

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### Metastable Solid Solutions in Silver-Platinum Alloys

W. KLEMENT and H. L. LUO, *Trans. Met. Soc. A.I.M.E.*, 1963, **227**, (5), 1253-1254.

X-ray diffraction data were obtained for alloys prepared from Ag and Pt powders. No flattening in the liquidus curve was detected such as often occurs with metastable gaps. The lattice spacings fit into progressively greater positive distortions in the sequences Au→Pt→Ir, Ag→Pd→Rh and Cu→Ni→Co→Fe→Mn. It is suggested that position in the periodic table must be considered when comparing lattice spacing-composition curves for alloys of these metals.

### Study of the Thermodynamic Properties of Iron-Platinum Alloys by the E.M.F. Method

M. SUNDARESEN, YA. I. GERASIMOV, V. A. GEIDERIKH and I. A. VASIL'EVA, *Zh. Fiz. Khim.*, 1963, **37**, (11), 2462-2466

An e.m.f. study of Fe-Pt alloys in the range 600-900°C showed the effects of alloy composition and temperature. Activities and activity coefficients were calculated. Functions were derived for the mixing of Fe and Pt at 923 and 1123°K, below and above the ordering temperature of Fe<sub>3</sub>Pt and FePt<sub>3</sub>. A complex relation existed with negative deviation from ideal behaviour. Fe<sub>3</sub>Pt had first order phase transition with  $\Delta H_{ord} = -1.8$  kcal/g-at. FePt<sub>3</sub> had an apparently second order transition. The Fe-Pt phase diagram was clarified in the Fe<sub>3</sub>Pt area.

### Heat Content, Heat-of-formation and Free Energy Data. Platinum and its Compounds

C. E. WICKS and F. E. BLOCK, *U.S. Bur. Mines Bull.* 605, *Thermodynamic Properties of 65 Elements - Their Oxides, Halides, Carbides and Nitrides*, 1963, 91-92

Data are tabulated for the metal Pt and for the halide compounds PtCl, PtCl<sub>2</sub>, PtCl<sub>3</sub>, PtCl<sub>4</sub>, PtBr, PtBr<sub>2</sub>, PtBr<sub>3</sub>, PtBr<sub>4</sub>, PtI, PtI<sub>2</sub>, PtI<sub>3</sub> and PtI<sub>4</sub>.

### Rates of Permeation and Diffusion Coefficients of Light and Heavy Hydrogen through Palladium

G. TODA, *Shokubai*, 1963, **5**, (1), 11-24, abs. in English

Calculated and observed values of the diffusion coefficients of H<sub>2</sub> and D<sub>2</sub> permeating Pd wire towards vacuum were in agreement. The permeation rate  $V_p^{H_2}$  for H<sub>2</sub> and its isotopic effect  $V_p^{H_2}/V_p^{D_2}$  were measured. The diffusion

coefficient  $D^H$  of H<sub>2</sub> and its isotopic effect  $D^H/D^D$  were also derived.

### Self-diffusion of Palladium in Silver-Palladium Alloys

R. L. ROWLAND and N. H. NACHTRIEB, *J. Phys. Chem.*, 1963, **67**, (12), 2817-2821

The self-diffusion coefficient  $D_{Pd} = D_{Pd}^0 \exp(bX)$  for Pd in Ag-Pd alloys, where  $b = -7.5$ ,  $X =$  atom fraction of Pd and  $D_{Pd}^0$  is the coefficient for pure Pd at a given temperature. Tests on 0 to 21 at.% Pd alloys at 850 and 896°C used Pd<sup>109</sup> as a tracer.  $D_{Pd}$  and  $D_{Ag}$  have similar exponential dependence on concentration and reduced temperature.  $D_{Pd}$  also equals  $0.0166 \exp(-17.21 T_m/T)$ , where  $T$  is the temperature and  $T_m$  is the melting point of the alloy.

### Properties of Palladium-Iron-Copper Alloys

A. T. GRIGOR'EV and G. V. POZHARSKAYA, *Zh. Neorg. Khim.*, 1963, **8**, (12), 2694-2699

The Brinell hardness, specific electrical resistance and temperature coefficient of resistance were measured for annealed alloys and tempered alloys of the Pd-Fe-Cu system. Results plotted showed the effect of the Fe:Cu ratio for various amounts of Pd and the effect of varying the %Pd while the Fe:Cu ratio remained equal to 1:1. The existence was indicated of Pd<sub>3</sub>FeCu which possessed a tetragonal lattice with  $a = 6.02$ ,  $c = 4.37$  Å and  $c/a = 0.726$ .

### The Crystal Structure of Pd<sub>2</sub>Al

L.-E. EDSHAMMER and V. BJÖRNSTJERNA, *Acta Chem. Scand.*, 1963, **17**, (6), 1803

Pd<sub>2</sub>Al was shown to be isostructural with orthorhombic Rh<sub>2</sub>Ge and to have lattice parameters  $a = 5.407$  Å,  $b = 4.061$  Å and  $c = 7.769$  Å.

### The Equilibrium Diagram of the System Molybdenum-Palladium

E. ANDERSON, *J. Less-Common Metals*, 1964, **6**, (1), 81-84

The Mo-Pd system was studied by X-ray, micrographic, and thermal analysis methods. Pd had maximum solubility in Mo at 6.5 at.% Pd; peritectic temperature  $1755 \pm 10^\circ\text{C}$ . At about 52 at.% Pd an h.c.p.  $\epsilon$ -phase was detected, which decomposed after quenching. The freezing-point maximum of Pd-rich alloys occurred at about 61 at.% Pd. Atomic volume/composition relations were discussed. The tendency in Group VIA—Group VIII C alloys for the solubility in the Group VIII C component to be greater was confirmed, i.e. Mo is more soluble in Pd than Pd is in Mo.

