

# ABSTRACTS

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

### PROPERTIES

#### **The Effect of Non-Metallic Additions on the Strength of Platinum at High Temperatures**

I. F. BELYAEV, *Tsvetnye Metal*, 1957, **30**, (6), 57-61 (*Chem. Abs.*, 1957, **51**, 17675g)

Metal-ceramic compacts of Pt with 0.05, 0.1 and 0.5% Al<sub>2</sub>O<sub>3</sub>, BeO, BaO and ZrO<sub>2</sub> were prepared by mixing solutions of (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>6</sub> and metal nitrate, drying and calcining at 1050° to give a sponge. This was powdered, briquetted and subjected to three cycles of sintering at 1500° and forging. Wires drawn from the compacts were several times stronger than wire made from pure Pt, and had the same ductility and corrosion resistance.

#### **Conductivity and Hall Constant**

##### **VII—Deformation and Recrystallisation in Pure Metals**

W. KÖSTER and W. SCHÜLE, *Z. Metallkunde*, 1957, **48**, (12), 634-636

The effect of deformation and recrystallisation on conductivity and Hall constant was studied for Cu, Ag, Au, Pd, Pt, Mo, W and Al. The resistivity increases on deformation, the increases varying from 0.2% for Pd to 10.2% for W. The change in Hall constant is negative except for Al and possibly Pd where it is positive and for Pt where there is no change. Since the increase in resistivity and decrease in mobility are about equal the perturbation of the lattice periodicity is considered to be the main reason for the resistivity increase.

#### **Mechanism of the Diffusion of Hydrogen through Active and Inactive Palladium**

O. N. SALMON, D. RANDALL and E. A. WILK, U.S. Atomic Energy Comm., Report KAPL-1672, 56 pp.

Experiments were carried out on flat Pd membranes, 0.0025-0.020 in. thick, at an upstream hydrogen pressure up to 50 cm. Hg and essentially zero downstream pressure, with a membrane temperature between 300 and 600°C. The factors involved in diffusion are discussed and an equation obtained which fits the experimental results quite well for active Pd membranes under the given conditions. The Pd membrane is rendered inactive by low true surface area due to lack of surface roughness and/or poisoning by impurity atoms or molecules occupying active sites on the surface. Hydrocarbon vapours and H<sub>2</sub>S poison the surface but SiF<sub>4</sub> and HCl (in

the absence of Fe) have no effect between 400 and 600° C. The membrane activity can be maintained if its temperature is held above 400° between runs in a good vacuum (10<sup>-5</sup> to 10<sup>-4</sup> cm. Hg) and if it is continuously protected from extraneous gases by two adjacent cold traps at -193° C. The rate of diffusion at high hydrogen pressures is determined by the rate of diffusion of protons through the lattice. At low pressures it is governed by the surface reactions: dissociation of hydrogen molecules and adsorption of the protons followed by their final desorption and recombination.

#### **Quenching Vacancies in Dilute Binary Platinum Solid Solutions**

S. PEARSON and F. J. BRADSHAW, *Phil. Mag.*, 1957, **2**, (Nov.), 1387-1388

The experiments described previously for Pt (*Platinum Metals Rev.*, 1957, **1**, (2), 62) were repeated using 1 at. % Rh-Pt and 0.5 at. % Au-Pt alloys. The vacancy formation energies deduced for both alloys were within  $\pm 0.1$  e.v. of the value for pure Pt. The resistance increases on quenching and the annealing behaviour does not differ significantly from that for pure Pt. From these results it was deduced that the vacancy-solute atom binding energies would not exceed 0.16 e.v. (Rh-Pt) and 0.23 e.v. (Au-Pt) and are probably much smaller than these values.

