

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### The Structural Diagram of the Titanium-Palladium System

A. A. RUDNITSKII and N. A. BIRUN, *Zhur. Neorg. Khim.*, 1960, 5, (11), 2414-2421

The system was investigated using thermal analysis, microscopic examination, measurements of resistivity and thermal e.m.f., and hardness and tensile tests. There is partial solubility of Ti and Pd in the solid state; a eutectic containing 60 at.% Ti is formed at 1160°C. The intermetallic compound Pd<sub>3</sub>Ti is formed at 1040°C. Small additions of Ti to Pd increase the specific resistivity of Pd, but reduce the temperature coefficient of resistivity and the ductility. The addition of 4 at.% Ti doubles the tensile strength.

### A Study of the Iron-Palladium-Silver System

A. T. GRIGOR'EV, L. A. PANTELEIMONOV, Z. P. OZEROVA and E. V. AKATOVA, *Zhur. Neorg. Khim.*, 1960, 5, (11), 2395-2402

Methods of thermal analysis, microstructure examination, and measurement of Brinell hardness, electrical resistivity and its temperature coefficient were used in this study. A phase diagram of the system shows a region of stratification, observed in the binary system Fe-Ag, extending into the ternary system up to 57 at.% Pd, a region of solid solution in the Pd corner of the diagram, and a central zone of mechanical mixture.

### A Study of the Palladium-Rhodium-Gold System

A. A. RUDNITSKII and A. N. KHOTINSKAYA, *Zhur. Neorg. Khim.*, 1960, 5, (12), 2781-2794

Alloys of the ternary system, in both the annealed and hardened condition, were studied by an examination of microstructure and measurement of hardness, electrical resistivity and its temperature coefficient, and integral thermal e.m.f. A phase diagram for the system was constructed. It was found that the mechanical properties of Pd-Rh are considerably improved by the addition of 2.5 to 10 wt.% Au. Properties of 59 alloys of the system are given in a table.

### An Investigation of the Electrical Resistivity of Nickel-Palladium Alloys in the Temperature Range 0° to 700°C

S. YAZLIEV, *Zhur. Neorg. Khim.*, 1960, 5, (11), 2440-2445

Isotherms for the resistivity and its temperature

coefficient of alloys of the system show the characteristics of a continuous series of solid solutions. It was established that, at high temperatures, the Matthiessen rule is obeyed for all compositions of the alloys.

### An Investigation of the Thermoelectric Properties of Nickel-Palladium Alloys

S. YAZLIEV, *Zhur. Neorg. Khim.*, 1960, 5, (11), 2446-2457

The integral thermal e.m.f., differential thermal e.m.f., absolute thermal e.m.f., thermoelectric potential and Thomson e.m.f. of the alloys were studied in the temperature range 0-1000°C. Results obtained, shown in both tabular and graphical form, establish the dependence of these properties on temperature and alloy composition.

### A Study of the Spectral Emissivities and Melting Temperatures of Osmium and Ruthenium

R. W. DOUGLASS and E. F. ADKINS, *Trans. Met. Soc. A.I.M.E.*, 1961, 221, (2), 248-249

The melting points of Os and Ru were determined as 3010 ± 10°C and 2250 ± 10°C, respectively. Relations derived for spectral emissivities are: Os,  $\log_{10} \epsilon_{\lambda=0.855} = 9510 [(157.8 - 0.160)/T (0.840T + 157.8)]$  and Ru,  $\log_{10} \epsilon_{\lambda=0.855} = 9510 [(172.0 - 0.183T)/T(0.817T + 172.0)]$ .

### The Platinum-Niobium System

H. KIMURA and A. ITO, *J. Jap. Inst. Metals*, 1961, 25, (1), 88-91

The system was investigated by X-ray and thermal analysis and by microscopic examination. The maximum solubility of Nb in the Pt phase ( $\alpha$ ) is 36 at.% and the resulting alloy melts at 2000°C. Two intermetallic compounds, PtNb<sub>2</sub> and PtNb<sub>3</sub>, are formed in this system. PtNb<sub>3</sub> is formed by the peritectic reaction: liquid + PtNb<sub>3</sub> ⇌ PtNb<sub>3</sub> at 1900°C, and forms a eutectic with  $\alpha$ -phase at 1700°C (45 at.% Nb). At about 2000°C there is a peritectic reaction: liquid + Nb ⇌ PtNb<sub>3</sub>. PtNb<sub>2</sub> and PtNb<sub>3</sub> have tetragonal and cubic structures, respectively. The solubility limit of Pt in Ni is < 1 at.%. Pt<sub>3</sub>Nb (25 at.% Nb) shows a disordered structure with a random array of Pt and Nb atoms on a f.c.c. lattice at high temperature.

### The Structures of Co<sub>2</sub>P, Ru<sub>2</sub>P and Related Phases

S. RUNDQVIST, *Acta Chem. Scand.*, 1960, 14, (9), 1961-1979

The crystal structures of the two phosphides,

which crystallise in the C23 structure type, were determined using single-crystal methods. Comparisons with related phosphides and silicides are given.

### Excess Free Energy in Dehydrogenated Palladium

J. M. SINGER and G. W. CASTELLAN, *J. Chem. Phys.*, 1960, **33**, (2), 633-634

Samples of Pd were alloyed with hydrogen by gas- and electrolytic-charging and dehydrogenated using Ce (SO<sub>4</sub>)<sub>2</sub> solution. Potential measurements indicate that the Pd lattice acquires an excess free energy in the hydrogenation-dehydrogenation cycle.

### Melting Points of Iron-Nickel-Palladium Alloys

L. A. PANTELEIMONOV, N. A. BIRUN and D. N. GUBIEVA, *Russ. J. Inorg. Chem.*, 1960, **5**, (7), 793-794 (Transl. of *Zhur. Neorg. Khim.*, 1960, **5**, (7), 1635-1636)

The system was studied by the method of thermal analysis and results are given in a table. The form of liquidus and solidus curves at a constant Pd content indicate that a continuous series of solid solutions is formed immediately on solidification.

### Complex Hydrides of Platinum

J. A. CHOPOORIAN, J. LEWIS and R. S. NYHOLM, *Nature*, 1961, **190**, (May 6), 528-529

(PPh<sub>3</sub>)<sub>4</sub>PtH<sub>2</sub>, (PPh<sub>3</sub>)<sub>3</sub>PtH<sub>2</sub>, and (PPh<sub>3</sub>)<sub>2</sub>PtH<sub>2</sub>, (Ph = phenyl), were prepared and their melting points determined as 116-118°, 125-130°, and 175-178°C, respectively. Evidence is given for the existence of a Pt-H bond in the complexes.