### Crystalline and Magnetic Structure of the Ordered Alloy $Mn_2Pd_3$

V. V. KLYSHIN and R. TSISHEVSKII, *Fiz. Met. i Metallod.*, 1963, 16, (5), 796-798

Neutron and X-ray analyses of the crystal structure of 40 at.% Mn-Pd confirmed that it has b.c. tetragonal structure with lattice parameters  $a=4.01$ ,  $c=3.58$  Å. Neutron measurements were made at  $-190^\circ\text{C}$  and room temperature with and without an applied magnetic field. Study of the ferro-antiferromagnetic transition in this alloy continues.

### Temperature Dependence of Solid Binary Alloys of Nickel with Palladium and Rhodium

I. I. KORNILOV and K. P. MYASNIKOVA, *Izv. Akad. Nauk S.S.S.R., Metallurgiya i Gornoe Delo*, 1963, (6), 146-151

The microstructure of Ni alloys was studied to determine the solubility of alloys with up to 60 at.% Rh. 61 at.% Rh-Ni alloy showed an anomalous increase in hardness caused by the formation of a disordered superstructure above  $800^\circ\text{C}$ . Pd-Ni alloys showed more resistance to plastic deformation than Rh-Ni alloys between 20 and  $500^\circ\text{C}$  but above  $500^\circ\text{C}$  this relation was reversed. Tests at  $800^\circ\text{C}$  showed that Rh-Ni alloys were more creep-resistant than Pd-Ni alloys.

### Structure and Electronic Properties of Niobium-Ruthenium Alloys

D. BENDER, E. BUCHER and J. MÜLLER, *Phys. kondens. Materie*, 1963, 1, (3), 225-231

Electronic specific heat, Debye temperature, paramagnetic susceptibility and superconducting transition temperature were measured for Nb-rich Nb-Ru alloys. A single phase region exists up to  $>45$  at.% Ru at low temperatures, with slow increase of tetragonal deformation above 37 at.% Ru. The transition temperature decreased by about  $0.65^\circ\text{K}$  for each 1% Ru. The transition point for pure Nb was estimated as  $9.49^\circ\text{K}$ . Electronic specific heat and susceptibility measurements on the same specimens indicated that van Vleck type paramagnetism played some part.

### The Iridium-Tungsten System

M. A. TYLKINA, V. P. POLYAKOVA and V. SH. SHEKHTMAN, *Zh. Neorg. Khim.*, 1963, 8, (11), 2549-2555

The W-Ir system contained two intermetallic phases when its phase diagram was constructed from results of melting-point, microstructural, X-ray and hardness tests. Stable h.c.p.  $\epsilon$ -phase existed from 23 to 52 at.% W with  $a=2.736$  Å,  $c=4.378$  Å at 22 at.% W;  $a=2.762$  Å,  $c=4.447$  Å at 50 at.% W. Separate tetragonal  $\sigma$ -phase existed from 69 to 72 at.% W above  $1850^\circ\text{C}$  with  $a=9.68$  Å,  $c=4.98$  Å,  $c/a=0.516$ .  $\sigma+\epsilon$  eutectic existed at 63 at.% W,  $2700\pm 25^\circ\text{C}$ . Ir was 3%

soluble in W at  $2000^\circ\text{C}$ , 1% at  $1000^\circ\text{C}$ . The W-Pt metal diagrams were compared. It was deduced that W-Rh should be similar to W-Ir in its properties.

### A Constitution Diagram for the Molybdenum-Iridium System

S. J. MICHALIK and J. H. BROPHY, *Trans. Met. Soc. A.I.M.E.*, 1963, 227, (5), 1047-1053

The diagram was derived from melting point and X-ray methods and from metallography. Ir solubility in Mo decreased from 16 at.% at  $2110^\circ\text{C}$  to 4.5 at.% at  $1560^\circ\text{C}$ . Mo solubility in Ir was 22 at.% between  $1720$  and  $1915^\circ\text{C}$  and was not much different between  $1500$  and  $2300^\circ\text{C}$ . Three intermediate phases were detected:  $\beta$ -phase  $Mo_3Ir$  with  $\beta$ -W structure formed at  $2110^\circ\text{C}$  peritectically;  $\sigma$ -phase with 29 at.% Ir and complex tetragonal structure; h.c.p.  $\epsilon$ -phase existing from 37 at.% Ir at  $2080^\circ\text{C}$  to 70 at.% Ir at  $1720^\circ\text{C}$ .

### New Semiconducting Arsenopyrite-type Compounds

F. HULLIGER, *Nature*, 1964, 201, (4917), 381-382

Lattice constants of monoclinic semiconducting crystals are tabulated for RuPS, RuAsS, RuSbS, RuPSe, RuAsSe, RuSbSe, RuAsTe, RuSbTe, OsPS, OsAsS, OsSbS, OsPSe, OsAsSe and OsAsTe, which were specially prepared. These substances are non-metallic and weakly diamagnetic. Their thermoelectric powers, energy gaps and magnetic susceptibilities are tabulated.

### Alloys of Thorium with Certain Transition Metals. I. The Systems Thorium-Ruthenium and Thorium-Rhodium

J. R. THOMSON, *J. Less-Common Metals*, 1963, 5, (6), 437-442

X-ray and metallographic studies of the Th-Ru and Th-Rh systems in the  $1000$ - $1500^\circ\text{C}$  range confirmed the existence of the intermetallic compounds  $Th_7Ru_3$ ,  $ThRu$ ,  $ThRu_2$ ,  $Th_7Rh_3$ ,  $ThRh$ ,  $ThRh_2$  and  $ThRh_3$ . Other compounds detected were tentatively designated  $Th_3Ru_2$ ,  $Th_3Rh_4$ ,  $Th_3Rh_5$  and  $ThRh_5$ . Preliminary constitution diagrams were prepared which covered the  $1000$ - $1500^\circ\text{C}$  range. Eutectics and crystal lattice parameters have been studied in several cases.