#### **Paramagnetic Studies on Hydrogenated Dilute Cobalt-Palladium Alloys**

J. P. BURGER and J. WUCHER, *Compt. rend.*, 1957, **245**, (Dec. 16), 2230-2233

Alloys containing 1, 2 and 4 at. % Co were saturated with hydrogen by subjecting them to electrolysis in an acidic bath. Addition of hydrogen neutralises the magnetic moment of Pd by causing the filling up of holes in the electronic *d*-band. A moment of about 5.2  $\mu$ B was obtained for Co alone which is similar to the value found in compounds containing Co<sup>2+</sup>. The paramagnetic Curie points of the alloys are sensitive to an excess of hydrogen.

#### **Electrical Resistivity of the Nickel-Palladium Alloy System between 300°K and 730°K**

A. I. SCHINDLER, R. J. SMITH and E. I. SALKOVITZ, *Phys. Rev.*, 1957, **108**, (Nov. 15), 921-923

Measurements were carried out, *in vacuo*, on the whole range of Ni-Pd alloys. The maximum resistivity moves from about 70 at. % Pd at 323°K to 50 at. % at 723°K, where all the alloys

are paramagnetic. Matthiessen's rule, which states that the rate of change of resistivity with temperature is independent of concentration in an alloy system, is obeyed only above the Curie temperature of the alloys, i.e. above 629°K. The asymmetry in the resistivity versus composition curves and the non-applicability of Matthiessen's rule at low temperatures is explained by the composition dependence of the filling of the two half *d*-bands in Ni. At higher temperatures the two halves of the *d*-band are equally filled and are composition independent.

### Neutron-Diffraction Observations on the Palladium-Hydrogen and Palladium-Deuterium Systems

J. E. WORSHAM JR., M. K. WILKINSON and C. G. SHULL, *Phys. Chem. Solids*, 1957, 3, (3/4), 303-310  
Neutron-diffraction investigations on powdered samples have shown that both hydrogen and deuterium atoms in  $\beta$ -phase Pd-H and Pd-D are located in octahedral positions in the Pd lattice. No conclusions could be drawn regarding the position of hydrogen in the  $\alpha$ -Pd lattice, since insufficient gas entered this phase even at low gas concentrations. The total neutron-scattering cross-section for hydrogen in the Pd-H system is abnormally low, indicating that the Pd-H bonds involved are weaker than normal chemical bonds.

### Superconductivity in the Nickel-Palladium-Arsenic System

S. GELLER and B. T. MATTHIAS, *Phys. Chem. Solids*, 1958, 4, (1/2), 156-157

The phases present in the following alloys were determined:  $(\text{Ni}_{0.75}\text{Pd}_{0.25})\text{As}$ ,  $(\text{Ni}_{0.25}\text{Pd}_{0.75})\text{As}$ , and  $(\text{Ni}_{0.12}\text{Pd}_{0.88})\text{As}$ . Both  $(\text{Ni}_{0.25}\text{Pd}_{0.75})\text{As}$  and  $(\text{Ni}_{0.12}\text{Pd}_{0.88})\text{As}$  were found to be superconducting with transition points at 1.6-1.34 and 1.39°K respectively. Since both alloys have the pyrite structure it appears that under the proper electronic conditions this structure is favourable to superconductivity.

### Sigma-Phase in the System Ruthenium-Tungsten

W. OBROWSKI, *Naturwiss.*, 1957, 44, (22), 581

The  $\sigma$ -phase is formed by peritectic reaction in the W-solid solution and has the composition  $\text{Ru}_2\text{W}_3$ . It is only stable above 1650°C, at lower temperatures it decomposes eutectically into W- and Ru-solid solutions.

### The Crystal Structures of the Monosilicides of Osmium, Iridium and Ruthenium

W. L. KORST, L. N. FINNIE and A. W. SEARCY, *J. Phys. Chem.*, 1957, 61, (11), 1541-1543

$\text{OsSi}$  has the cubic  $\text{FeSi}$  structure.  $\text{IrSi}$  has the orthorhombic  $\text{MnP}$  structure.  $\text{RuSi}$  exists in two modifications one with the  $\text{CsCl}$  structure and the other with the  $\text{FeSi}$  structure. Space groups and cell dimensions are given.

