

# ABSTRACTS

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

### PROPERTIES

#### The Zirconium-Platinum Alloy System

E. G. KENDALL, C. HAYS and R. E. SWIFT, *Trans. Met. Soc. A.I.M.E.*, 1961, 221, (3), 445-452

Phase relationships in the region 0-50 at.% (68.2 wt.%) Pt were investigated by metallographic, incipient melting, and X-ray diffraction techniques. Phase fields in the Pt-rich region were outlined. The maximum solubility of Pt in  $\beta$ Zr is  $13.5 \pm 1$  wt.% and the minimum solubility in  $\alpha$ Zr is  $< 1.0$  wt.%. Zr solubility in pure Pt is  $< 1.0$  wt.%. A eutectic exists between  $\beta$ Zr and Zr<sub>2</sub>Pt at  $36 \pm 1$  wt.% and 1185°C, and a eutectoid reaction between  $\beta$ Zr and  $\alpha$ Zr + Zr<sub>2</sub>Pt occurs at  $8.5 \pm 1$  wt.% Pt and 826°C. Zr<sub>2</sub>Pt is formed peritectically at about 51.7 wt.% Pt and 1725°C. ZrPt and ZrPt<sub>2</sub> occur at 68.2 and 86.5 wt.% Pt, respectively, with melting points at 2100°C and  $> 2120$ °C, respectively.

#### Constitution Diagrams of the Palladium-Tungsten System

M. A. TYLKINA, V. P. POLYAKOVA and E. M. SAVITSKII, *Zhur. Neorg. Khim.*, 1961, 6, (6), 1471-1474

The system was investigated by thermal analysis, microscopic and X-ray analysis, and measurement of hardness, microhardness and absolute thermal e.m.f. No chemical compounds were observed in the system. A peritectic reaction occurs at  $2175 \pm 25$ °C.  $\alpha$  solid solution of W in Pd extends up to 28 wt.% W and its melting point increases steadily from 1552°C to 2100°C for the alloy containing 25 wt.% W. A narrow  $\beta$ -phase solid solution based on W extends up to 2 wt.% Pd. Between the  $\alpha$ - and  $\beta$ -solid solutions there is a two-phase ( $\alpha + \beta$ ) region.

#### Kirkendall Effect and Diffusion in the Gold-Platinum System

##### I. The Kirkendall Effect

A. BOLK, *Acta Met.*, 1961, 9, (7), 632-642

Sandwich-type diffusion couples of pure Au and pure Pt (poly- and single-crystalline), and of pure Au and a 73.5 at.% Au-Pt alloy were prepared by welding platelets of Au on both sides of a platelet of Pt or the Au-rich alloy. Diffusion took place in a furnace and the Kirkendall effect was measured as a function of temperature and time. A displacement of the marker interface in the direction of the highest Au concentration was observed. A difference in the magnitude of the effect in couples with polycrystalline Pt and in

those with single-crystalline Pt is interpreted in terms of an extra diffusion transport along the grain boundaries in polycrystalline Pt. Porosity and dimensional and structural changes were also studied.

##### II. The Concentration Penetration Curves and the Diffusion Coefficients

*Ibid.*, 643-652

Concentration penetration curves were determined and the overall diffusion coefficient was calculated according to the graphical method of Matano. Partial diffusion coefficients may be calculated from the observed Kirkendall displacement and data concerning the concentration gradient and the concentration in the marker interface. A method of expressing an observed Kirkendall effect in a numerical value between 1 and 0 is given.

#### An Investigation of the Ageing of Platinum-Rich Alloys of Platinum with Silver

A. A. RUDNITSKII and N. A. BIRUN, *Zhur. Neorg. Khim.*, 1961, 6, (6), 1342-1346

Vickers hardness measurements were made on alloys containing 5, 10, 15, 20, 25 and 30 wt.% Ag which had been aged for various periods in the range 10 min-3½ h at 400°, 500°, 600° and 700°C. The alloys were also aged at 500°C for periods in the range 11-75 h and then hardness-tested. Alloys containing 15-30 wt.% Ag show the greatest ageing effect which is obtained by soaking at 500°C for 10-20 h.

#### Ternary Carbon Alloys of Palladium and Platinum with Magnesium, Aluminium, Zinc, Gallium, Germanium, Cadmium, Indium, Tin, Mercury, Thallium and Lead

H. H. STADELMAIER and W. K. HARDY, *Z. Metallkunde*, 1961, 52, (6), 391-396

The crystal structure of 22 ternary alloy systems was examined. True ternary phases of the Al and related structures were found in the Pd-In-C, Pd-Sn-C, Pd-Pb-C, Pt-Mg-C, Pt-Al-C, Pt-Ga-C, Pt-In-C, Pt-Sn-C and Pt-Pb-C systems. The structures of PdMg, Pd<sub>2</sub>Zn, Pd<sub>3</sub>Tl, Pt<sub>3</sub>Mg, PtMg, Pt<sub>3</sub>Al, Pt<sub>3</sub>In and Pt<sub>3</sub>Hg were also determined.

#### Metal-Optical Investigations on Silver-Palladium and Nickel-Chromium Alloys

H.-E. SCHMIDT and R. E. HUMMEL, *Z. Metallkunde*, 1961, 52, (5), 337-343

Optical constants of mechanically polished samples were determined using incident visible

light of different wave-lengths. Reflected intensity and phase of the originally plane polarised light were observed and the refractive coefficient and absorption coefficient were calculated as a function of intensity ratio and principal angle of incidence. Data obtained are used to study the application of the free conduction electron model to the alloys studied.

### Ferromagnetism in Dilute Solutions of Cobalt in Palladium

R. M. BOZORTH, P. A. WOLFF, D. D. DAVIS, V. B. COMPTON and J. H. WERNIK, *Phys. Rev.*, 1961, **122**, (4), 1157-1160

Magnetic moments were measured in fields up to 12k oersteds at temperatures down to 1.3°K. Ferromagnetism exists in the 0.1 at.% Co-Pd alloy even though the Co atoms are about 10 at. diameters apart. The Curie point of this alloy is 7°K. It was found that the moment associated with one Co atom increases from 1.7 Bohr units in pure Co to 9 to 10 units in the maximum dilution. The onset of ferromagnetism at about 10 at.% Co was indicated by measurement of lattice constants.