### II. The Systems Thorium-Osmium, Thorium-Iridium and Thorium-Platinum

*Ibid.*, 1964, 6, (1), 3-10

The Th-Os, Th-Ir, and Th-Pt systems were studied by X-ray methods and metallography in the range  $1000$ - $1500^\circ\text{C}$ .  $Th_7Ir_3$ ,  $ThIr$ ,  $ThIr_2$ , and  $ThIr_5$  were studied and  $ThIr_3$  may also exist.  $Th_3Pt_3$ ,  $ThPt$  and  $Th_3Pt_5$  are known to exist and there is evidence for  $Th_3Pt_4$ ,  $ThPt_2$ ,  $ThPt_4$  and  $ThPt_5$  as well.  $Th_3Os_3$  and  $ThOs_2$  were studied and an intermediate compound between their compositions was detected.

## The Crystal Structure of RuB<sub>2</sub>, OsB<sub>2</sub> and IrB<sub>1.35</sub> and Some General Comments on the Crystal Chemistry of Borides in the Composition Range MeB-MeB<sub>3</sub>

B. ARONSSON, *Acta Chem. Scand.*, 1963, 17, (7), 2036-2050

The lattices and atomic positions of the most B-rich phases in these systems were studied by X-ray methods. Orthorhombic RuB<sub>2</sub> has a=4.645, b=2.865, c=4.045 Å and is isomorphous with OsB<sub>2</sub> which has a=4.684, b=2.872, c=4.076 Å. Monoclinic IrB<sub>1.35</sub> has a=10.525, b=2.910, c=6.099 Å and  $\beta=91^{\circ}4'$ . Other B-rich borides are compared with these structures.

## CHEMICAL COMPOUNDS

### Metal Olefin Compounds. IV. The Preparation and Properties of Some Aryl and Alkyl Platinum(II)-Olefin Compounds

C. R. KISTNER, J. H. HUTCHINSON, J. R. DOYLE and J. C. STORLIE, *Inorg. Chem.*, 1963, 2, (6), 1255-1261

The preparation and physical properties are reported for a series of compounds of the type (olefin)PtR<sub>2</sub> or (olefin)PtRI, where R is an alkyl or aryl group, by the partial or complete replacement of halide groups in Pt(II)-olefin compounds containing cyclic diolefins under the action of alkyl or aryl Grignard reagents. Possible structures are proposed on the basis of chemical and spectral data.

### Five-Coordinate Hydrido-Carbonyl Complexes of Rhodium and Iridium and their Analogy with CoH(CO)<sub>4</sub>

S. S. BATH and L. VASKA, *J. Am. Chem. Soc.*, 1963, 85, (21), 3500-3501

Infrared and proton magnetic resonance spectra illustrated the similarities of the isostructural compounds IrH(CO)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>3</sub> and RhH(CO)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>3</sub> to CoH(CO)<sub>4</sub>. These Ir and Rh compounds are quinequivalent, diamagnetic and thermally- and air-stable. IrH(CO)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>3</sub> was prepared by treating ethanolic IrCl(CO)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub> with aqueous 95% N<sub>2</sub>H<sub>4</sub> and the Rh compound was prepared similarly.

### New Cyclopentadienyl Complexes of Rhodium

R. J. ANGELICI and E. O. FISCHER, *J. Am. Chem. Soc.*, 1963, 85, (23), 3733-3735

New complexes derived from the di- $\pi$ -cyclopentadienylrhodium(III) cation have been prepared. These include  $\pi$ -cyclopentadienyl-(1-*exo*-phenylcyclopentadiene)-rhodium,  $\pi$ -cyclopentadienyl-( $\pi$ -phenylcyclopentadienyl)-rhodium(III) cation, polymeric [(C<sub>5</sub>H<sub>5</sub>)RhBr<sub>2</sub>]<sub>x</sub> and (C<sub>5</sub>H<sub>5</sub>)RhBr<sub>2</sub>(py), where (py)=pyridine. Further compounds were obtained by the reaction of the first cation with Na cyclopentadienide.

## Complexes of Iridium(III) with 1:10-Phenanthroline

B. CHISWELL and S. E. LIVINGSTONE, *J. Inorg. Nucl. Chem.*, 1964, 26, (1), 47-51

Chelated complexes of three types have been prepared: [Ir(phen)<sub>3</sub>]X<sub>3</sub>.nH<sub>2</sub>O where X=Cl, Br, I, ClO<sub>4</sub>; [Ir(phen)<sub>2</sub>X<sub>2</sub>]X.nH<sub>2</sub>O, X=Cl, Br; [Ir(phen)<sub>2</sub>X<sub>2</sub>] [Ir(phen)X<sub>4</sub>].nH<sub>2</sub>O, X=Cl, Br, I. Complexes containing Ir(III) and 1:10-phenanthroline had not been reported previously.

## The Reaction of Ruthenium Tetroxide with Pyridine

Y. KODA, *Inorg. Chem.*, 1963, 2, (6), 1306-1307

The addition compound RuO<sub>4</sub>.2C<sub>5</sub>H<sub>5</sub>N was prepared from CCl<sub>4</sub> solutions of RuO<sub>4</sub> and C<sub>5</sub>H<sub>5</sub>N. Heat decomposed the greenish-black crystals without melting. The solubility in various solvents was observed. Aqueous solutions at 2 p.p.m. concentration could still be detected by the colour.

## High-temperature Chemistry of the Ruthenium-Oxygen System

W. E. BELL and M. TAGAMI, *J. Phys. Chem.*, 1963, 67, (11), 2432-2436

RuO<sub>2</sub> was shown to be the only stable condensed oxide in the 800-1500°C temperature range with O<sub>2</sub> pressures ranging from 0.01 to 1.0 atm. Its dissociation pressure was 1.0 atm at 1540°C. RuO<sub>3</sub> and RuO<sub>4</sub> vapours were detected, depending on the O<sub>2</sub> pressure. The heats of formation  $\Delta H^{\circ}_{298}$  and standard entropies  $S^{\circ}_{298}$  were measured as RuO<sub>3</sub>(s), -72.2±2.0 kcal/mole and 12.5±2.0 e.u.; RuO<sub>3</sub>(g), -18.0±4.0 kcal/mole and 63.7±4.0 e.u.; RuO<sub>4</sub>(g), -46.7±5.0 kcal/mole and 65.5±5.0 e.u.