### A Further Study of Ti<sub>2</sub>Ni-Type Phases Containing Titanium, Zirconium or Hafnium

M. V. NEVITT, J. W. DOWNEY and R. A. MORRIS, *Trans. Met. Soc. A.I.M.E.*, 1960, **218**, (6), 1019-1023

Binary and ternary alloys of Ti, Zr or Hf with the Pt metals and other transition metals were prepared by arc melting and examined by metallographic, X-ray, and density determination techniques. Oxygen was the third constituent of many of the alloys. Ti<sub>2</sub>Ni-type phases were identified and lattice parameters were measured.

### The Palladium-Chlorine System at High Temperature

W. E. BELL, U. MERTEN and M. TAGAMI, *J. Phys. Chem.*, 1961, **65**, (3), 510-517

The system was studied over the range 500°-1500°C at chlorine pressures up to 1 atm. The melting point of the solid chloride PdCl<sub>2</sub> was determined as 680 ± 2°C under 1 atm chlorine pressure. The liquid in equilibrium with Pd at 980°C contains 61 at. % Cl and has a dissociation pressure of 1 atm. The main gaseous species at

1 atm chlorine pressure are Pd<sub>3</sub>Cl<sub>10</sub> below 980°C, and PdCl<sub>2</sub> above 980°C.

### The High-Temperature Oxidation of the Platinum Metals and Their Alloys

W. BETTERIDGE and D. W. RHYS, 1st International Congress on Metallic Corrosion, London, Apr. 1961, Preprints, 64-69

The formation of solid surface oxides and of volatile oxides by heating the pure metals in air or oxygen is described. Volatile oxides are formed at higher temperatures, usually above 1000°C. The increase in volatility of the metals compared with that on heating in an inert atmosphere varies in the order: Pd < Pt < Rh < Ru < Ir. Oxidation of Pt and Pd alloys occurs either on the surface, with the formation of oxide films or scales, or internally. The nature of the alloying constituent, its concentration and the operating temperature determine the form of oxidation. Among the alloys discussed are Pt-Pd and alloys of Pt or Pd with Ir, Rh, Au, Ag, W, Mo, Ru, Sn, In, Ti, Zr and Al.

### The Variation with Temperature of the Magnetic Susceptibility of Some of the Transition Elements

H. KOJIMA, R. S. TEBBLE and D. E. G. WILLIAMS, *Proc. Roy. Soc., Series A*, 1961, **260**, (1301), 237-250

Measurements of paramagnetic susceptibility,  $\chi$ , were made in the temperature range 20 to 1800°C. Values obtained at 20°C in 10<sup>-6</sup> e.m.u./g are: Ti, 3.36; Zr, 1.33; Hf, 0.38; V, 5.64; Nb, 2.3; Ta, 0.85; Mo, 0.82; W, 0.29; Re, 0.35; Ru, 0.34; Rh, 1.03; Ir, 0.14; Pd, 5.4; Pt, 0.97. Results obtained do not support the theory of Kriessman that  $d\chi/dT$  alternates in sign for successive columns of the periodic table. The results are discussed in relation to the band theory of metals.

### Thermodynamic Properties of Gaseous Ruthenium Chlorides at High Temperature

W. E. BELL, M. C. GARRISON and U. MERTEN, *J. Phys. Chem.*, 1961, **65**, (3), 517-521

A study was made of thermodynamic properties in the temperature range 600°-1500°C at chlorine pressures from 0.1 to 1.5 atm. The important vapour species, RuCl<sub>4</sub> and RuCl<sub>3</sub>, were identified by determining the dependence of vapour pressure on chlorine pressure.

### Constitutional Diagrams Ta-Ru, W-Ru, Ta-Os

E. J. RAPPERPORT and M. F. SMITH, *J. Metals*, 1961, **13**, (1), 86. Paper presented at the Annual Meeting, Met. Soc. A.I.M.E., St. Louis, Feb.-Mar., 1961

The diagrams were determined by techniques which included lattice parameter extrapolation

and electron microbeam probe analysis. Ru is soluble in Ta to about 45 at.% and Ta is soluble in Ru to 28 at.%. There are two intermediate Ta-Ru phases, one from 50 to 60 at.% Ru, and one, which decomposes peritectoidally at 1667°C, at 62 at.% Ru. The mutual maximum solubilities of Ru and W are 23 and 48 at.%, respectively. A  $\sigma$ -phase forms peritectically in the W-Ru system at 40 at.% Ru,  $\sim 2300^\circ\text{C}$ , and decomposes eutectoidally at 1667°C. Os is soluble in Ta to 22 at.% and Ta is soluble in Os to  $>25$  at.%. A  $\sigma$ -phase forms in the Ta-Os system at about  $2500^\circ\text{C}$ , extending from 21 to 43 at.% Os; another intermediate phase is formed peritectically at  $2420^\circ\text{C}$  and 57 at.% Os.

#### Solid Solubilities of Carbon in Cu-Pd-Ni and Cu-Pd-Ag Alloys

M. E. NICHOLSON, *J. Metals*, 1961, **13**, (1), 86  
Paper presented at the Annual Meeting, Met. Soc. A.I.M.E., St. Louis, Feb.-Mar., 1961

The solubility of C was determined by saturating the samples with C at  $900^\circ\text{C}$  in an atmosphere of CO in equilibrium with graphite. Precision lattice parameter, magnetic susceptibility, and Hall coefficient measurements were made. It appears that the solid solubility of C in the ternary systems is determined primarily by their electronic structure and is proportional to the density of states at the Fermi surface of the "d" band.

#### Diffusion of Hydrogen through Palladium

R. C. HURLBERT and J. O. KONECNY, *J. Chem. Phys.*, 1961, **34**, (2), 655-658

Hydrogen, maintained at constant pressure upstream, was allowed to diffuse through a Pd disc, about  $4\text{ cm}^2$  in area, into vacuum downstream at  $350^\circ\text{C}$ . The effects on diffusion rates of upstream pressures from 1 to 7 atm and of membrane thicknesses from 10 to  $150\mu$  were determined. The effect of temperature on diffusion rates through membranes of different thickness was shown. It was found that the surface reaction is not rate-limiting for membranes thicker than  $20\mu$ . Under the given conditions,  $\log F = 3.70 + 0.68 \log P - 623/T - \log L$ , where  $F$  = diffusion rate ( $\text{cm}^2$  STP/ $\text{cm}^2$  min),  $P$  = upstream pressure (atm),  $L$  = thickness of Pd membrane (microns), with  $L \geq 20\mu$ .

#### Absorption of Deuterium by Palladium

T. B. FLANAGAN, *J. Phys. Chem.*, 1961, **65**, (2), 280-284

Deuterium was absorbed by Pd wire specimens from a 0.02N DCl solution at  $25^\circ\text{C}$  and 1 atm pressure. The course of the absorption was followed by measurement of changes in the electrode potentials and relative resistances of the Pd wires. Co-existence of  $\alpha$ - and  $\beta$ -phases is indicated by a region of constant electrode potential at  $31.0 \pm 0.5$  mV. The absorption rate is constant over almost all the absorption range and is slower than that for hydrogen. The heat of

absorption was calculated as  $-8795$  cal/mole  $\text{D}_2$  after measurement of the temperature coefficient of the electrode potential in the two-phase region.