## ELECTROCHEMISTRY

### Surface States of the Platinum Anode (II) The Structural Change of Platinum Oxides by Heat Treatment

T. INOUE, *J. Electrochem. Soc. Japan*, 1957, 25, (8), E87-88 (English summary)

Pt hydroxides were prepared by two methods and the structural changes occurring in the temperature range 110-900°C were determined by X-ray analysis. No change in crystal structure was observed on heating below 200°C; above 200° partial decomposition of the oxide to Pt metal occurs and above about 750° this conversion is complete.

### Oxygen Coatings on Noble Metal Electrodes II—Smooth Iridium Electrodes

M. BREITER, K. HOFFMANN and C. A. KNORR, *Z. Elektrochem.*, 1957, 61, (9), 1168-1176

The oxygen coating on smooth Ir electrodes in  $\text{H}_2\text{SO}_4$  solution within a definite range of reference potential was examined by means of potentiostatic anodic current-voltage curves and cathodic charge curves. The decrease in anodic current density with increasing reference potential can be explained by the formation of an anion adsorption layer. The coating is much larger on Ir than on Pt under the same conditions.

### The Action of Cations on the Polarisation Potential of Platinum Anodes and on the Overpotential of Oxygen, Respectively

T. ERDEY-GRUZ and I. SAFARIK, *Acta Chim. acad. sci. Hung.*, 1957, 13, (1-2), 159-178 (In German)

At low current densities ( $10^{-1}$ — $10^{-2}$  amp./sq.cm.) in  $\text{H}_2\text{SO}_4$  solution only oxygen is formed at the Pt anode and the polarisation potential increases linearly with the log of current density. Above  $10^{-1}$  amp./sq.cm. persulphates are formed and the polarisation increases rapidly. When metal sulphates are dissolved in the  $\text{H}_2\text{SO}_4$  electrolyte the polarisation is increased, the effect of the various ions being as follows:  $\text{K}^+ > \text{Al}^{3+} > \text{NH}_4^+ > \text{Zn}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{Li}^+$ . The action was similar in 2N and 9N  $\text{H}_2\text{SO}_4$  and also in the absence of acid. The  $\text{K}^+$  ion showed identical action on smooth and platinised Pt and on Ni electrodes, the effect increasing linearly with concentration of  $\text{K}^+$ . Interpretation of the results is effected by assuming the metal cations to be adsorbed in the diffuse portion of the double layer, by the ions  $\text{SO}_4^{2-}$  and  $\text{HSO}_4^-$  which are directly adsorbed on the metal surface.

### Effect of Alternating Current on the Overpotential of Oxygen on Platinum Anodes in Solutions of Sulphuric Acid—I

T. ERDEY-GRUZ and I. SAFARIK, *Acta Chim. acad. sci. Hung.*, 1957, 13, (1-2), 201-213 (In German)

Changes in the polarisation potential of a Pt anode under the influence of A.C. superposed

on D.C., were examined in 2N and 9N H<sub>2</sub>SO<sub>4</sub>. Low frequency A.C. reduces the polarisation by 0.05v in 2N H<sub>2</sub>SO<sub>4</sub> and by 0.35v in 9N H<sub>2</sub>SO<sub>4</sub>. In both solutions there is a maximum depolarising action at ~ 1000 Hz after which the polarisation increases again. At low current densities, where oxygen evolution is the main electrode process, the depolarisation is independent of current density, but when persulphate is being formed the action of the A.C. decreases with increasing current density until at 1 amp./sq.cm. it has no effect at all. It is assumed that the superposition of A.C. affects the surface oxides of Pt by a periodic alternation of oxidation and reduction. Since A.C. is ineffective when persulphate is being formed it is concluded that the surface oxides of Pt can play no part in determining the rate of formation of persulphate.