### Magnetic Coupling in Palladium-Dilute Iron Group Alloys

E. O. WOLLAN, *Phys. Rev.*, 1961, **122**, (6), 1710-1713

The magnetic properties of Pd and its alloys with Fe group metals is discussed in terms of the splitting of the *d* orbitals. Data already obtained for the Curie point temperatures of Pd-Fe alloys and ferromagnetic saturation moments of Pd-Fe and Pd-Ni alloys are shown graphically.

### Néel Temperatures and Thermoremanent Magnetisation of $Mn_xPd_{100-x}$ Alloys ( $34 \leq x \leq 42$ )

R. WENDLING, *Compt. rend.*, 1961, **252**, (21), 3207-3209

The susceptibilities of alloys quenched at 1200°C show a sharp maximum at temperatures  $T_N$  which increase as *x* increases. After annealing at 450°C, the thermoremanent magnetisation is very feeble. The susceptibility maxima for alloys cooled slowly after melting are less sharp. Thermoremanent magnetisation induced by annealing at 450°C disappears at  $T_N$ .

### The Hall Effect in Some Pd-Co-H Alloys

J.-P. BURGER, *Compt. rend.*, 1961, **252**, (24), 3763-3765

Pd and Co-Pd alloys containing 2, 4 and 7 at.% Co were studied before and after hydrogenation. The ferromagnetic Curie points of the 2, 4, and 7% Co-Pd alloys before hydrogenation are <80°, 175° and 248°K, respectively. The Hall effect of the hydrogenated paramagnetic alloys

was measured and a term proportional to paramagnetic magnetisation proposed.

### Crystallography of the Ru-B and Os-B Systems

C. P. KEMPTER and R. J. FRIES, *J. Chem. Phys.*, 1961, **34**, (6), 1994-1995

The systems were studied by X-ray powder diffraction. The existence of the hexagonal Ru<sub>3</sub>B<sub>3</sub> phase was confirmed and the hexagonal phases RuB<sub>2</sub>, Ru<sub>2</sub>B<sub>3</sub>, OsB<sub>2</sub> and Os<sub>2</sub>B<sub>3</sub> were found. Crystallographic data are given.

### Arsenides of the Transition Metals

#### IV. A Note on the Platinum Metal Arsenides

R. D. HEYDING and L. D. CALVERT, *Canad. J. Chem.*, 1961, **39**, (4), 955-957

Binary alloys corresponding to M<sub>3</sub>As, M<sub>2</sub>As, MAs, MAs<sub>2</sub> and MAS<sub>3</sub> (M=Ru, Rh, Pd, Os, Ir, or Pt) were prepared and their structures were examined by X-ray powder diffraction techniques. The compounds Pd<sub>3</sub>As, Rh<sub>2</sub>As, RuAs, RhAs, RuAs<sub>2</sub>, OsAs<sub>2</sub>, PdAs<sub>2</sub>, PtAs<sub>2</sub>, RhAs<sub>3</sub>, and IrAs<sub>3</sub> were detected and their structures are discussed.

### Ruthenium Hexafluoride

H. H. CLAASSEN, H. SELIG, J. G. MALM, C. L. CHERNICK and B. WEINSTOCK, *J. Amer. Chem. Soc.*, 1961, **83**, (10), 2390-2391

RuF<sub>6</sub> was prepared by heating the metal powder in a F atmosphere at 300 mm pressure. The resultant dark brown solid melts at 54°C and decomposes at 200°C according to the reaction: RuF<sub>6</sub> → RuF<sub>5</sub> + ½F<sub>2</sub>.

### Experimental Study of Intermetallic Diffusion in Large Temperature Gradients

C. J. MEECHAN, *J. Appl. Phys.*, 1961, **32**, (5), 954-950

Diffusion couples of Au/Ni, Cu/Ni, γFe/Ni, γFe/Pd, and Ni/Pd were fabricated by a sintering technique and temperature gradients in the range 2000°C/cm to 3000°C/cm were applied across the specimen interfaces. Diffusion zone widths were measured by microhardness, colouration and etching techniques. It is shown that diffusion is influenced by the temperature gradient. Some of the factors which may be affected by the temperature gradient are noted.

### Kinetics of the Oxidation of Platinum

G. C. FRYBURG and H. M. PETRUS, *J. Electrochem. Soc.*, 1961, **108**, (6), 496-503

Oxidation rates of Pt ribbons electrically heated in normal oxygen were determined over the temperature range 900°-1500°C under pressures from 15μ to 1 atm. It was found that the oxidation rate is a function of the temperature of the Pt and the temperature and pressure of the oxygen. The activation energy, obtained from temperature-dependence data, is 42.5 kcal/mole. Back-reflection of volatile PtO<sub>2</sub> by the surrounding

gas molecules is thought to cause a decrease in the oxidation rate with increased pressure.

### Vaporisation of Iridium and Rhodium

M. B. PANISH and L. REIF, *J. Chem. Phys.*, 1961, **34**, (6), 1915-1918

Knudsen effusion and Langmuir evaporation techniques were used in the study. The vapour pressure of Ir over the temperature range 2100°-2600°K is represented by the equation:  $\log p_{\text{mm}} = 10.46 - (33980/T)$ , and that for Rh over the temperature range 2050°-2200°K by the equation:  $\log p_{\text{mm}} = 10.28 - (28300/T)$ . Heats of vaporisation calculated are: Ir,  $\Delta H_{298} = 158.4 \pm 0.5$  kcal/mole, and Rh,  $\Delta H_{298} = 132.8 \pm 0.3$  kcal/mole. Boiling points are estimated for Ir and Rh as 4800°K and 3980°K, respectively.