#### Relationships between Electrical Resistance and the Hydrogen Content of Palladium

T. B. FLANAGAN and F. A. LEWIS, *Z. Phys. Chem. (Frankfurt)*, 1961, **27**, (1/2), 104-111 (In English)

Hydrogen was absorbed by preactivated Pd wires from hydrogen-saturated HCl solutions, or was introduced electrolytically. Resistance measurements were made and the hydrogen content of the specimens was determined by vacuum outgassing. Data for the relationship between relative resistance ( $R/R_0$ ) and atomic ratio (H/Pd) over the temperature range  $0^\circ$ - $55^\circ\text{C}$  are given. The temperature coefficient of resistance,  $\alpha$ , at each hydrogen content was calculated.

#### The Effect of Alkali Metal Halides on the Amount of Hydrogen Adsorbed on Platinum Black

D. V. SOKOL'SKII and G. D. ZAKUMBAEVA, *Proc. Acad. Sci. U.S.S.R., Phys. Chem. Section*, 1960, **130**, (1-6), 167-169 (Transl. of *Doklady Akad. Nauk S.S.S.R.*, 1960, **130**, (5), 1078-1080)

The rate of reduction of  $\text{PtO}_2$  to Pt black was investigated, and the amount of hydrogen adsorbed on the Pt black in the presence of KCl, KBr, and KI in 50%  $\text{C}_2\text{H}_5\text{OH}$  solutions was determined. It was found that the amount of hydrogen adsorbed is decreased in the presence of halides and, in the cases of KCl and KBr, is practically independent of their concentration.

#### The Exchange of Hydrogen Isotopes on Palladium

G. N. TRUSOV and N. A. ALADZHALOVA, *Proc. Acad. Sci. U.S.S.R., Phys. Chem. Section*, 1960, **130**, (1-6), 47-50 (Transl. of *Doklady Akad. Nauk S.S.S.R.*, 1960 **130**, (2), 370-373)

The rate of hydrogen exchange between an electrolyte enriched with deuterium or tritium and a layer of hydrogen adsorbed on a Pd cathode was measured in the reactions:  $\text{Pd}(\text{H})_n + \text{D}_2\text{O} \rightarrow \text{Pd}(\text{H})_{n-1}\text{D} + \text{HDO}$ , and  $\text{Pd}(\text{H})_{n-1}\text{T} + \text{H}_2\text{O} \rightarrow \text{Pd}(\text{H})_n + \text{T}_2\text{O}$ . The true rate of exchange was compared with the rate calculated from extrapolated overvoltage curves. A mechanism involving a "catalytic" exchange reaction is proposed.

#### Passivity and Corrosion Resistance of Titanium and Its Alloys

N. D. TOMASHOV, R. M. ALTOVSKY and G. P. CHERNOVA, *J. Electrochem. Soc.*, 1961, **108**, (2), 113-119

Possible methods of increasing the corrosion resistance of Ti in  $\text{H}_2\text{SO}_4$  and HCl solutions are reviewed. Results of corrosion tests on alloys of Ti with Pd, Mo, and Cr are given. The increased resistance of Pd-Ti, Mo-Ti, Pd-Mo-Ti, and

Pd-Cr-Ti alloys is shown. Electrochemical characteristics of the alloys were investigated and are correlated with corrosion behaviour. Increased corrosion resistance is obtained by cathodic alloying to give a shift of potential in the noble direction and by the addition of metals which increase the tendency of Ti to passivate and increase its thermodynamic stability.

## ELECTROCHEMISTRY

### The Behaviour of Platinum Electrodes Part 2. Effects of Anodic Electrolysis in Acid Solution

A. MITUYA and T. OBAYASHI, *J. Res. Inst. Catalysis, Hokkaido Univ.*, 1960, **8**, (2), 79-85

A Pt wire electrode, after neutron irradiation, was anodically polarised in 0.1N HCl in air and in hydrogen. The polarisation was measured with reference to a Ag/AgCl electrode in air and to a platinised Pt electrode in hydrogen. After each electrolysis, the electrolyte was concentrated and its radioactivity was measured. Pt disintegration was detected after anodic polarisation in air by about 1.9V against the reversible hydrogen potential, but not after electrolysis in hydrogen.

### The Anodic Behaviour of a Cathodically Pre-polarised Bright Platinum Electrode in Sulphuric Acid Solution

S. SHIBATA, *Bull. Chem. Soc. Japan*, 1960, **33**, (12), 1635-1640

Anodic charging curves of the working Pt electrode in 1N H<sub>2</sub>SO<sub>4</sub> were studied with a mechanical oscillograph. The behaviour of an initial horizontal stage of the curves with steady potential is ascribed to the molecular hydrogen accumulated near the electrode during cathodic prepolarisation. It is shown that the decrease of this accumulated hydrogen with time is similar to the decrease in a first order chemical reaction.

### The Effect of Irradiation on the Potential of a Platinum Electrode in a Solution of Sulphuric Acid

D. V. KOKOULINA, P. I. DOLIN and A. N. FRUMKIN, *Proc. Acad. Sci. U.S.S.R., Phys. Chem. Section*, 1960, **132**, (1-6), 469-472 (Transl. of *Doklady Akad. Nauk S.S.S.R.*, 1960, **132**, (4), 880-883)

The behaviour of a Pt electrode in 0.8N H<sub>2</sub>SO<sub>4</sub> was studied over a wide range of radiation dosage and of dose intensity. It was found that the potential under irradiation reaches the reversible hydrogen value after the absorption of  $3.5 \times 10^{18}$  eV/cm<sup>2</sup>, independently of the dose intensity. A stable potential of 0.85V is reached eventually at a dose which is partly dependent on the composition of the electrode surface and the rate of exchange between the solution and gaseous reaction products.

### The Potential of a Platinum Electrode in an Irradiated Sulphuric Acid Solution

G. Z. GOCHALIEV, TS. I. ZALKIND and V. I. VESELOVSKII, *Proc. Acad. Sci. U.S.S.R., Phys. Chem. Section*, 1960, **132**, (1-6), 461-464 (Transl. of *Doklady Akad. Nauk S.S.S.R.*, 1960, **132**, (4), 872-875)

Experiments were carried out in 0.8N H<sub>2</sub>SO<sub>4</sub> at a dose power of  $6.1 \times 10^{16}$  eV/cm<sup>2</sup>/sec. Curves showing the relationship between the potential of the Pt electrode and duration of the irradiation were obtained. The Pt electrode is selective towards the reducing products of the radiolysis of water and a potential of 10-20 mV is established. If a gas phase is present, the potential increases to 0.85V at doses  $> 2 \times 10^{20}$  eV/cm<sup>2</sup>.