## Some Halido- and Hydrido-alkyl and -aryl Complexes of Ruthenium(II) and Osmium(II)

J. CHATT and R. G. HAYTER, *J. Chem. Soc.*, 1963, (Dec.), 6017-6027

Complex alkyl and aryl derivatives of Ru(II) and Os(II) were prepared. The compounds are the first reported to have both an H atom and an organic group attached to the same transition metal by  $\sigma$ -bonds. Their general formulae are *cis*-[MR<sub>2</sub>(disphosphine)<sub>2</sub>], and *cis*- and *trans*-[MXR(disphosphine)<sub>2</sub>], where M=Ru, Os; X=Cl, Br, I, SCN, H; R=alkyl, aryl; disphosphine=Me<sub>2</sub>P.CH<sub>2</sub>.CH<sub>2</sub>.PMe<sub>2</sub>, Ph<sub>2</sub>P.CH<sub>2</sub>.CH<sub>2</sub>.PPh<sub>2</sub> or Ph<sub>2</sub>P.CH<sub>2</sub>.PPh<sub>2</sub>. Properties and structure are discussed.

## The Structure of Compounds in the Osmium-Chlorine System

N. I. KOLBIN, I. N. SEMENOV and YU. M. SHUTOV, *Zh. Neorg. Khim.*, 1963, 8, (11), 2422-2427

The formation and properties of OsCl<sub>4</sub> and OsCl<sub>3</sub> were reviewed and their lattice spacings were

tabulated. The dissociation of these compounds to Os and Cl<sub>2</sub> and of (NH<sub>4</sub>)<sub>2</sub>OsCl<sub>6</sub> to Os, Cl<sub>2</sub> and NH<sub>4</sub>Cl were analysed quantitatively.

## ELECTROCHEMISTRY

### Hydrogen: Electrolytic Technique for Purifying it and Removing it from a Gas Stream

S. H. LANGER and R. G. HALDEMAN, *Science*, 1963, **142**, (3589), 225-226

Better than 98% pure H<sub>2</sub> was produced by impressing a voltage across a cell with two efficient electrodes separated by a barrier electrolyte which allowed H<sub>2</sub> to pass towards the anode. Electrodes tested were Pd or Pt on stainless steel screens, Rh, and Pt on Ta screen. Acidic and basic electrolyte membranes were used. The electrode area, membrane resistance and temperature controlled the purification rate. CO in the input gas tended to poison the H<sub>2</sub>-electrode. Output H<sub>2</sub> burnt in a fuel cell could self-power this type of purification unit.

### The Effect of Acidity on the Differential Capacity of Polarised Platinum Electrodes

M. C. BANTA and N. HACKERMAN, *J. Electrochem. Soc.*, 1964, **111**, (1), 114-119

Maxima on differential capacity-potential curves for activated Pt electrodes in molar nitrate and chloride solutions of various pH were attributed to adsorption and desorption processes. The H<sub>3</sub>O<sup>+</sup> discharge → H<sub>2</sub>O discharge transition occurred at pH 3-4. Cl<sup>-</sup> ion inhibited O<sub>2</sub>-layer formation, particularly at low pH and high Cl<sup>-</sup> concentration. Results supported the zero point of charge for Pt being at -0.05 V on the saturated calomel scale. SO<sub>4</sub><sup>2-</sup>, ClO<sub>4</sub><sup>-</sup> and Cl<sup>-</sup> are specifically adsorbed on Pt electrodes in acid solution but NO<sub>3</sub> is not.

### Voltammetric Study of Halide Ion Adsorption on Platinum in Perchloric Acid Solutions

M. W. BREITER, *Electrochim. Acta*, 1963, **8**, (12), 925-935

Halide ion concentration affected the H<sub>2</sub> and O<sub>2</sub> adsorption at a smooth Pt surface in 1 N HClO<sub>4</sub>. Periodic current/potential curves at 30 mV/sec and impedance measurements at 1000 c/s under the same conditions showed that approximately a monolayer of halide ions was present when the concentrations of Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> were 10<sup>-2</sup>M, 10<sup>-4</sup>M and 10<sup>-5</sup>M respectively. Further effects occurred at higher concentrations, partly due to halide deposition.

### Comparative Voltammetric Study of Methanol Oxidation and Adsorption on Noble Metal Electrodes in Perchloric Acid Solutions

*Ibid.*, 973-983

Periodic current/potential curves and impedance measurements using Pt, Pd, Ir, Rh and Au

electrodes showed similarities for Pt and Pd and for Ir and Rh. Little CH<sub>3</sub>OH oxidation occurred at Au. CH<sub>3</sub>OH adsorption was dependent on the O<sub>2</sub> layers formed electrochemically on the Pt metals.

### Passivation of Iridium in Hydrochloric Acid Solutions

J. LLOPIS and L. JORGE, *Electrochim. Acta*, 1964, **9**, (1), 103-111

Ir is generally more resistant to corrosion than Pt under both a.c. and d.c. conditions. Polarisation curves for Ir in HCl showed that for concentrations below 3 N there is passivation of Ir even at low current densities but for concentrations above 4 N the curves were in two parts corresponding to anodic corrosion of Ir and to evolution of Cl<sub>2</sub> and O<sub>2</sub> on passivated Ir. Anodic and cathodic charging curves permitted an estimate of the "oxidised" area after passivation and this decreased with greater HCl concentration. The effect of Cl<sup>-</sup> adsorption is discussed.