### Heat Capacity and Resistivity Anomalies in Palladium Hydride

P. MITACEK and J. G. ASTON, *Nature*, 1961, **191**, (Jul. 15), 271

Slow exothermal processes were observed near 150°K and above 200°K on cooling solutions of hydrogen in polycrystalline Pd. Heat capacity measurements with H/Pd ratios of 0.25 and 0.125 show a maximum at 55°K coinciding with that previously reported for a H/Pd ratio of 0.50. A migration of hydrogen from the  $\alpha$ - to  $\beta$ -phase at low temperatures is suggested. Resistivity and heat capacity data are compared.

### The Electrical Resistance of Alpha Hydrogen-Palladium

W. T. LINDSAY and F. W. PEMENT, *Bull. Amer. Phys. Soc., Series II*, 1961, **6**, (4), 353 (Abstract of paper presented at the 1961 Summer Meeting, Mexico City, June 1961)

Resistance measurements were made on gas-charged alloys in the range 100°-400°C. The increase of resistance of Pd resulting from hydrogen addition is proportional to the hydrogen concentration, and the proportionality constant is independent of temperature. Results obtained combined with those obtained previously may be represented in the range 75°-400°C by the equation  $(R/R^0) - 1 = (2.41 \pm 0.04)m$ , where  $R$  = resistance of  $\alpha$ H-Pd,  $R^0$  = resistance of H-free Pd, and  $m = \text{H}:\text{Pd}$  atom ratio.

### The Kinetics of Oxygen Absorption at Vapour-Coated Fe, Ni or Pt Layers and Alloys

C. WEISSMANTEL, K. SCHWABE and G. HECHT, *Werkstoffe u. Korrosion*, 1961, **12**, (6), 353-359

The rate of oxygen sorption on layers of metal about 500Å thick was measured manometrically in the temperature range 25°-450°C. The effect of the simultaneous addition of H<sub>2</sub>O vapour was studied. The exchange rate between combined

oxygen and gas-phase oxygen was examined with the O<sup>18</sup> mass spectrometer. Pt and Ni, compared with Fe, have a much slower sorption rate. The atmospheric behaviour of the coatings was observed during several months.

### Some Specific Chemical Reactions at the Surfaces of Noble Metals

A. KEIL, *Metall*, 1961, **15**, (7), 655-657

Reactions which occur at room temperature include the formation of Ag<sub>2</sub>S and diffusion of Ag<sub>2</sub>S on Au surfaces. Conditions for the occurrence of this phenomenon are discussed. Adsorption and polymerisation reactions of organic vapours on Pt metal surfaces are described. The atmospheric oxidation of Ag, Au, and the Pt metals at high temperatures is discussed. (14 references)

### Rates of Chemisorption of Hydrogen on Hydrogen-Covered Ruthenium Surfaces

M. J. D. LOW, *J. Phys. Chem.*, 1961, **65**, (5), 887-888

Hydrogen was pre-adsorbed on a 0.5% Ru/Al<sub>2</sub>O<sub>3</sub> catalyst at 257°C. The rate of hydrogen uptake on the pre-adsorbed gas was then measured at 257°C. Data obtained for the chemisorption kinetics indicate that the chemisorption mechanism requires a surface which changes in character during adsorption.

## ELECTROCHEMISTRY

### The Fundamental Behaviour of Passive Alloys

H. H. UHLIG, *Werkstoffe u. Korrosion*, 1961, **12**, (7), 413-416

The mechanism of passivation of a base metal by alloying, as in the addition of Cr to Fe, is discussed. Passivation achieved by the addition of alloying constituents of lower overvoltage, exemplified by the addition of 0.1% Pd to Ti and 18/8 stainless steel, is also described. Critical alloy compositions for Cr-Fe and Ni-Cu alloys are discussed.

### Possibilities of Protecting Titanium from Corrosion

W. R. FISCHER, *Techn. Mitt. Krupp*, 1961, **19**, (2), 16-72

The possible corrosion protection of Ti is predicted from a study of potential-pH (Pourbaix) diagrams for the Ti-TiO<sub>2</sub>-H<sub>2</sub>O system and of current-voltage curves for Ti in aqueous solutions. Cathodic and anodic methods of protection in aqueous solutions are described. Methods of anodic protection include the addition of oxidising substances to the corrosive medium, the application of impressed currents, and galvanic contact of the Ti with Pt metals by coupling or coating. The corrosion resistance of Ti in HCl and H<sub>2</sub>SO<sub>4</sub> is greatly improved by alloying with small amounts of Pt or Pd; the addition of 0.2% Pd is sufficient.

Alloying with base metals such as Mo, Ta, V, and Zr is also mentioned. The corrosion properties of Ti in non-aqueous solutions and gases are also discussed.

### **An Investigation of the Mechanism of the Electrochemical Corrosion of Titanium III. The Corrosion and Electrochemical Behaviour of Titanium and of its Platinum and Palladium Alloys in Sulphuric and Hydrochloric Acid Solutions**

N. D. TOMASHOV, G. P. CHERNOVA and R. M. AL'TOVSKII, *Zhur. Fiz. Khim.*, 1961, **35**, (5), 1068-1077 (English summary)

The polarisation in  $H_2SO_4$  and HCl solutions of anodes and cathodes of Ti and its alloys with 1% and 2% Pt and Pd was investigated by potentiostatic methods. It was shown that increases in both acid concentration and temperature cause an increase in the passivation current and a shift of the total passivation potential in the positive direction. Alloying of Ti with Pt or Pd lowers the cathodic hydrogen overvoltage with a positive shift of the steady state potential. Consequently the corrosion resistance of the alloys is increased.