### Platinum-Plated Anode Wins Chlorine Test

ANON., *Chem. Week*, 1961, **88**, (12), 153-160  
The successful plant-scale operation for 15 months of a diaphragm type chlorine cell using platinised Ti anodes is reported. Advantages over the use of graphite anodes are emphasised. Operating data show a 25% increase in output, savings in power consumption, a 100% increase in diaphragm life, a constant production rate at a high level, and increased anode life. The quality of the chlorine and NaOH produced by the process is significantly improved.

### Electrical Impedance at the Surface of Pd/H/H<sub>2</sub> Electrodes

J. C. BARTON, F. A. LEWIS, D. S. McILHAGGER and R. K. QUIGG, *Naturwiss.*, 1961, **48**, (7), 216-217 (In English)

Measurements of impedance were made between pairs of palladised Pd wires in hydrogen-saturated 1.0N HCl at 25°C. A balancing circuit independent of frequency over the range 20-5000 c.p.s. was devised.

### The Influence of Alternating Current on the Anodic Behaviour of Metals

R. JUCHNIEWICZ, 1st International Congress on Metallic Corrosion, London, Apr. 1961, Preprints, 436-439

Corrosion measurements were made on anodically polarised Pt, platinised Ti, 2% Ag-Pb, and 2% Ag-6% Sb-Pb electrodes in NaCl solutions. It was found that, with the exception of the Pb alloys, superimposed a.c. increases the corrosion. Impedance measurements indicate that a.c. may affect the anodic behaviour of different metals by different mechanisms.

### Anodic Polarisation of Lead-Platinum Bi-electrodes in Chloride Solutions

L. L. SHREIR, *Corrosion*, 1961, **17**, (3), 90-96

Potential-time studies were carried out to determine the effect of a Pt microelectrode on the behaviour of Pb in chloride solutions. Experimental results show the effect of the relative areas

of Pt/Pb, and of withdrawal and insertion of Pt. Current through the Pt microelectrode and weight change during anodic polarisation were measured. The mechanism of formation of  $\text{PbO}_2$  films and the role of the Pt microelectrode in (i) limiting the initial formation of  $\text{PbCl}_2$ , (ii) oxidising Pb ions to  $\text{PbO}_2$ , and (iii) acting as a "chlorine valve", are discussed. The possible application of the bielectrodes in cathodic protection systems is mentioned.

#### **Anodic Behaviour of a Lead-Platinum Bielectrode in Chloride Electrolytes**

E. L. LITTAUER and L. L. SHREIR, 1st International Congress on Metallic Corrosion, London, Apr. 1961, Preprints, 18-25.

A study was made of the electrode processes of Pb and the Pb-Pt bielectrode over a range of pH and NaCl concentration, using galvanostatic and potentiostatic techniques. The bielectrode consisted of 2% Cu-Pt wire inserted into, and projecting 2 mm from, a Pb rod. The Pt microelectrode limits the formation of  $\text{PbCl}_2$  and acts as a nucleus for the deposition of  $\text{PbO}_2$ . Initially,  $\text{PbO}_2$  forms over the surface of previously formed  $\text{PbCl}_2$ , which is then converted to  $\text{PbO}_2$ .  $\text{PbO}_2$  is not formed when the bielectrode is polarised in  $\text{NaCl} > 1.3\text{M}$ .

#### **Kinetics of Hydrogen Evolution at Zero Hydrogen Partial Pressure**

S. SCHULDINER, *J. Electrochem. Soc.*, 1961, **108**, (4), 384-387

Potential curves for the hydrogen evolution reaction on Pt and Rh were determined in 1M  $\text{H}_2\text{SO}_4$  solution rapidly stirred with helium. The Pt and Rh electrodes used were wire terminated by small spheres. Results indicate that, for both Pt and Rh, the electrochemical desorption of hydrogen is the predominant rate-controlling step in the lowest current density range. With increased current density, the rate-controlling step is the combination of adsorbed hydrogen atoms. Kinetic equations are derived.

#### **On Electrical Phenomena of Palladium Filament Occluding Hydrogen. II. Investigation of Hirota and Horiuti's Results**

G. TODA, *J. Res. Inst. Catalysis, Hokkaido Univ.*, 1960, **8**, (3), 203-208

A Pd filament was cathodically electrolysed in a 0.1N  $\text{H}_2\text{SO}_4$  solution until its resistance had increased about 1.65 times, corresponding to a H/Pd ratio = 0.7. The concentration of dissolved hydrogen decreased as a result of anodic electrolysis or by exposure of the filament to air at room temperature. A deposit of Hg on the hydrogen-charged filament checked the passage of hydrogen through its surface. It was not possible to reproduce phenomena observed by Hirota and Horiuti when using a hydrogen-charged Pd filament as one arm of a Wheatstone bridge.

#### **The Kinetics of Absorption and Evolution of Hydrogen by Palladium and Palladium/Platinum Electrodes**

T. B. FLANAGAN and F. A. LEWIS, *J. Electrochem. Soc.*, 1961, **108**, (5), 473-477

Measurements of electrode potential and electrical resistance were made on Pd and Pt-Pd wires containing 2.79, 5.73, 8.80, 12.03, 15.42 and 18.99 at. % Pt at 25°C in HCl solutions stirred by hydrogen at 1 atm. The specimens were preactivated by anodisation before absorption of hydrogen and equilibrium with hydrogen was established before desorption was studied. A kinetic analysis is applied to the results obtained which are correlated with those found previously when the desorption rate could be neglected.

## **ELECTRODEPOSITION**

#### **A Survey of Progress in the Electrodeposition of Precious Metals**

W. T. LEE, *Metal Finishing J.*, 1961, **7**, (74), 63-70

Operating conditions and bath compositions for the plating of Pt, Pd, Rh, Ag and Au are discussed. Applications of electrodeposited Pt, Pd, Rh and Au in the electrical and electronic industries are outlined. Both vat and barrel plating are described, as are the various factors which require control in economic specification plating.

#### **Electrodeposition of Ruthenium**

F. H. REID and J. C. BLAKE, *Trans. Inst. Metal Finishing*, 1961, **38**, (2), 45-51

A number of electrolytes consisting of aqueous solutions of Ru salts and nitrosyl derivatives were tested. Of these, the most useful electrolyte for prolonged operation is prepared from ruthenium nitrosyl-sulphamate with 5g Ru/l as the optimum concentration. Using a current density of 8A/dm<sup>2</sup> at 70°C, smooth, bright deposits up to 0.0002 in. thick may be obtained. Internal tensile stress of the deposits is in the order of 20-30 tons/in<sup>2</sup>. Fine cracking may occur in deposits over 0.0001 in. thick, but it may be reduced by the addition of  $\text{Al}_2(\text{SO}_4)_3$  to the electrolyte. Slightly superior deposits may be obtained initially from ruthenium sulphamate solution and an electrolyte based on the reaction between sodium tetranitro-nitrosyl-ruthenate and sulphamic acid, but neither electrolyte is stable in operation. In all cases, cathode efficiencies are low.