### The Performance of Platinised Titanium Anodes in Electrolysis of Cobalt Chloride

K. P. BATASHEV, *Tsvetnye Metally*, 1964, (1), 28-31

Platinised Ti anodes with 0.01-2.0μ Pt deposits were tested for electrolysis of aqueous Co chloride solutions. A film of Co(OH)<sub>3</sub> on the anodes shifted the Cl<sup>-</sup> discharge potential to more electro-positive and more of it formed at higher current densities. Cumulative durability tests lasted up to two months. The Pt dissolution rate of 10<sup>-4</sup>μ/hr (0.88μ/yr) was equivalent to 2.0-4.8g Pt per ton Co deposited at the cathode. When Pt deposits became reduced to 0.14-0.15μ the anodes required replacement. Satisfactory reconditioning by replating followed cleaning and/or stripping. 94% of dissolved Pt was recovered from the electrolyte. No Pt was detected in the Co cathode.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Engineering Applications of Electrochemistry. 6. Platinum Metal Plating

F. H. REID, *Metal Finishing J.*, 1963, **9**, (107), 431-439, 449

This review emphasises the importance of Rh plating for many electronic components and instruments applications. The growing importance of Pd and Pt plating is described. Ru and Ir plating are under study. Electroless plating of Pt metals is reported. (36 refs.)

### Reflecting Films of Platinum for the Vacuum Ultraviolet

G. F. JACOBUS, R. P. MADDEN and L. R. CANFIELD, *J. Opt. Soc. Am.*, 1963, **53**, (9), 1084-1088

An induction heating technique has been de-

veloped for evaporating Pt films on to glass and other substrata to give mirrors with 24% maximum reflectance in the ultra-violet at 584 Å by optimum conditions, i.e. substrate temperature above 250–300°C, deposition rate 5–15 Å/sec and film thickness 120–140 Å. Only 1–2% deterioration in reflectance was noticed after up to one year's storage. Optical constants were determined for the films at various wavelengths.

## LABORATORY APPARATUS AND TECHNIQUE

### Constancy of Weight of 3% Iridium-Platinum Alloy Apparatus in Analytical Operations

G. REINACHER, *Werkstoffe u. Korrosion*, 1964, 15, (1), 84–88

Comparisons with Pt apparatus showed that 3% Ir-Pt crucibles have equally good weight constancy and resist distortion better. Trials included such typical analytical operations as heating at temperatures of up to 1000°C, heating on a waterbath with HNO<sub>3</sub> and HCl for 24 hours, and KHSO<sub>4</sub> and NaKCO<sub>3</sub> fusions. Results were confirmed in practical laboratory work.

### Design and Performance of a High-temperature X-ray Diffractometer Furnace

R. J. SCOTT and E. RUH, *J. Am. Ceram. Soc.*, 1963, 46, (11), 513–515

A furnace was constructed to fit a General Electric XRD-5 diffractometer. The sample holder consisted of 40% Rh-Pt sheet and the heating element of 40% Rh-Pt wound on a spline-shaped mandrel to produce kinks to allow for thermal expansion and with a refractory high-alumina composition cast round the mandrel to hold the wire in position. The combustible mandrel was then burned away. A thin slurry of Al<sub>2</sub>O<sub>3</sub> protected the element for use at 2700°F. The element was held at 2700°F for up to 48 hours without deterioration and at 2800°F for short periods. Studies of the polymorphic inversions of silica demonstrated the unit's capabilities.

## CATALYSIS

### Measurement of Active Pt-Surfaces on Supported Catalysts

G. WEIDENBACH and H. FÜRST, *Chem. Techn.*, 1963, 15, (10), 589–591

The activity of Pt/Al<sub>2</sub>O<sub>3</sub> decreases with increase in the size of the Pt crystals on the support because of the decrease in Pt surface area. Tests showed that the F ratio (atoms of Pt exposed/total atoms of Pt on support) is related to crystal size by  $S = \frac{5M}{L \cdot b \cdot \zeta \cdot F} - \frac{8.46}{F} \cdot 10^{-8} \text{cm}$ , where S is the crystal cube side, M is atomic wt. of Pt, L is the Loschmidt number, b is surface area of Pt

atom and  $\zeta$  is the Pt thickness. Methods used were O<sub>2</sub> adsorption at room temperature and H<sub>2</sub> retention from a stream of O<sub>2</sub>-free N<sub>2</sub>.

### Effect of Water on the Activity of Platinum-on-Alumina Catalysts with Varying Metal Content

I. I. LEVITSKII, M. G. GONIKBERG, KH. M. MINACHEV and D. A. KONDRAT'EV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1963, (11), 2065–2066

0.3 and 3.0% Pt/Al<sub>2</sub>O<sub>3</sub> catalysts were treated with pure H<sub>2</sub> at 550°C and subsequently with a water vapour mixture. The effects of these treatments on C<sub>6</sub>H<sub>6</sub> hydrogenation and C<sub>6</sub>H<sub>12</sub> dehydrogenation were compared with previous results using 0.005% Pt/Al<sub>2</sub>O<sub>3</sub>. H<sub>2</sub>O tended to reactivate catalysts deactivated by pure H<sub>2</sub>. The initial activity of the catalysts rose with Pt content although the activity per unit wt. of Pt fell. The deactivating effect of H<sub>2</sub> and reactivating effect of H<sub>2</sub>O both decreased as the Pt content rose.

### Kinetic Evidence for the Migration of Reactive Intermediates in Surface Catalysis

J. H. SINFELT and P. J. LUCCHESI, *J. Am. Chem. Soc.*, 1963, 85, (21), 3365–3367

When C<sub>2</sub>H<sub>4</sub> was hydrogenated over one part of 0.05% Pt/SiO<sub>2</sub> catalyst mixed with nine parts of Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub>, the rate of hydrogenation was greater with the Al<sub>2</sub>O<sub>3</sub> mixture than could be accounted for by adding the individual activities of Al<sub>2</sub>O<sub>3</sub> and Pt/SiO<sub>2</sub>. This was taken to indicate migration of reactive intermediates (active H<sub>2</sub>) from Pt/SiO<sub>2</sub> catalyst centres to centres on Al<sub>2</sub>O<sub>3</sub>, which chemisorbed C<sub>2</sub>H<sub>4</sub> more than SiO<sub>2</sub>, and accounted for the greater hydrogenation with the Al<sub>2</sub>O<sub>3</sub> mixture than with the SiO<sub>2</sub> mixture.