### **Electrochemical Properties of Anodically Prepared Oxide Layers on Platinum**

K. NAGEL and H. DIETZ, *Electrochim. Acta*, 1961, **4**, (1), 1-11

Conditions for the formation of thick oxide layers on Pt by anodic treatment with pure d.c. or with superposed a.c. were investigated. Cathodic charging curves obtained with the Pt oxide electrodes thus produced show a plateau region. Rest values obtained with intermittent current indicate that the equilibrium potential of the  $PtO_2$  electrode should be close to  $U_H = 0.80$  V, the rest value measured with thin layers. An explanation of the electrochemical behaviour of the Pt oxide electrode is given.

### **Potential-Activity Diagram for Important Electrode Reactions in the System Platinum/Platinum Oxide/Solution**

K. NAGEL and H. DIETZ, *Electrochim. Acta*, 1961, **4**, (2-4), 141-154

The dependence of  $U_H$  values for electrode reactions in the system on the activity  $a_i$  of dissolved reactants is shown graphically in a  $U(a)$  diagram. The possibilities of determining equilibrium values of the Pt oxide electrode are discussed.

### **The Anodic Oxidation of Oxalic Acid on Platinum. I. Passivation Effect of a Bright Platinum Electrode**

J. GINER, *Electrochim. Acta*, 1961, **4**, (1), 42-54

The mechanism of the anodic passivation of a bright Pt electrode in 1N  $H_2SO_4$  for the reaction  $H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2e^-$  was studied. A

layer of chemisorbed oxygen is formed on the Pt electrode by oxygen separated from the  $H_2O$ . This passivating oxygen layer may be removed either by cathodic reduction or by reduction by the  $H_2C_2O_4$ . It is suggested that the anodic oxidation of  $H_2C_2O_4$  is effected by intermediate active oxygen.

### **Mechanisms for the Evolution and Ionisation of Oxygen at Platinum Electrodes**

A. C. RIDDIFORD, *Electrochim. Acta*, 1961, **4**, (2-4), 170-178

Observations by other workers on the oxygen electrode process support the suggestion that it follows the same path in both acid and alkaline solution. The path is identified.

### **Effect of Adsorption of Anions on the Discharge of Hydrogen on Palladium and the Ionisation of Hydrogen Dissolved in Palladium**

L. T. SHANINA, *Proc. Acad. Sci. U.S.S.R., Phys. Chem. Section*, 1960, **133**, (1-6), 647-649 (Transl. of *Doklady Akad. Nauk S.S.S.R.*, 1960, **133**, (2), 417-419)

Polarisation measurements on a palladised Pt electrode were made in HCl, HBr, KI + 1N  $H_2SO_4$ , and KI + 1N NaOH at 20°C, and anode charging curves were plotted. Charging curves plotted in HCl (0.1N, 0.5N and 2N) differ little from those plotted in 1N  $H_2SO_4$ . The reversibility of the process is disrupted in the presence of  $Br^-$  and there is an even greater deviation in the presence of  $I^-$ .

### **Effect of Surface Oxidation on the Behaviour of Platinum Electrodes. The Fe(III)-Fe(II) Couple in Sulphuric Acid and Perchloric Acid**

F. C. ANSON, *Analyt. Chem.*, 1961, **33**, (7), 934-939

Chronopotentiometric studies showed that a film of platinised Pt is formed on the surface of an electrode which has been oxidised and reduced electrolytically. The behaviour of the electrode is influenced by the presence of this film as well as by that of a Pt oxide film. The oxide film is chemically reduced rapidly by Fe(II) in 1M  $H_2SO_4$ , but in 1M  $HClO_4$  solutions of Fe(III) and Fe(II) it persists on the electrode and causes decreases in the reversibility of the reduction and oxidation of Fe(III) and Fe(II).

### **The Problem of Hydrogen Overpotential on Platinum**

YA. M. KOLOTYRKIN and A. N. CHEMODANOV, *Proc. Acad. Sci. U.S.S.R., Phys. Chem. Section*, 1960, **134**, (1-6), 819-822 (Transl. of *Doklady Akad. Nauk S.S.S.R.*, 1960, **134**, (1), 128-131)

Determination of the hydrogen concentration in the vicinity of a functioning Pt microcathode by means of oscillographic polarography was used to examine the theory that, for low potentials, the rate of evolution of hydrogen in acid media is

controlled by the rate of diffusion of molecular hydrogen from the cathode surface into the liquid.

### Intermediate Temperature Fuel Cells

G. V. ELMORE and H. A. TANNER, *J. Electrochem. Soc.*, 1961, **108**, (7), 669-671

The construction and performance of two types of gas cell operating from 125° to 200°C is described. A Pd foil, 0.0005 in. thick, hydrogen electrode and Teflon-treated Ag powder oxygen electrode are used in an alkaline cell with a NaOH-KOH-Ca(OH)<sub>2</sub> electrolyte. In a H<sub>3</sub>PO<sub>4</sub>-SiO<sub>2</sub> electrolyte, carbon coated with Teflon and Pt or Pd is used for both the hydrogen and oxygen electrodes. Current densities up to about 100 ma/cm<sup>2</sup> have been attained.

### Electrochemical Corrosion of Platinum in Hydrochloric Acid Solutions

J. LLOPIS and A. SANCHO, *J. Electrochem. Soc.*, 1961, **108**, (8), 720-726

Anodic corrosion of Pt by d.c. ( $i_a$ ) is increased by increasing temperature, high Cl<sup>-</sup> concentration, high acidity and by superimposing a.c. ( $i_a$ ). Corrosion by a.c. at frequencies below 50 c/s was studied. Using a 10 c/s square wave, intense corrosion is increased by increasing acidity and temperature. Corrosion is nil until  $i_a$  reaches a critical value above which it increases, and with solutions of low acidity, it goes through a maximum with increasing  $i_a$ . Oscillographic cathodic and anodic charging curves were studied and interpreted.