## **METAL WORKING**

#### **The Powder Metallurgy of Ruthenium**

R. G. COPE and D. W. RHYS, *Powder Metallurgy*, 1961, (7), 139-155

Sintered compacts were prepared from Ru powder obtained by the reduction of ammonium ru-

thorium chloride with hydrogen. The specific surface area and tap density of the powder and their inter-relationship were measured, and the density, grain size, mechanical properties, and ease of working of the compacts were examined. A relationship between the properties of the powder and the conditions of its preparation was observed. The effects of temperature and compacting pressure on sintering were studied. Maximum compact densities may be obtained by sintering at 1500°C at a pressure which gives high density and open porosity at 1200°C. Gas evolution occurs at 1200°C. Specimens for working may be obtained by vacuum sintering compacts prepared from powder with a surface area 2-5 m<sup>2</sup>/g using pressures up to 25 tons/in<sup>2</sup>. A relationship between the workability of the sintered compacts and surface area of the powder was observed.

### Brazing René 41

G. S. HOPPIN, *Metal Progress*, 1960, **78**, (5), 75-79  
Processing and service factors which influence the choice of brazing material are discussed. Three alloys suitable for brazing a Ni-base high temperature alloy (René 41) are J-8600 (4% Si-24%Pd-33%Cr-39%Ni), J-8100 (10%Si-19%Cr-71%Ni), and J-8500 (5%In-35%Ni-60%Cu). J-8600 may be used for vacuum brazing at 2150°F. J-8100 and J-8500 are satisfactory for capillary and wide-gap brazing, respectively, of Ni-plated René 41 in hydrogen at 2200°F.

## CATALYSIS

### Platinum Metal Catalysis in Organic Chemistry

P. N. RYLANDER, *Abstracts of Papers*, 28-29 N, Div. of Med. Chem., 139th Meeting, A.C.S., St. Louis, Mar. 1961

Pd is an effective catalyst for the reduction of  $-C=C-$ ,  $>C=C<$ ,  $-C\equiv N$ ,  $>C=N-$ , nitroso, and nitro groupings for hydrogenolysis of activated functional groups, for selective reduction of acid chlorides, and preferential reduction of multiple unsaturation. The above functional groups, various aromatic systems, and non-activated carbonyl functions are reduced with Pt catalysts. Rh is active for the reduction of some aromatic systems under mild conditions and for functional groups such as  $>C=N-$  and  $>C=O$ . Ru is suitable for low pressure reduction of carbonyl compounds, and high pressure reduction of aromatic systems, with the avoidance of hydrogenolysis. The synergistic effects of mixed Pt metals catalysts are described. The effect of solvent, pressure, temperature, agitation, and catalyst concentration on selectivity of hydrogenation and the role of Pt metals in vapour- and liquid-phase dehydrogenation are discussed.

### Kinetics of Liquid Phase Hydrogenation II. Hydrogenation of Aromatic and Aliphatic Nitrocompounds over a Colloidal Platinum Catalyst

H.-C. YAO and P. H. EMMETT, *J. Amer. Chem. Soc.*, 1961, **83**, (4), 796-799

The rates of hydrogenation of *p*-C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> and other nitrocompounds were studied under constant hydrogen pressure at 25°C. Factors found to affect the order of reaction were the amount of catalyst, the nature of the solvent, and of the nitrocompounds, and the acidity of the solution. The rate for the aliphatic compounds is slower than that of aromatic compounds and there is evidence of poisoning of the catalyst surface by reaction products. Addition of acid or base increases the rate for the aromatic compounds, but decreases the rate for aliphatic compounds.

### III. The Nature of Platinum Oxide Catalysts *Ibid.*, 799-801

Reduced PtO<sub>2</sub> catalyst was prepared by suspending PtO<sub>2</sub> in 1% polyvinyl alcohol aqueous solution and reducing with hydrogen at 25°C. The rate of hydrogenation of C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> and CH<sub>3</sub>NO<sub>2</sub> with reduced catalyst in various liquids increases in the order: neutral solution < alkaline solution < acid solution < glacial CH<sub>3</sub>COOH. The activity of the catalyst for the hydrogenation of nitrocompounds is very low until partial reduction of the PtO<sub>2</sub> occurs. The reduction of C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> and CH<sub>3</sub>NO<sub>2</sub> over reduced catalyst is first order with respect to hydrogen pressure in the range 300 mm-850 mm, and with small amounts of catalyst, first order with respect to the nitrocompound concentration.

### Some Structural Problems of Hydrogenation Catalysis. III.

A. N. MAL'TSEV, N. I. KOBOZEV, T. V. SEMENOVA and E. I. KARPOVA, *Russ. J. Phys. Chem.*, 1960, **34**, (6), 568-573 (Transl. of *Zhur. Fiz. Khim.*, 1960, **34**, (6), 1190-1200)

The hydrogenation of hept-1-ene, cyclohexene, methylenecyclohexane, and 1,3-cyclohexadiene in C<sub>2</sub>H<sub>5</sub>OH at 25°C on a Pt/SiO<sub>2</sub> gel catalyst was studied. It was shown that hydrogenation takes place on the active centres [Pt<sub>2</sub>], [Pt<sub>6-7</sub>], and [Pt<sub>12</sub>] for all the hydrocarbons studied. The theory of active ensembles is applied to the results obtained for specific activity.

### Oxidation Reactions of the Olefins

I. I. MOISEEV, M. N. VARGAFIK and YA. K. SYRKIN, *Proc. Acad. Sci. U.S.S.R., Phys. Chem. Section*, 1960, **130**, (1-6), 115-118 (Transl. of *Doklady Akad. Nauk S.S.S.R.*, 1960, **130**, (4), 820-823)

Experimental work was carried out on the oxidation of olefins by oxygen in the presence of a solution of PdCl<sub>2</sub> and a Cu<sup>II</sup> salt. C<sub>2</sub>H<sub>4</sub> was converted to CH<sub>3</sub>CHO using a PdCl<sub>2</sub>/CuBr<sub>2</sub>/CuCl<sub>2</sub> catalyst and propylene was converted to CH<sub>3</sub>COCH<sub>3</sub> and propyl aldehyde with a PdCl<sub>2</sub>/CuBr<sub>2</sub>/CuSO<sub>4</sub> catalyst. CH<sub>3</sub>COCH<sub>2</sub>CH<sub>3</sub> was

obtained from butylene-2. The formation of intermediate  $\pi$ -complexes and their decomposition are discussed.

#### The Effect of Irradiation of Solid Catalysts

H. C. ANDERSEN, G. COHN, C. D. KEITH and P. N. RYLANDER, *U.S.A.E.C. Report NYO-2836*, Sep. 30, 1960, 30 pp.

Measurements made on a large number of supported Pt metals catalysts showed no effect on their activity for liquid phase hydrogenations at ordinary temperatures. Most gas phase reactions tested also showed no irradiation effects, but changes in activity were found with 5% PdO/ $\text{Al}_2\text{O}_3/\text{SiO}_2$ . The rate of the oxygen-hydrogen reaction at 25°C was increased 2-4 times, while rates of CO oxidation at 125°C and of  $\text{N}_2\text{O}$  decomposition near 400°C were halved.