### Electrochemical Behaviour of the Palladium-Hydrogen System

#### I—Potential-Determining Mechanisms

S. SCHULDINER, G. W. CASTELLAN and J. P. HOARE, *J. Chem. Physics*, 1958, 28, (1), 16-19

The potential of saturated  $\alpha$ -Pd in hydrogen-stirred solution with respect to a Pt/H<sub>2</sub> reference electrode is  $0.0495 \pm 0.0005$ v. It is proposed that the potential determining reaction is an equilibrium between H<sup>+</sup> in solution and H atoms dissolved in the metal, which is independent of hydrogen pressure. Pd in solution spontaneously absorbs H to form  $\alpha$ -Pd having a H/Pd ratio of 0.025. Between H/Pd = 0.03 and 0.36  $\alpha$ - and  $\beta$ -phases coexist but the  $\alpha$ -phase determines the potential, between 0.36 and 0.6 the potential is a function of the hydrogen content of the Pd. When H/Pd = 0.6 ( $\beta$ -phase) the potential is zero.

#### II—Thermodynamic Considerations

*ibid.*, 20-21

From thermodynamic principles a value of 0.048v is obtained for the potential of  $\alpha$ -Pd against Pt/H<sub>2</sub>, which agrees with the observed value of 0.050v. In the gas-charged alloy the  $\beta$ -Pd phase is stable at 1 atm. pressure but in the electrolytically charged alloy the  $\beta$ -phase loses H spontaneously and reverts to a composition corresponding to a point in the two-phase region. These facts can only be reconciled by assuming that electrolytic charging gives an alloy with a higher free-energy content than the gas-charged alloy.

#### III—Gas-Charged Palladium Alloys

*ibid.*, 22-24

Experimental evidence is presented to support the proposed difference in electrochemical properties between  $\beta$ -(gas-charged) and  $\beta^1$ -(electrolytically-charged) Pd-H alloys. The  $\beta$ -Pd/H<sub>2</sub> electrode is a true equilibrium hydrogen electrode. The presence of a passivating film explains the insensitivity of this electrode to

changes in hydrogen pressure. Pd in gaseous hydrogen forms  $\beta$ -Pd, but in hydrogen-stirred acid solution it forms  $\alpha$ -Pd. This is explained by a change in the sign of the surface charge on passing from Pd to  $\alpha$ -Pd, due to absorption of hydrogen, which blocks any further absorption in the presence of water molecules.

### Electrolytic Preparation of Perchlorates

K. C. NARASIMHAM, A. NARAYANASWAMI and B. B. DEY, *J. Sci. Indust. Res.*, 1957, 16A, (11), 512-516

Optimum conditions for the electrolytic oxidation of chlorate to perchlorate were established with a view to designing a large-scale unit for the production of ammonium and potassium perchlorates. The electrolytic cell was constructed of mild steel which acts as the cathode, the anodes were of Pt foil and the electrolyte composition (g./l.) was: NaClO<sub>3</sub> 600, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 0.6, K<sub>2</sub>CrO<sub>4</sub> 0.6 and MgCl<sub>2</sub> 1. On a laboratory scale a maximum current efficiency of 96% was obtained under the following conditions: temperature 30-35°C, current density 40 amp./sq.dm., voltage 5.0-5.5v and pH 6-7. This corresponds to a power consumption of about 1.046 kWh/lb. of NaClO<sub>4</sub>. Experiments were extended to a 2l. cell, similar in design to the smaller one, in which an efficiency of 85.2% was obtained under the optimum conditions, both in batch and continuous operations. Conversion of the NaClO<sub>4</sub> in the electrolyte to KClO<sub>4</sub> and NH<sub>4</sub>ClO<sub>4</sub> is described, respective yields of 81% and 67% with purities of 99.87 and 99.5% were obtained.