### Electrochemical Applications of Platinised Titanium

C. E. TIRRELL, *Crucible Titanium Rev.*, 1961, **9**, (2), 2-6

The electrochemical properties of Ti and Pt-coated Ti anodes are discussed, and methods of applying Pt to Ti are outlined. Applications in which Pt/Ti anodes have been used include fuel cells, impressed current cathodic protection systems, electro dialysis cells, and caustic-chlorine cells. In chlorine production, Pt/Ti anodes may be used in concentrated brine cells with current densities ranging from 100 to 300 A/sq. ft. A fifteen-month plant-scale test with a diaphragm cell has resulted in reduced power consumption, increased diaphragm life and improved chlorine and NaOH quality.

## ELECTRODEPOSITION

### Immersion Plating of the Platinum Group Metals

R. W. JOHNSON, *J. Electrochem. Soc.*, 1961, **108**, (7), 632-635

Pd, Rh, and Pt may be deposited on Cu from chloride solutions, while Ru is deposited from solutions based on ammonium nitroso ruthenium

chloride or ruthenium sulphamate. Plating solutions containing 5 g metal/l and 250 ml HCl (32%)/l are recommended with operating temperatures of 25°C for Rh and Pd and 95°C and 65°C for Ru and Pt, respectively. Deposits of Pd, Rh, Pt, and Ru up to thicknesses of 50, 30, 65, and 100 μin., respectively, may be obtained. The coatings are sealed by immersion in a replacement Au solution, in boiling H<sub>2</sub>O, or in NH<sub>4</sub>OH. The adhesion, tarnish and corrosion resistance, and solderability of the deposits are discussed.

### Barrel Plating by Means of Electroless Palladium

R. N. RHODA, *J. Electrochem. Soc.*, 1961, **108**, (7), 707-708

Experimental work was carried out using a bath of composition: Pd (as chloride of tetrammine amine complex) 2.5-20 g/l, Na<sub>2</sub>EDTA 8 g/l, and NH<sub>4</sub>OH 280 g/l. The effect on plating rates of variations in temperature (25°-45°C), addition rates of the N<sub>2</sub>H<sub>4</sub> reducer, and Pd concentration were studied. The maximum rate (0.1 mil Pd deposited in 1½h) is obtained at 45°C with the addition of 0.096 g N<sub>2</sub>H<sub>4</sub>/15 min and 10g Pd/l. Operating techniques for long and short runs, storage of the baths, and pretreatment of substrates are discussed.

### Crack-free Rhodium Deposits

F. H. REID, *Metalloberfläche*, 1961, **15**, (2), 33-37

Two modified plating baths have been developed. Rh deposits containing Al and Mg, which are practically crack-free, are suitable for applications where corrosion resistance is most important and surface quality is of less importance. These coatings must be polished for applications in electrical engineering. Rh deposits containing Se have good surface quality and, though not truly crack-free, have enhanced protective properties.

## LABORATORY APPARATUS AND TECHNIQUE

### Induction Heated Pressure Vessel for Growing Oxide Single Crystals

A. FERRETTI, D. G. WICKHAM and A. WOLD, *Rev. Sci. Instr.*, 1961, **32**, (5), 566-568

The pressure vessel consists basically of a water-cooled stainless steel tube. This contains an Al<sub>2</sub>O<sub>3</sub> tube which surrounds a radio frequency load coil. The heating chamber, located in the cylindrical space enclosed by the load coil, consists of a 20% Rh-Pt crucible sheathed by fused Al<sub>2</sub>O<sub>3</sub> and heated by Rh-Pt-Al<sub>2</sub>O<sub>3</sub> ring elements the whole assembly being contained in a fused Al<sub>2</sub>O<sub>3</sub> crucible. Two Pt:10% Rh-Pt thermocouples are mounted in the heating chamber. The furnace, which operates at 1600°C and 75 atm oxygen pressure, has been used to grow ferrite crystals.

### Oxygen Gauge

J. WEISSBART and R. RUKA, *Rev. Sci. Instr.*, 1961, **32**, (5), 593-595

A galvanic cell which measures oxygen partial pressure and oxygen pressures in vacuum systems, both at high temperatures, is described. The gauge consists of a  $\frac{3}{4}$  in. diameter tube of Ca stabilised  $ZrO_2$  sealed to a Kovar metal flange through a graded glass seal. The flat bottom of the tube, coated on both sides with a porous Pt film, acts as the electrolyte. The electrodes are connected by Pt wire leads to a potentiometer. A Pt:10% Rh-Pt thermocouple measures the cell temperature.

## CATALYSIS

### Plants Tests on the Decomposition of Nitrous Oxide over a Heated Rhodium Catalyst

L. T. LAKEY, *U.S.A.E.C. Report IDO-14545*, 11 pp.

Dissolver off gases containing 14.2 to 19.8 vol.%  $N_2O$  were passed over a 0.5% Rh/ $Al_2O_3$  catalyst bed in a stainless steel reactor. It was found that, with outlet temperatures maintained between 1300° and 1500°F, the  $N_2O$  content of the off gases may be reduced to < 0.05 vol.%. Suggestions for the design of a single, double-pass reactor are given.

### Reaction of Ethane with a Clean Rhodium Film

R. W. ROBERTS, *Nature*, 1961, **191**, (Jul. 8), 170

$C_2H_6$  at low pressure was brought into contact with a Rh film 30Å thick at 27°C and 100°C. At 27°C the  $C_2H_6$  decomposed to yield gaseous  $CH_4$  and an adsorbed residue with the composition  $CH_{1.8}$ . It was found that the rate of reaction is a function of the surface temperature and of surface cleanliness.

### The Selective Hydrogenation of Linolenic Acid

J. G. WILLARD and M. L. MARTINEZ, *J. Amer. Oil Chem. Soc.*, 1961, **38**, (6), 282-286

Methyl linoleate was hydrogenated in the presence of Rufert Ni, reduced NiO, Cu chromite, or Pd-Pb catalysts. It was found that variation of catalyst, catalyst concentration, solvent, temperature, and pressure had little influence on the selectivity. Differences in relative reactivity of the 9, 12, and 15 double bonds of the methyl linoleate were found.