#### Reductions with Ruthenium II. Its Use in the Hydrogenation of Pyridines

M. FREIFELDER and G. R. STONE, *Abstracts of Papers*, 33N, Div. of Med. Chem., 139th Meeting, A.C.S., St. Louis, Mar. 1961

The use of  $\text{RuO}_2$  as a hydrogenation catalyst at 90°C to 100°C and 70 atm pressure is described. With 0.1%  $\text{RuO}_2$  and a temperature of 200°C, reduction of  $\text{C}_6\text{H}_5\text{N}$  is completed in about 1.5h. Decarboxylation occurs during hydrogenation of nicotinic acid, but may be prevented by the presence of  $\text{NaHCO}_3$ . Advantages of the use of Ru and the effects on hydrogenation of substituents in the  $\text{C}_6\text{H}_5\text{N}$  ring are discussed.

#### Aging of Platinum Reforming Catalysts

C. G. MYERS, W. H. LANG and P. B. WEISZ, *Ind. Eng. Chem.*, 1961, 53, (4), 299-302

Experimental reforming of Mid-Continent naphtha was carried out under standard conditions of temperature, pressure, hydrogen/naphtha ratio, and catalyst concentration. Pt/ $\text{Al}_2\text{O}_3/\text{SiO}_2$ , Pt/ $\text{Al}_2\text{O}_3$  and Pt/ $\text{SiO}_2$  gel catalysts were used. The aging of the catalysts caused by several different hydrocarbon constituents of the naphtha was studied. A generalised poisoning mechanism involves the formation of unsaturated reaction intermediates, their reversible adsorption on the Pt sites and migration to the acid sites where they are reversibly adsorbed. The reversibility of the poisoning reactions is shown by the catalyst reactivation with nitrogen, hydrogen, and hydrogen-naphtha mixtures.

#### The Catalytic Synthesis of Hydrogen Peroxide from the Elements on Palladium

##### I. Conditions for the Formation of Hydrogen Peroxide

T. A. POSPELOVA, N. I. KOBOZEV and E. N. EREMIN, *Zhur. Fiz. Khim.*, 1961, 35, (2), 298-305 (English summary)

The catalysis of oxy-hydrogen gas to  $\text{H}_2\text{O}$  and to  $\text{H}_2\text{O}_2$  was investigated. It was shown that on Pd black, Pd/ $\text{SiO}_2$ , Pd/ $\text{Al}_2\text{O}_3$ , Pd/ $\text{WO}_3$  and Pd/C

the principal product is  $\text{H}_2\text{O}_2$ . Stabilisation of the  $\text{H}_2\text{O}_2$  is achieved by the presence of HCN and by HCl in dilute acid solutions. The overall reaction rate and  $\text{H}_2\text{O}_2$  yield are affected by acid concentration, composition of the gaseous mixture, temperature, and catalyst support.

#### The Isomerisation of Saturated Bicyclic Hydrocarbons by a Platinum Catalyst on an Acid Support

R. MAUREL and J.-E. GERMAIN, *Compt. rend.*, 1960, 251, (22), 2551-2553

The hydrogenation at 250°C of methyl-2-bicyclo-[2,2,1] heptane and bicyclo-[3,2,1] octane, using a Pt/ $\text{Al}_2\text{O}_3/\text{SiO}_2$  catalyst, was studied. Structures of the four principal constituents of the catalysate were the same as those previously obtained by the isomerisation of the corresponding olefins.

#### Investigations of the Kinetics of Catalytic Hydrogenation in the Liquid Phase. II. Diffusion of Dissolved Hydrogen to the Catalyst Surface

F. NAGY, D. MÓGER and I. NYITRAY, *Acta. Chim. Acad. Sci. Hung.*, 1960, 25, (2), 177-191 (In German)

The rate constant ( $k_2$ ) of diffusion was investigated, using a platinised Pt electrode as catalyst, in  $\text{H}_2\text{O}$  and in 0.1N  $\text{H}_2\text{SO}_4$  solutions at varying stirrer velocities. At low stirrer velocities,  $k_2$  is proportional to the square root of the velocity and the Lewitsch equation is satisfied. At higher velocities,  $k_2$  is hardly affected by changes in velocity and the Lewitsch equation does not hold.

#### Catalysed Reaction between $\text{NH}_3$ and NO

A. KRAUSE, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1960, 8, (7), 331-332 (In German)

A mechanism involving a NH-radical is discussed for the reaction between  $\text{NH}_3$  and NO on a Pt catalyst at 500°-530°C.

#### Kinetics of the Catalysed Oxidation of Hydrogen, Carbon Monoxide, and Methane by Oxygen in a Flowing Stream of Helium

C. D. SCOTT, *U.S.A.E.C. Report ORNL-3043*, 23 pp.

Tests were made on the oxidation of a gas mixture using a fixed bed Pt catalyst. Results obtained were used in the design of catalytic oxidisers for gas-cooled reactor helium purification systems.

#### The Catalytic Synthesis of Hydrogen Peroxide from the Elements on Palladium

##### II. The Active Centres of Palladium in the Synthesis of Hydrogen Peroxide

T. A. POSPELOVA and N. I. KOBOZEV, *Zhur. Fiz. Khim.*, 1961, 35, (3), 535-542 (English summary)

The dependence of the total and specific activities upon the degree of coverage of Pd/ $\text{SiO}_2$  gel adsorption catalysts was investigated. A comparison of Pt/ $\text{SiO}_2$  and Pd/ $\text{SiO}_2$  showed that Pt/ $\text{SiO}_2$

gives negligible yields of  $H_2O_2$  in the presence of poisons and that Pd is a specific catalyst for the synthesis of  $H_2O_2$  from the elements. The specificity is explained by the preservation of the  $-O-O-$  link due to the primary adsorption of hydrogen and secondary adsorption of oxygen.

#### Review of Recent U.S.A. Patents on Catalysts

H. HEINEMANN and P. A. LEFRANCOIS, *World Petroleum*, 1961, **32**, (3), 68, 69 and 79

The sixty-eight patents discussed in this review relate to Pt metal and base metal catalysts for reforming, cracking, isomerisation, hydrodesulphurisation, hydrogenation, polymerisation, oxidation, and butadiene production processes.

#### The Deuteration of Some Cyclic Olefins on Iron and Other Transition Metal Films

J. ERKELENS, A. K. GALWEY and C. KEMBALL, *Proc. Roy. Soc., Series A*, 1961, **260**, (1301), 273-292

The deuteration of cyclohexane on films of Ni, Pd, Pt and W was carried out at  $-35^\circ C$  and  $0^\circ C$  and the reaction products were determined by means of a mass spectrometer. The distribution of products of the deuteration of cyclohexene, cyclopentene, cycloheptene and other cyclic olefins on Fe films was also studied. Two types of reaction are postulated to account for the product distributions.