## LABORATORY APPARATUS AND TECHNIQUE

### Automatic Temperature Programming and Recording for a Platinum-Rhodium Furnace

J. M. CUTTER and R. DERRY, *J. Sci. Instruments*, 1958, 35, (1), 26-27

Because of the large increase in the resistance of 10% Rh-Pt furnace windings with temperature, the voltage applied to the winding must be adjusted continuously as the temperature changes and it is preferable that this should be done automatically. This was achieved by means of a servo-mechanism. The temperature control instrument is a proportional on-off programming unit which operates from a thermocouple in the furnace.

### An Oxidising Atmosphere Furnace for use with an X-Ray Diffractometer

S. W. KENNEDY and L. D. CALVERT, *J. Sci. Instruments*, 1958, 35, (2), 61-62

A furnace wound with 10% Rh-Pt wire for use with the Norelco diffractometer is described. It enables the investigation of rigid specimens or powders to be carried out in controlled atmospheres or vacuum.

## CATALYSIS

### Combined Catalysts as Revealed by Electron Diffraction

S. YAMAGUCHI, *J. Chem. Physics*, 1957, 27, (Nov.), 1114-1115

Solid catalysts combined with promoters,  $ZnCr_2O_4$ -ZnO, Cu-NiO and  $Al_2O_3$ -Pt, were investigated by electron diffraction using alternate hard and soft wavelengths. Three types of catalyst are distinguished from the results obtained. In  $ZnCr_2O_4$  the ZnO crystallites are enveloped in the chromite substrate, in Cu-NiO the NiO particles are scattered on the surface of the Cu, whereas the diffraction pattern of  $Al_2O_3$ -Pt shows a homogeneous mixture of components with the probability of bonding between the Pt and the  $\gamma$ - $Al_2O_3$ .

### Infra-Red Studies of Carbon Monoxide Chemisorbed on Rhodium

A. C. YANG and C. W. GARLAND, *J. Phys. Chem.*, 1957, 61, (11), 1504-1512

The infra-red spectrum of CO chemisorbed on Rh supported on a high area alumina was investigated in the region 1700-4000  $cm^{-1}$ . The mode of adsorption of CO, deduced from its spectrum, varies with the amount of Rh on the catalyst and with its heat treatment, whether sintered or unsintered. The results indicate that three types of adsorption occur: (a) two CO molecules/site, (b) a single linear CO molecule/site, and (c) a bridged CO between two sites already having a linear CO. With 2% Rh in the catalyst only type (a) occurs; with 8-16% Rh and a high coverage of CO all three types occur, but with a low coverage only type (b).

### Carbon Dioxide Chemisorption on Evaporated Metal Films

A. C. COLLINS and B. M. W. TRAPNELL, *Trans. Faraday Soc.*, 1957, 53, (11), 1476-1482

The interaction of  $CO_2$  with evaporated films of 12 metals was studied between  $-78$  and  $70^\circ C$ . Among the transition metals the chemisorption on Rh, Pt and Pd is very slight but on W, Mo, Fe and Ni it is extensive, fast and irreversible. Very little CO is liberated during  $CO_2$  chemisorption indicating that this is non-dissociative. Carboxylate ions are probably formed indicating that the low activity of the Pt metals may be due to their high work functions. The relevance of the results to the catalysis of isotopic exchange between CO and  $CO_2$  is discussed.

### Selectivity in Chemical Reactions

H. I. WATERMAN and A. B. R. WEBER, *J. Inst. Petroleum*, 1957, 43, (Dec.), 315-322

Simultaneous reactions are divided into three types, consecutive, side and parallel, and reaction courses are calculated for each assuming first-order kinetics. The method is applied to the

hydrogenation of linoleic esters on Pt-C and Ni-kieselguhr catalysts. At high pressures the reaction course is in accordance with the assumption of a consecutive first-order reaction, but there are unexpected deviations at low temperatures. The derivation of sound theoretical functions is practically impossible for many complex simultaneous reactions but the course of these reactions can be described to a good approximation by functions containing two constants, where the reaction products are considered as pseudo-three-component systems. These functions are applied to some reactions described in the literature.

