solution containing Ag and Pd nitrates and precipitating a finely divided alloy of Pd-Ag by the addition of a reducing agent, e.g.  $H_3PO_2$ , which reduces both metals.

#### Noble Metal Alloy Having High Specific Electrical Resistance

DEUTSCHE GOLD- UND SILBER-SCHNEIDANSTALT  
*British Patent* 1,005,292

An alloy of high specific electrical resistance consists of 18-75 wt. % Au, 20-75 wt. % Pd, 2-15 wt. % Fe and 0.4-5 wt. % of one or more of Al, B, Ga or In, any balance being unavoidable impurities.

#### Ruthenium Alloy of Improved Workability

THE INTERNATIONAL NICKEL CO.  
*U.S. Patent* 3,194,657

The workability of Ru metal is improved by permeating the molten Ru in a non-oxidising medium with 0.005-5 wt. % Zn, Bi, Cd, Ba, Ge, Hf or a lanthanide, maintaining the metal in a molten

state until it is substantially quiescent and free from gas evolution and then allowing it to solidify.

#### Self-lubricating Bearing

THE BOEING CO.  
*U.S. Patent* 3,199,934

The running surface is a composite of 7.5-22.5 % Ag, 7.5-22.5 % Pt, 26.25-78.25 %  $MoS_2$ , 5.45-22.75 % PbO and 0.4-1.2 %  $SiO_2$ .

#### Palladium Alloy Permeable to Hydrogen

NIPPON JUNSUISO K.K. *German Patent* 1,199,242  
The alloy consists of Pd with 2-40% of at least one Group IB element and at least 0.1-20% of other Group VIII elements, e.g. Pd with 20-30% Ag, 3-10% Au and 0.1-5% Ru.

## ELECTROCHEMISTRY

### Use of Platinum Anodes in Electrolytic Processes

MONSANTO CO. *U.S. Patent* 3,193,475  
A Pt anode and a Hg cathode have been used in various reactions involving the electrolytic