### Electron Spin Resonance Investigations of Platinum-Carbon System

I. URSU, A. BÓDI and P. POPESCU, *Acad. Repub. Pop. Rom. Inst. Fiz. Atom.*, 1963, (May), 21–IS

### Simultaneous Isotopic Exchange and Catalytic Oxidation of Hydrogen Reactions on Platinum-Carbon

I. URSU, D. STRUGARU and M. PALADI, *Ibid.*, 22–IS

### Electron Spin Resonance Investigations of the Platinum-Carbon System in Different Gaseous Atmospheres

I. URSU and I. BARBUR, *Ibid.*, 23–IS

These papers indicate that unpaired spins may have acted as active centres for simultaneous H-D isotope exchange and oxidation of 3% Pt/C catalyst but that O<sub>2</sub> poisoned the isotope exchange reaction. 3 and 12% Pt/C catalysts were prepared on C by the reduction of H<sub>2</sub>PtCl<sub>6</sub> with H<sub>2</sub> at 200°C, with N<sub>2</sub>H<sub>4</sub> in alkaline solution and with formalin in alkaline solution. E.S.R. tests on these catalysts treated in various ways showed that the concentration of spins/g depended on the conditions of reduction and increased with tempera-

ture. The concentration of spins/g was greatly decreased in air or O<sub>2</sub>, but in N<sub>2</sub> or H<sub>2</sub> was about the same as in vacuo.

### Catalytic Conversions of Spiro-(5, 5)-undecane on a Platinum Catalyst

N. V. ELAGINA, A. K. MIRZAEVA, KH. E. STERIN and B. A. KAZANSKII, *Neftekhimiya*, 1963, 3, (5), 663-667

Hydrogenation and dehydrogenation of spiro-(5, 5)-undecane over 15% Pt/C caused the breaking of a C-C bond at the quaternary C atom joining the two cyclohexane rings and the production of *N*-amyl benzene, together with much smaller quantities of benz-cycloheptane,  $\alpha$ - and  $\beta$ -methyl naphthalene, naphthalene and  $\alpha$ -ethyl indane

### Microdispersions of Metals on Electrochemical Platinum Black. I. Catalytic Activity

G. LA PLUYE, *Bull. Soc. chim. France*, 1963, (10), 2287-2292

Platinised Pt electrodes were treated by the deposition of base metals and the effect on catalytic activity was estimated from the hydrogenation of ethyl *trans*-cinnamate to ethyl *trans*-hydrocinnamate. The activity of Pt decreased exponentially with the addition of Ag. With increasing amounts of Cu there was some recovery of activity after initial decrease, indicating a complex electrochemical mechanism. The decreases in activity for Pb, Zn or Cd were linear and suggested the formation of crystals of those metals.

### A Correlation between the Catalytic Activity of Platinum and its Ability to Adsorb Hydrogen

T. C. FRANKLIN and D. C. McCLELLAND, *J. Phys. Chem.*, 1963, 67, (11), 2436-2439

Studies at platinised Pt wire electrodes on the hydrogenation of *p*-benzoquinone and on the catalytic decomposition of H<sub>2</sub>O<sub>2</sub> indicated that the former process occurred over the whole surface whereas the latter only took place at certain sites. This supported the presumed existence of two forms of surface H<sub>2</sub>. The Pt surface area was measured by H<sub>2</sub> adsorption.

### Catalytic Fission of the Carbon-Halogen Bond. Part 2. Reactions of Tertiary Butyl Chloride with Hydrogen and Deuterium on Evaporated Platinum and Palladium Films

J. S. CAMPBELL and C. KEMBALL, *Trans. Faraday Soc.*, 1963, 59, (11), 2583-2593

Catalytic hydrogenolysis of (CH<sub>3</sub>)<sub>3</sub>CCl on evaporated Pt and Pd films was initially rapid at -35°C or higher temperatures. (CH<sub>3</sub>)<sub>3</sub>CH and HCl were formed but the latter poisoned the reaction. Films pretreated with HCl were studied and the kinetics on Pt were examined. Deuterolysis produced isotopic isobutanes, the distribution of which

helped to explain the mechanism of hydrogenolysis.

### Catalytic Hydrogenation and Electrochemical Reduction of Quinone on Dispersed Palladium-Gold Alloys

I. A. MOSEVICH, I. P. TVERDOVSKII and ZH. L. VERT, *Zh. Fiz.Khim.*, 1963, 37, (12), 2683-2687

In the hydrogenation of quinone, as of maleic acid and *m*-nitrophenol, the catalytic activity depended on the catalyst composition. It remained constant for Pd and alloys up to 60% Au-Pd but more Au decreased the activity and Au was inactive. A potential of about 0.7 V was required in all cases. Electroreduction occurred on all Pd-Au alloys and Pd and at a slightly higher rate on Au. An electronic mechanism for the process is discussed.

### The Reaction between Deuterium and Dialkylacetylenes on Palladium Catalysts

E. F. MEYER and R. L. BURWELL, *J. Am. Chem. Soc.*, 1963, 85, (19), 2877-2880

2-Butyne and D<sub>2</sub> reacted on 0.03% Pd/Al<sub>2</sub>O<sub>3</sub> to form *cis*-2-butene-2,3-*d*<sub>2</sub> with 99% selectivity and stereospecificity at 14°C and the by-products still only amounted to 6% at 58°C. Using an H-D mixture, the H-D exchange was greatly inhibited. Similar results were obtained for 3-hexyne and D<sub>2</sub> over 13.8% Pd/Al<sub>2</sub>O<sub>3</sub> but the by-product proportion was larger. Isotope effects and reaction mechanisms are discussed.

### The Reaction between Deuterium and 1-Butyne, 1,2-Butadiene, and 1,3-Butadiene on Palladium-on-Alumina Catalyst

*Ibid.*, 2881-2887

0.03% Pd/Al<sub>2</sub>O<sub>3</sub> was used in these reactions which produced various isomers of butene. Product ratios of 1-butene, *cis*- and *trans*-2-butene are discussed and the isotopic distribution is considered for each reaction.