### The Hydrogenation of Monovinylacetylene

A. RIECHE, A. GRIMM and H. ALBRECHT, *Brennstoff-Chem.*, 1961, **42**, (6), 177-185

Known methods of partial hydrogenation of monovinylacetylene to butadiene are reviewed. A number of Pd, Pt, and Ni catalysts on various bases were used in the hydrogenation reactions

and in some cases complete hydrogenation to butane was found. The optimum yield of butadiene (69%), given with a Pd/ $BaSO_4$  catalyst, was accompanied by 21% butene-1, 5.5% *trans*-butene-2, 3.5% *cis*-butene-2 and 1% butane. Further hydrogenation of butadiene-(1, 2) and -(1, 3), butine-(1) and butine-(2) was investigated in the liquid- and gas-phases. Hydrocarbons with 12-16 C atoms are produced in the gas phase.

### Catalytic Reforming

F. G. CIAPETTA, *Petroleum Eng.*, 1961, **33**, (5), C19-C31

The history of the development of the catalytic reforming process is outlined. Various reactions which occur in the reforming of petroleum naphthas are discussed and the functions of the constituents of Pt/ $SiO_2$ , Pt/ $Al_2O_3$ / $SiO_2$  and other reforming catalysts in these processes are described. Factors which affect the activity, selectivity and life of Pt catalysts are discussed in detail. These include boiling range of the feed, feed composition, the presence of catalyst poisons, and variations in operating temperature, pressure, space velocity and hydrogen recycle rate. (88 references)

### Alumina: Catalyst and Support. VI. Aromatisation of 1,1-Dimethylcyclohexane, Methylcycloheptane, and Related Hydrocarbons over Platinum/Alumina Catalysts

H. PINES and T. W. GREENLEE, *J. Org. Chem.*, 1961, **26**, (4), 1052-1057

Catalysts prepared by impregnating aluminas of various intrinsic acidities with a solution of  $Pt(NH_2NO_2)_2$  were used in the investigation. Aromatisation of 1,1-dimethylcyclohexane (I), 4,4-dimethylcyclohexene (II), methylcycloheptane (III), and 5,5-dimethylcyclohexadiene was studied at 350°C. The composition of the aromatised product is affected by the relative acidities of the aluminas and the method of platinising them. Absorption of the Pt complex probably neutralises the acid sites of the  $Al_2O_3$ . Isomerisation, with the production of xylenes, accompanies the aromatisation of I and II and the extent of isomerisation is related to the intrinsic acidity of the  $Al_2O_3$ . Aromatisation of (III) gives  $C_6H_5CH_3$ ,  $C_6H_5C_2H_5$  and xylenes.

### Ethylene Oxidation: Low-Cost Route to Acetaldehyde Manufacture

ANON., *Chem. Eng.*, 1961, **68**, (10), 66-68

The Aldehyd G.m.b.H. process is described. An aqueous solution of  $CuCl_2$  containing a small amount of PdCl<sub>2</sub> acts as the oxygen-carrier in the conversion of  $C_2H_4$  to  $CH_3CHO$ . In a one-stage oxidation,  $C_2H_4$ , oxygen, and recycle gas are boiled together with the catalytic solution under slight pressure, the gaseous effluent is scrubbed with  $H_2O$  and the resulting aqueous  $CH_3CHO$  solution is distilled. When air is used instead of

oxygen, the spent catalyst is regenerated in a separate reactor before recycling. Operating costs for the one- and two-stage processes are given.

### Preparation of Some Condensed Ring Carbazole Derivatives

H. M. GROTTA, C. J. RIGGLE and A. E. BEARSE, *J. Org. Chem.*, 1961, **26**, (5), 1509-1511

A Pt/MgO catalyst was used in the vapour phase cyclodehydrogenation of N,N'-diphenylphenylenediamines. Indolo [3, 2-*b*] carbazole and indolo [2, 3-*b*] carbazole were prepared from N,N'-diphenyl-*p*-phenylenediamine and N,N'-diphenyl-*m*-phenylenediamine, respectively. Benzocarbazoles were prepared from phenylnaphthylamines by a similar method.

### Catalytic Fission of the Carbon-Halogen Bond

#### Part I. Reactions of Ethyl Chloride and Ethyl Bromide with Hydrogen on Evaporated Metal Films

J. S. CAMPBELL and C. KEMBALL, *Trans. Faraday Soc.*, 1961, **57**, (5), 809-820

Evaporated films of Pd, Pt, Ni, Fe, W and Rh were used as catalysts in a study of the hydrogenolysis of the ethyl halides. The principal reaction observed was:  $C_2H_5X + H_2 \rightarrow C_2H_6 + HX$ , but with Ni and Fe,  $C_2H_4$  was also formed. Some  $CH_4$  was formed over Rh. No exchange of the alkyl halides with deuterium was found up to 450°C. The distributions of isotopic ethanes formed by deuterolysis of the halides was observed. Kinetic results and reaction mechanisms are discussed.

#### A Study of the Catalytic Hydrogenation of Hydroxybenzenes over Platinum and Rhodium Catalysts

H. A. SMITH and B. L. STUMP, *J. Amer. Chem. Soc.*, 1961, **83**, (12), 2739-2743

Adams' Pt and 5% Rh/Al<sub>2</sub>O<sub>3</sub> were used in the hydrogenation of phenol, catechol, resorcinol, hydroquinone, phloroglucinol and pyrogallol. Reduction rates were found to be of the same order as those for corresponding methyl- and methoxybenzenes. It is suggested that, in the reduction of the phenols, cyclohexenols are formed as intermediates and that these are reduced to form cyclohexanols, isomerised to form cyclohexanones or cleaved to form cyclohexanes. Kinetic data are given.