#### The Activation of Molecular Hydrogen by Platinum

A. I. KRASNA, *J. Amer. Chem. Soc.*, 1961, **83**, (2), 289-291

The exchange reaction:  $H_2 + HDO \rightleftharpoons HD + H_2O$  was studied by suspending  $PtO_2$  or  $PtCl_2$  in 10%  $D_2O$  in a hydrogen atmosphere. Parahydrogen conversion in  $H_2O$  in the presence of the same catalysts was also studied. Both reactions were very fast and the rates were independent of the concentration of  $PtO_2$  in the range 0.5-20 mg. It is suggested that the Pt catalyses a gaseous reaction between hydrogen and water vapour. In 100%  $D_2O$ , there is no parahydrogen conversion and more  $D_2$  than HD is formed in the exchange reaction. A homolytic split of the hydrogen is probable.

#### Catalytic Treatment of Nitric Acid Plant Tail Gas

H. C. ANDERSEN, W. J. GREEN and D. R. STEELE, *Ind. Eng. Chem.*, 1961, **53**, (3), 199-204

Experimental work on the removal of nitrogen oxides was carried out on a semi-pilot plant scale with a synthesised tail gas containing 0.2-0.5%  $NO + NO_2$ , 2.0-5%  $O_2$ , balance  $N_2$ . Reducing gases used included  $NH_3$ , CO, hydrogen, bleeder gas, natural gas, coke oven gas, and vapourised kerosine. Supported Pd, Rh and Pt catalysts were used. It was found that Pd is most suitable for use with  $CH_4$  while Pt is preferred for use with other hydrocarbons and  $NH_3$ . The catalytic

process may also be adapted for the generation of heat if higher inlet temperatures or lower space velocities are used. Selective removal of NO and  $NO_2$  without removal of oxygen is obtained with  $NH_3$  as the reducing gas. Operating data for various fuels, catalysts and inlet gas mixtures are given.

#### Nitric Acid Production

D. T. AUSTIN and J. G. SLOAN, *Indust. Chemist.*, 1961, **37**, (434), 159-166

The new  $HNO_3$  production plant at Ardeer (*Plat. Met. Rev.*, 1961, **5**, (2), 54-56) is described in detail. Advantages of operating the dual-pressure process—oxidation of  $NH_3$  over Rh-Pt gauze at 1 atm and adsorption of nitrous gases in  $H_2O$  at 4 atm—are discussed.

#### Hydrogenation and Hydrogenolysis. IV. Catalytic Reductions of Cinnamyl Alcohols and 3-Phenylpropargyl Alcohol

S. NISHIMURA, T. ONODA and A. NAKAMURA, *Bull. Chem. Soc. Japan*, 1960, **33**, (10), 1356-1359

The reductions were studied using oxides of Pt, Pd, Rh and Rh-Pt as catalysts. Hydrogenation was carried out at  $20^\circ-25^\circ C$  and 1 atm pressure. Maximum hydrogen adsorption is obtained with Pt, and hydrogenolysis is decreased by the addition of Rh to Pt. In  $CH_3COOH$ , the activities of the catalysts are in the order: Rh-Pt oxide  $>$  PdO  $>$  Pt oxide. The absorption of hydrogen increases with respect to the solvents in the order:  $C_2H_5OH$ ,  $CH_3COOH$ ,  $C_2H_5OH/HCl$ ,  $CH_3COOH/HCl$ .

#### V. Rhodium-Platinum Oxide as a Catalyst for the Hydrogenation of Organic Compounds

S. NISHIMURA, *Bull. Chem. Soc. Japan*, 1961, **34**, (1), 32-36

Hydrogenation of various organic compounds was carried out at S.T.P. using a Rh-Pt (3:1) oxide catalyst. The activity of the catalyst was compared with that of  $PtO_2$  and PdO under ordinary conditions, using both  $C_2H_5OH$  and  $CH_3COOH$  as solvents. Rh-Pt oxide proved to be the most active catalyst, especially in the hydrogenation of compounds with C-O linkages susceptible to hydrogenolysis.

#### Platinum Metal Catalysts in Nitric Acid Manufacture

J. SAGOSCHEN, *Chem. - Z.*, 1961, **85**, (6), 179-184

The  $NH_3$  oxidation process for the manufacture of  $HNO_3$  is described and the importance of the Pt metal catalysts used is emphasised. Details are given of the manufacture of Rh-Pt gauze catalysts, the possibilities of their contamination and mechanical loss, and the recovery of Pt. The purification of the process tail gas using supported Pt metal catalysts is also described. Residual nitrogen oxides may be removed together with

oxygen by reduction with fuel gases, or they may be reduced selectively with  $\text{NH}_3$ .

### Hydrogenation of Benzene on Platinum Catalysts. II. Poisoning

J. E. GERMAIN and Y. BOURGEOIS, *Bull. Soc. Chim. France*, 1961, (3), 521-525

Poisoning curves (relative speed of hydrogenation *v.* concentration of poison) were obtained for Pt/SiO<sub>2</sub> gel catalysts in the hydrogenation of C<sub>6</sub>H<sub>6</sub> at 20°C in the presence of thiophene. It is deduced that the energy of activation is independent of the degree of poisoning and that the susceptibility to poisoning does not depend on temperature in the range 15°-35°C. The relative effect of thiophene is the same in the hydrogenation of C<sub>6</sub>H<sub>6</sub> and C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, but thiotoluene is a more effective poison.

### Decarbonylation of Aromatic Aldehydes

J. O. HAWTHORNE and M. H. WILT, *J. Org. Chem.*, 1960, 25, (12), 2215-2216

Various aromatic aldehydes were heated with 5% Pd/C powder in an initial CO atmosphere. In most cases decarbonylation occurred within 2h. When *n*-C<sub>6</sub>H<sub>13</sub>CHO was treated similarly, the reaction time was 9h and decarbonylation was accompanied by dehydrogenation, isomerisation and polymerisation.

## CATHODIC AND ANODIC PROTECTION

### Use of Anodic Passivation for Corrosion Mitigation of Iron and Alloy Steels

D. A. SHOCK, J. D. SUDBURY and O. L. RIGGS, 1st International Congress on Metallic Corrosion, London, Apr. 1961, Preprints, 144-148

The essential requirements for anodic protection are explained. A basic circuit consisting of the vessel to be protected, an inert Pt-clad brass electrode, a reference electrode, and a current-potential controller is described. Limitations imposed on the system by the presence of halogen ions and the effect of anodic passivation on stress-corrosion cracking are discussed. Applications of the process are found in the protection of H<sub>2</sub>SO<sub>4</sub> storage tanks and sulphonation process vessels.