### Organic Syntheses by means of Noble-Metal Compounds. Part 3. Reaction of $\pi$ -Allylpalladium Chloride Complex with Carbon Monoxide

J. TSUJI, J. KIJII and M. MORIKAWA, *Tetrahedron Letters*, 1963, (26), 1811-1813.

$\pi$ -Allylpalladium chloride reacted with CO in C<sub>2</sub>H<sub>5</sub>OH in a stainless steel autoclave to form ethyl-3-butenolate. The Pd complex was formed during the CO reaction by using ethanolic solution of allyl alcohol or chloride in the presence of PdCl<sub>2</sub> as catalyst. Pd metal, Pt and Rh compounds also catalysed the formation of ethyl-3-butenolate. The yield with PdCl<sub>2</sub> from allyl chloride was 52%, from allyl alcohol 43.5%.

### Palladium-catalysed Olefine Isomerisation

N. R. DAVIES, *Nature*, 1964, 201, (4918), 490-491  
Results from the synthesis of C<sub>5</sub>H<sub>11</sub>.CD<sub>2</sub>CH=CH<sub>2</sub> and its isomerisation are consistent with

stepwise migration of the double bond in the presence of  $\text{PdCl}_2$  by the movement of H atoms from one C atom to the next only. This was indicated by no D becoming attached to the terminal C atom. It is suggested that an olefine complex of Pd is involved in the reaction mechanism.

### Oxidation of Butylenes into Methyl Ethyl Ketone in the Presence of Palladium Chloride

B. L. KOZIK, S. V. PESTRIKOV and A. R. SAVEL'EV, *Khim. i Tekhnol., Topliv. i Masel*, 1963, (11), 11-15  
Butylene fractions containing 70% *n*-butylene were oxidised to methyl ethyl ketone in the presence of  $\text{PdCl}_2$ . 70-90% of the reaction products was methyl ethyl ketone. The gas conversion rate under steady conditions was 4-5%. Catalytic activity was reduced for pH below 1.8-2.0 and when  $\text{SO}_4^{2-}$  and  $\text{ClO}_4^-$  were present. The use of  $\text{CuCl}_2$  with  $\text{PdCl}_2$  to maintain the catalytic activity is discussed.

### Synthetical Applications of Activated Metal Catalysts. XIX. A Comparison of the Efficiencies of Catalysts Derived from the Metals of Group VIII and from Copper in the Formation of Biaryls from Pyridine and Quinoline

G. D. F. JACKSON, W. H. F. SASSE and C. P. WHITTLE, *Austral. J. Chem.*, 1963, 16, (6), 1126-1131

Of 26 catalysts tested only Pd/C and Raney Ni were of value in producing 2,2'-bi-pyridyl from pyridine. These catalysts were also of some value in producing 2,2'-biquinolyl from quinoline but far better action was obtained using Rh/C. Results for all catalysts tested are tabulated.

### Kinetics of Ethane Hydrogenolysis on Ru/SiO<sub>2</sub> Catalyst

F. B. GONEIM, A. A. BALANDIN and T. A. SLOVKHOTOVA, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1963, (11), 1905-1910

5% Ru/SiO<sub>2</sub> catalyst was used in studying hydrogenolysis of C<sub>2</sub>H<sub>6</sub>. The composition of the C<sub>2</sub>H<sub>6</sub>-H<sub>2</sub> mixture affected the reaction. When Ar was added to the reaction mixture the three partial pressures affected the results. The apparent activation energies for 9% H<sub>2</sub>-91% C<sub>2</sub>H<sub>6</sub> and 28% H<sub>2</sub>-72% C<sub>2</sub>H<sub>6</sub> in the temperature range 200-250°C were 11 and 14.6 kcal/mole respectively.

### Oxidation Reaction of Steroid Alcohols by Ruthenium Tetroxide

H. NAKATA, *Tetrahedron*, 1963, 19, (12), 1959-1963  
RuO<sub>4</sub> oxidised steroid alcohols to the corresponding ketones with >90% yields in neutral media. RuO<sub>3</sub> produced during the reactions was reconverted to RuO<sub>4</sub> by using the O<sub>2</sub>-donor Na metaperiodate in excess, enabling only catalytic amounts of RuO<sub>4</sub> to be required. Na metaperiod-

ate has low solubility in non-polar solvents but the oxidation was slower when Pb tetraacetate replaced it. Using RuO<sub>4</sub> and Na metaperiodate, >80% yield of 3, 17-dione corresponding to 5 $\alpha$ -androstane-3 $\beta$ -ol-17-one was obtained. Cholestane-3 $\beta$ ,5 $\alpha$ ,6 $\beta$ -triol 3-acetate was converted to cholestane-3 $\beta$ ,5 $\alpha$ -diol-6-one 3-acetate with 76% yield.

## FUEL CELLS

### Electrochemical Behaviour of a Palladium Hydrogen-Diffusion Electrode

L. LEDERER and N. D. GREENE, *Electrochim. Acta*, 1963, 8, (11), 883-886

The use of Pd diffusion membranes as H<sub>2</sub> electrodes for fuel cells was shown to be feasible by electrochemical studies on 0.01 in. Pd foil electrodes containing H<sub>2</sub> at 0-10 p.s.i.g. Pd oxide catalyst was formed by heating the foils in air at 600°C and gave maximum current densities of 75 mA/cm<sup>2</sup> at 24°C and of 140 mA/cm<sup>2</sup> at 43.5°C, when using 1 N H<sub>2</sub>SO<sub>4</sub> electrolyte. Platinised Pd electrodes were less efficient.

### The Use of Palladium Electrodes for the Diffusion of Hydrogen in Fuel Cells Working at Ambient Temperature

N. BUSSON, M. JACQUIN and R. BUVET, *J. Chim. phys.*, 1963, 60, (11-12), 1355-1364

Pd foils treated chemically and thermally by various methods were found to be suitable for fuel cell use at 200°C but not at room temperature. The quantity of H<sub>2</sub> diffused was increased sufficiently to give 40 mA/cm<sup>2</sup> current density when 10% Ag-Pd alloy was used in 2 N KOH electrolyte but this remained insufficient for fuel cell purposes at ambient temperatures.