#### Catalytic Activation of Molecular Hydrogen by Ruthenium (III) Chloride Complexes

J. F. HARROD, S. CICCONE and J. HALPERN, *Canad. J. Chem.*, 1961, **39**, (6), 1372-1376

Ru (III) in aqueous HCl solution was found to catalyse the homogeneous reduction by hydrogen of Ru<sup>IV</sup> and of Fe<sup>III</sup>. Ru<sup>III</sup> itself is resistant to reduction by hydrogen. The rate law for the reduction of Ru<sup>IV</sup> and Fe<sup>III</sup> is  $-d[H_2]/dt =$

$k_1[H_2][Ru^{III}]$ , where  $k_1 = 4.0 \times 10^{14} \exp[-23,800/RT] M^{-1} \text{ sec}^{-1}$ . Mechanisms of the reduction reactions are discussed.

#### Adsorption of Hydrogen on Low Percentage Pt/Al<sub>2</sub>O<sub>3</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> Catalysts in the Liquid Phase

D. V. SOKOL'SKII and E. I. GIL'DEBRAND, *Proc. Acad. Sci. U.S.S.R., Chem. Section*, 1960, **133**, (1-6), 855-857 (Transl. of *Doklady Akad. Nauk S.S.S.R.*, 1960, **133**, (3), 609-612)

Catalysts containing 0.05 to 3.47% of the metal were prepared, suspended in a buffer solution (CH<sub>3</sub>COOH/NaOH), and saturated with hydrogen by shaking. The adsorbed hydrogen was determined by shaking the catalyst with quinone and determining the hydroquinone formed. It was found that as the concentration of Pt and Pd in the catalyst is increased, their adsorption capacities decrease sharply at first and then more slowly. The adsorption capacity of Pd is less than that of Pt. The phenomenon of excess paramagnetism developed by the Pt and Pd during hydrogenation reactions is discussed.

#### Annual Review of U.S.A. Patents on Petroleum Refining and Processing

H. HEINEMANN and P. A. LEFRANCOIS, *World Petroleum*, 1961, **32**, (8), 53-59, 112

183 patents are reviewed. The processes covered by the patents include catalytic reforming and petrochemical production, hydrocracking, catalytic cracking, hydrogenation, dehydrogenation, alkylation, dealkylation, isomerisation, and desulphurisation. Pt metal catalysts are employed in many of the processes.

#### Reforming the 60°-140° Benzene Fraction and Standard B-70 Benzene of Bakinski Petroleum on a Platinum Catalyst

N. I. SHUKIN, KH. M. MINACHEV, V. S. ALIEV, I. I. SIDORCHUK and M. A. RYASHENTSEVA, *Zhur. Priklad. Khim.*, 1961, **34**, (2), 461-463

Reforming was carried out at 480°-500°C, 40-50 atm hydrogen pressure, and space velocity 2-3/h in the presence of a 0.5% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. Under the given conditions, 45.8-57.9% aromatic hydrocarbons were produced from the 60°-140° benzene fraction and 38.6% from the B-70 benzene. Five-membered ring compounds and alkanes were also present in the catalysate.

#### Catalytic Isomerisation of *n*-Pentane on a Platinum Catalyst

N. R. BURSIAI and G. N. MASLYANSKII, *Khim. Prom.*, 1961, (3), 18-20

A supported 0.6% Pt catalyst was used in the isomerisation process which was carried out under pressure. The effect of variations in the hydrogen: *n*-pentane ratio, pressure, temperature, and volumetric flow rate was studied. Optimum parameters found were: temperature, 400-420°C;

molar ratio of hydrogen:*n*-pentane, 3:1; the rate of addition of *n*-pentane, 1 volume/volume of catalyst/h. The yield of *iso*-pentane under these conditions was 50%, and that of C<sub>1</sub>-C<sub>4</sub> gases below 1.5%.

## GLASS TECHNOLOGY

### Galvanic Corrosion of Glass Tank Refractories

F. J. SHONEBARGER, *Glass Technol.*, 1961, 2, (2), 53-59

Cells consisting of molten glass as the electrolyte and a refractory bar and coiled Pt wire as electrodes were used to investigate the corrosion of refractories by molten glass. The refractory bars were supported by Pt tie wires. It was found that the corrosion of refractories may be accelerated by the electrical potentials established by refractory combinations exposed to molten glass.

### New Plant Features Latest Look in Making Glass Fibres

N. P. CHOPEY, *Chem. Eng.*, 1961, 68, (10), 136-139

The processes operated at the Aiken, S. C., Owens-Corning plant are described briefly and a flow-sheet is given. Glass filaments are drawn directly from the forehearth of recuperative furnaces through Rh-Pt bushings, treated with a binder material, and wound on spindles. New features of the winding process are mentioned.

### Mechanical Strength of Polycrystalline Materials Produced from Glasses Containing Platinum

M. TASHIRO, S. SAKKA and M. WADA, *Yogyo Kyokai Shi*, 1960, 68, 223 (*Br. Ceram. Abs.*, 1961, 60, (5), 215A)

The effect of the addition of Pt on the bend-strength of glasses containing Li<sub>2</sub>O, MgO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> was investigated. 0.01% Pt is sufficient to cause complete devitrification of some glasses. The bend-strength of devitrified glass increases with increasing Pt content and is influenced by the Li<sub>2</sub>O content.

## ELECTRICAL ENGINEERING

### The Transfer of Material between Contacts of Precious Metal Alloys and Its Dependence on Heat Treatment

W. MERL, *Metall*, 1961, 15, (7), 672-674

Contact materials used in the investigation were 40% Cu-Pd, 3% Co-Au, 10% Ni-Au and 16% Ni-Au alloys. The electrical and thermal conductivities of these alloys may be increased by lattice changes (Cu-Pd) or precipitation processes (Co-Au, Ni-Au). The mechanisms of bridge transfer and coarse transfer are discussed.

### Mechanics of Electrical-Contact Failure Caused by Surface Contamination

S. W. CHAIKIN, *Electro-Technol.*, 1961, 68, (2), 70-75

Methods of examining sealed relays contaminated by base metals and organic material are described. Non-conducting deposits may be formed on contact surfaces, either spontaneously or during friction, by the polymerisation of organic vapours evolved by insulating materials. The contamination of Pd and Au contacts under static conditions was studied, and frictional polymers formed on Au, Ag, Pd and Au alloy contacts were also examined. It is concluded that the latter are produced by the combined effects of catalysis and electron emission. Contamination may be controlled by chemical and ultrasonic cleaning, selection of insulating and contact materials, and the use of carbon pellet "getters".