### Anodic Protection

C. EDELEANU and J. G. GIBSON, *Chem. & Ind.*, 1961, (10), 301-308

Requirements which must be satisfied to achieve passivity of metals by anodic polarisation are stated. Some experimental work supporting the proposed theory is described. The conditions upon which the economic operation of the protective system depends are given; the problem of throwing power is discussed. It is concluded that anodic protection is a promising method for corrosion control, especially in acid solutions.

## Electrochemical Principles of the Corrosion and Protection of Metals

T. P. HOAR, *J. Appl. Chem.*, 1961, 11, (4), 121-130

Anode and cathode reactions occurring in corrosion in aqueous media are described and the combination of these reactions in "natural" corrosion is discussed. Methods of influencing corrosion rates—anodic attack and cathodic protection; anodic passivation or protection and cathodic activation; anodic and cathodic inhibition and stimulation; resistance inhibition—are described. (39 references.)

## GLASS TECHNOLOGY

### Crystal Orientation as Influenced by Platinum Nucleation

G. E. RINDONE, *Bull. Amer. Ceram. Soc.*, 1961, 40, (4), 229 (Abstract of paper presented at the 63rd Annual Meeting of the Amer. Ceram. Soc., Toronto, Apr. 1961)

Orientation of Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> crystals with respect to a glass surface may be prevented in varying degrees by crystallisation on Pt nuclei. Experiments showed the depth beneath the surface to which orientation occurs in Pt-nucleated and Pt-free glasses under varying heat treatment conditions.

### Wetting and Adherence in Metal-Glass Systems

J. A. PASK, *Bull. Amer. Ceram. Soc.*, 1961, 40, (4), 277 (Abstract of paper presented at the 63rd Annual Meeting of the Amer. Ceram. Soc., Toronto, Apr. 1961)

Wetting characteristics of the Na<sub>2</sub>SiO<sub>5</sub>-Au, -Pt, and -Fe systems were determined by measurement of the contact angle in the sessile drop method. The importance of the reduction of the surface energy of the metal in the wetting process of these systems is discussed. Factors which lead to the formation of a chemical bond at the surface, with resultant good adherence, are analysed.

## TEMPERATURE MEASUREMENT

### Thermocouples for Use in Carbon Atmospheres

M. R. NADLER and C. P. KEMPTER, *Rev. Sci. Instr.*, 1961, 32, (1), 43-47

Factors which limit the selection of materials for use as thermocouples above 2000°C are discussed. Experimental work using W:Re, W:25% Re-W, Re:25%Re-W, graphite:Re, and graphite:Ir combinations in the temperature range 0°-2300°C is described. Temperatures of reaction between the oxide insulators (ThO<sub>2</sub>, UO<sub>2</sub>, and Y<sub>2</sub>O<sub>3</sub>) and C were measured.

### Vacuum Radiation Furnace with Precise Control of Temperature Gradients for Crystal Growth by Sublimation

A. C. PRIOR, *J. Sci. Instr.*, 1961, **38**, (5), 198-201

The furnace, designed to operate between 700°C and 850°C, is described in detail. Temperature gradients in the centre of the furnace, which do not exceed about 0.1°C/cm, are measured by a five-fold differential system of 1% Rh-Pt:13% Rh-Pt thermocouples. A high degree of temperature uniformity and rapid response times are achieved by minimising the mass of heated material and by the use of water-cooled reflecting Ag surfaces for the walls. A regulating system controls the temperature to 0.1°C.

### Effect of Pressure on E.M.F. of Thermocouples

F. P. BUNDY, *J. Appl. Phys.*, 1961, **32**, (3), 483-488

Thermal e.m.f.'s were measured for Pt, 10% Rh-Pt, Ni, Cu, Constantan, Alumel, Chromel, and 18% Mo-Ni at pressures up to 72 kbar for a

$\Delta T$  of 100°C. From these results, corrections due to pressure are deduced for common thermocouples made of pairs of these metals. Several thermocouple pairs were compared at pressures up to 58 kbar and temperatures up to 1200°C. Below 200° to 300°C, pressure deviations between them may be correlated with data on single metals taken at a  $\Delta T$  of 100°C, but at higher temperatures the deviations decrease and generally reverse.

### Thermocouple Calibration

ANON., *Instr. Practice*, 1961, **15**, (4), 428-431

Methods of calibration used at the National Bureau of Standards are described in detail. Base metal thermocouples are compared with a Pt resistance thermometer over the range -190° to 538°C and with a standard 10% Rh-Pt:Pt thermocouple up to 1100°C. Pt thermocouples are compared with the standard thermocouple, or are calibrated at fixed points on the International Temperature Scale. Thermocouple wires of various compositions and potentiometers also are calibrated.

## NEW PATENTS

### Electrical Resistance Alloy

JOHNSON, MATTHEY & CO. LTD. *British Patent* 861,646

A ductile stable high resistance alloy is composed of 16-90% palladium, 5-64% gold and 2.5-20% molybdenum apart from impurities.

### Separating Palladium from other Platinum Group Metals

CANADIAN COPPER REFINERS LTD. *British Patent* 863,286

Palladium is separated from other platinum group metals by adding to an aqueous solution of compounds of palladium and other platinum metal or metals, maintained in an acid condition by the presence of a strong acid, a water-soluble iodide in amount at least stoichiometrically equivalent to the palladium present to form PdI<sub>2</sub> so as to precipitate the palladium as PdI<sub>2</sub>, the solution containing a concentration of sulphur dioxide (0.3-4 g/l) sufficient to prevent the solution of PdI<sub>2</sub> by conversion thereof to PdI<sub>4</sub>.

### Separation of Platinum from other Metals

THE MOND NICKEL CO. LTD. *British Patent* 863,517

In the refining of platinum by precipitation as ammonium hexachloroplatinate from an acid chloride solution containing one or more other noble metals, the necessary ammonium ions are provided by hydrolysis of an amide in the

solution. Urea, acetamide or formamide may be used.

### Catalytic Isomerisation

ENGELHARD INDUSTRIES INC. *British Patent* 863,688

A C<sub>4</sub> to C<sub>6</sub> n-paraffinic-containing hydrocarbon feed is isomerised by contacting it in vapour phase with a catalyst, containing 0.01-2% of a platinum group metal and 3-20% of boria supported on activated alumina, at 500-800°F, superatmospheric pressure and in the presence of hydrogen and while providing 1-25% by wt. based on the feed of a hydrogen halide (atomic number of halogen 35-85).

### Isomerisation Catalyst

THE M.W. KELLOGG CO. *British Patent* 863,800

A catalyst for isomerisation processes is composed of an inorganic carrier, preferably alumina, rhodium, iridium, ruthenium or osmium, and at least 2% by wt. of a boron compound, preferably 5-25% of boron oxide. 0.05-5% by wt. of the platinum group metal is present.

### Isomerisation Catalyst

THE M.W. KELLOGG CO. *British Patent* 863,801

A hydrocarbon is isomerised by subjecting it to contact under isomerisation conditions with a catalyst comprising platinum or palladium, alumina and at least 5% by wt. of boron oxide.