### Palladium Hydrogen Diffusion Electrode, Working at High Temperature in Fused Chloride Medium

R. BARDE and R. BUVET, *Ibid.*, 1365-1371

Current densities from 0.5 to 2.0 A/cm<sup>2</sup> were achieved from the electrochemical oxidation of H<sub>2</sub> diffusing through a Pd electrode immersed in molten LiCl-KCl eutectic electrolyte. The effect of basic oxides, thickness of Pd foil, and temperature were evaluated.

### Electrochemical Oxidation of Methane in Phosphoric Acid [Electrolyte] Fuel Cells at 150°C.

W. T. GRUBB and C. J. MICHAELSKE, *Nature*, 1964, 201, (4916), 287-288

Tests on a CH<sub>4</sub>-O<sub>2</sub> fuel cell using Pt electrodes in 14.6 M (85 wt. %) H<sub>3</sub>PO<sub>4</sub> electrolyte at 150°C showed that, despite the usual inertness of saturated hydrocarbons, there is an e.m.f. higher than from the C<sub>3</sub>H<sub>8</sub>-O<sub>2</sub> system up to a current density of 20 mA/cm<sup>2</sup> and that at 40 mA/cm<sup>2</sup> the

e.m.f. is only 0.5 V from the reversible H<sub>2</sub> potential in the same electrolyte. The almost complete electro-oxidation of CH<sub>4</sub> means that further study of saturated hydrocarbons and their relation to electro-oxidation is necessary.

### Investigation of Current Transport between a Catalyst Suspension Fuel Charge and Brush Electrodes

J. HELD and H. GERISCHER, *Ber. Bunsengesell. Phys. Chem.*, 1963, **67**, (9/10), 921-929

A fine catalyst slurry of Pt or Pd black, or Raney Ni, was suspended in the electrolyte (1 N NaOH was tested in each case and 2 N H<sub>2</sub>SO<sub>4</sub> with Pt or Pd black). H<sub>2</sub>, CH<sub>3</sub>OH and CH<sub>3</sub>COOH fuels were oxidised by O<sub>2</sub> bubbled into the cell and current was collected at Pt or Pd electrodes. Current density depended on catalyst and fuel concentrations, on electrode material, on stirring, and on temperature.

### Physical Chemistry and Construction of Fuel Cells. I. Physicochemical Problems of the Fuel Cell

G. FEUILLADE, *La Technique Moderne*, 1963, **55**, (12), 600-608

Basic principles of the fuel cell, its thermodynamics and kinetics are described. Metals with catalytic activity are used as electrodes. At lower temperatures these are principally Pt, Pd and

Rh-Pt alloys at the H<sub>2</sub> electrode, and Au, Pt, Pd and Ag at the O<sub>2</sub> electrode. Above 400°C the order of catalytic activity at the H<sub>2</sub> electrode is Co < Pt < Au < 10% Ir-Pt < Cu < Pd < 10% Rh-Pt < Ag < Ni and at the O<sub>2</sub> electrode is Au < 10% Ir-Pt < Pt < Co < Cu < 10% Rh-Pt < Ag < C < Ni < Pd, but in the latter group only Au, Cu, Pd and Pt and its alloys have an oxidation potential greater than that of O<sub>2</sub> and are therefore corrosion-resistant.

## TEMPERATURE MEASUREMENT

### Thermocouples for Prolonged and Deep Temperature Measurement of Liquid Steel in Moulds

M. RÉDR, Z. KOŽUŠNÍK and B. LONSKÝ, *Hutnické Listy*, 1963, **18**, (7), 465-471 (in Czech)

Metal-clad thermocouples are more robust than those protected only by a ceramic covering. They are cheaper and their start-up time is short. Diagrams illustrate Pt:10% Rh-Pt and 6% Rh-Pt:30% Rh-Pt assemblies used in tests on the properties of protected thermocouples. They worked well for 13 hours while immersed 76 cm into liquid steel in a 10 ton ingot and were then switched off. Possible direct immersion of a metal-ceramic clad thermocouple of simple design is considered.

## NEW PATENTS

### Electrodeposition of Ruthenium

INTERNATIONAL NICKEL CO. (MOND) LTD.  
*British Patent* 938,164

Provides a process whereby Ru is electro-deposited from an aqueous acidic solution of a soluble tetra sulphamato nitrosyl ruthenate. The Na salt is used preferably which the solution should contain to the extent of 2.5 to 20 g/l.

### Production of Carbonyl Compounds

FARBWERKE HOECHST A. G.  
*British Patents* 938,831-938,838

A series of patents relating to a process for the production of aldehydes, ketones, and/or acids which comprises reacting an olefine with O<sub>2</sub> and H<sub>2</sub>O in a neutral or acid medium and in the presence of a Pt group metal and a redox system.

### Catalytic Hydrogenation of Methyl-butynol

LABORATORI RIUNITI STUDI E RICERCA S.P.A.  
*British Patent* 938,849

Method for the production of 2-methyl-3-buten-2-ol comprises catalytically hydrogenating 2-methyl-3-butyne-2-ol at 40°C in the presence of a metallic Pd/BaSO<sub>4</sub> catalyst.

### Production of Aliphatic or Cyclo-aliphatic Carboxylic Compounds

SHELL INTERNATIONAL RESEARCH N.V.  
*British Patent* 938,854

Process for the production of the above-mentioned compounds comprises passing the corresponding aliphatic or cyclo-aliphatic primary or secondary alcohol in the gaseous state through two heated zones containing a Pt group metal dehydrogenation catalyst.

### Catalytic Hydrogenation of Pyridine Compounds

ABBOTT LABORATORIES. *British Patent* 938,909  
Relates to the catalytic reduction of pyridine or C-substituted derivatives to piperidine or corresponding derivatives thereof using a Ru catalyst, preferably in an amount of from 0.5% to 2.0% by wt. based on the pyridine.

### Removal of HCN from Gases

ENGELHARD INDUSTRIES INC.  
*British Patent* 939,254  
HCN-containing gas is passed over a Pd, Pt, Rh or Ru catalyst. The catalyst metal, which is pre-