## ELECTRONICS AND TELECOMMUNICATIONS

### The Selection of Contact Materials for Telephone Switching

L. BORCHERT, *Nachrichtentech. Z. (N.T.Z.)*, 1961, 14, (4), 175-179

The suitability of Ag, Pd, Pd-Ag, Ni-Au, Ni-Pt, and W-Pt contact materials is discussed. Pd-Ag alloys containing 30-50% Pd are recommended for use in relays and selectors. Their satisfactory performance in the presence of H<sub>2</sub>S, organic vapours, and under various climatic conditions, is described. (20 references)

## TEMPERATURE MEASUREMENT

### Calibration of Platinum Resistance Thermometers

ANON., *Nat. Bur. Stds. Tech. News Bull.*, 1961, 45, (4), 62-65

The calibration of long stem-, capsule-, and calorimetric-type resistance thermometers is described. Stem-type thermometers are calibrated at the boiling points of oxygen (-182.97°C), water, and sulphur (444.6°C), and at the triple point of water (0.01°C). The calorimetric-type are calibrated at the triple point, steam point, and near 50°C. Capsule-type thermometers are calibrated over the range -263° to -183°C in a hydrogen bath against N.B.S. standard resistance thermometers. Resistance measurements are made using a Mueller-type bridge.

### Accurate Recording of Fast-Changing Temperatures

D. H. NALLE, *I.S.A.J.*, 1961, 8, (6), 58-59

A system consisting of a Pt resistance thermometer, a Wheatstone bridge, a carrier-amplifier and a direct-recording oscillograph is described. Applications include the measurement of average and differential temperatures.

### High Temperature Black Body Radiation Source

H. P. BEERMAN, *Bull. Amer. Ceram. Soc.*, 1961, 40, (5), 308-309

A standard radiation source consists of 40% Rh-Pt wire wound on an  $Al_2O_3$  core which has a conical cavity, blackened with a fired-on Pt paste.

A Pt:10% Rh-Pt thermocouple is embedded in the counterbore of the cone close to its apex. The core is insulated by bubble  $Al_2O_3$  and diatomaceous earth. The operating range may be extended from 1650° to 1850°C by using a Rh winding, an Ir:40% Rh-Ir thermocouple, and different core and insulating materials.

## NEW PATENTS

### Hydrogenation of Nitrosamines

FOOD MACHINERY & CHEMICAL CORP. *British Patent* 868,147

An N, N - disubstituted hydrazine is prepared by reacting a dialkyl or substituted dialkyl nitrosamine or a heterocyclic nitrosamine with hydrogen in the presence of a palladium catalyst and an iron salt in the proportion of about 0.5 millimole of iron per g of catalyst. The catalyst consists of 5 parts palladium and 95 parts of active carbon.

### Brazing of Beryllium

ASSOCIATED ELECTRICAL INDUSTRIES LTD. *British Patent* 869,607

Beryllium is brazed to a metal base by the use of palladium in the brazed joint. The palladium may be present in the brazing alloy, i.e. an alloy of silver, copper and palladium may be used or the palladium may be electrodeposited on the beryllium after the latter has been copper plated. Suitable for brazing a beryllium window to an X-ray tube.

### Anode for Cathodic Protection

ENGELHARD INDUSTRIES INC. *British Patent* 870,086

An anode assembly for cathodically protecting pipes, the walls of which come into contact with an electrolyte, is formed of a flexible wire anode surrounding one end part of a rod of insulating material, an inner conductive wire being provided for connecting the anode wire to a positive potential. The anode may be in the form of a helix or a wire mesh sleeve of platinum or other platinum group metal.

### Electrolytic Anodes

METAL & PIPELINE ENDURANCE LTD. *British Patent* 870,277

An anode, primarily for cathodic protection of steel structures, consists of a body of lead or lead alloy (10-16% silver-lead alloy) in intimate contact with a platinum group metal, part or all of which is on the outside of the lead body and exposed to the electrolyte in use. The platinum group metal is preferably in the form of a wire embedded in the lead.

### Beryllium Brazing

ASSOCIATED ELECTRICAL INDUSTRIES LTD. *British Patent* 870,780

Beryllium is brazed to another metal by interposing between the parts a palladium-containing solder, heating the assembly to below the solidus of the solder but high enough to cause interdiffusion between the beryllium and the solder, and holding this temperature long enough to cause limited interdiffusion and then raising the temperature above the liquidus to effect brazing. Solder alloy preferably 55-70% Ag, 20-30% Cu and 10-20% Pd.

### Electric Switch Contacts

DEUTSCHE GOLD-UND SILBER-SCHNEIDANSTALT *British Patent* 871,660

Electric switch contacts, e.g. circuit-breaker contacts in the weak current field, are formed of an alloy of 1-20% rhenium and remainder palladium. Up to 50% of the rhenium may be replaced by tungsten.

### Electrochemical Diode Rectifiers

UNION CARBIDE CORP. *British Patent* 871,675

An electrochemical diode rectifier comprises a vessel containing an electrolyte (reversible redox system in solution) and in which are mounted a pair of platinum electrodes, one of which is substantially greater in active surface area than the other.

### Purification of Nitrogen

ENGELHARD INDUSTRIES INC. *British Patent* 871,755

Nitrogen, containing oxides of nitrogen as impurities, is purified by adding hydrogen to the gas and contacting the mixture with palladium metal or other palladium-containing catalyst at reaction temperature (50°-700°F).

### Hydrogenation of Acetylene

BADISCHE ANILIN- & SODA-FABRIK A.G. *British Patent* 871,804

Acetylene compounds are partially hydrogenated in the presence of a palladium catalyst which has