### Possibility of Enhanced Catalytic Reactions

M. J. D. LOW, *J. Chem. Physics*, 1957, 27, (Oct.), 979

It is suggested that the enhancement of the rate and extent of gas-solid chemisorption reactions by gaseous electrodeless discharges is due to a chain mechanism initiated by the reaction of an active particle with a surface atom. Thus, if hydrogen adsorption is a prerequisite for hydrogenation on Pd, the action of the catalyst should be increased by energising the gas mixture above the catalyst. The energising could be accomplished by high or low energy electro-magnetic or corpuscular radiation or even by ultrasonics.

### Catalytic Exchange between Deuterium and Saturated Hydrides

J. R. ANDERSON, *Rev. Pure Appl. Chem.*, 1957, 7, (Sept.), 165-194

A review of catalytic exchange reactions in the gaseous phase over various catalysts, including the Pt metals. Among the reactions discussed are those in the hydrogen-deuterium system, in saturated hydrocarbons, ammonia and water and in certain aromatic amines and alcohols. (93 references)

### The Exchange between Hydrocarbons and Deuterium on Palladium Catalysts

R. L. BURWELL, JR., B. K. C. SHIM and H. C. ROWLINSON, *J. Amer. Chem. Soc.*, 1957, 79, (19), 5142-5148

The results of isotopic exchange between deuterium and twelve alkanes and cycloalkanes are reported. The catalyst used was mainly Pd- $Al_2O_3$ , but some work was done with evaporated Pd and Rh films. At about  $150^\circ$  the results on both Pd catalysts were similar and resembled those on Ni, but below  $100^\circ$  Pd- $Al_2O_3$  favoured more extensive multiple exchange than Ni.

### Contact Oxidation of Sulphur Dioxide and Hydrogen Sulphide by Platinised Nickel-Chromium in the form of a Complex Spiral

N. Z. KOTELKOV, *Zhur. Priklad. Khim.*, 1957, 30, (No. 3), 470-474

Tests were carried out using catalysts of platinised Ni-Cr and for comparison, Ni-Cr and platinised

Pt. The degree of oxidation on Ni-Cr at 450° C is 76.7 and 69.4% at bulk velocities of 68 and 234 respectively. Preliminary heat treatment of the Ni-Cr causes the temperature of maximum oxidation to increase and the maximum degree of oxidation to decrease. The degree of oxidation of SO<sub>2</sub> on platinised Ni-Cr and platinised Pt is 99.7% at 450° C and a bulk velocity of 214. On platinised Ni-Cr about 99% of H<sub>2</sub>S is oxidised at a bulk velocity of 97 and about 97% at a bulk velocity of 194, the temperature being 450° C.

#### Oxycat Burner Handles Flue Gases

L. RESEN, *Oil Gas J.*, 1958, **56**, (Jan. 6), 110-111  
An Oxycat unit has been installed at the Stanotex El Paso plant to burn flue gases from the Houdrifiow catalytic cracker. The flue gases, consisting of residual oil and carbon monoxide, together with oxygen are passed at 800° F over Oxycat ceramic bricks coated with Pt-Al<sub>2</sub>O<sub>3</sub> catalyst. Excess oxygen is always present to ensure complete combustion.

#### Heat Recovery by Catalytic Oxidation of the Tail-Gases from the Thermoform Catalytic Cracking Unit at the Refinery at Donges

R. MOREL and P. SIMONNIN, *Bull. Assoc. Franc. Techn. Petrole*, 1957, (Nov.), 493-497

A Houdry "Oxycat" unit has been installed at the refinery of Antar-Petroles de l'Atlantique at Donges in order to recover heat from the waste gases of the 12,500 b/d cracking unit. The gases are passed over a combustion catalyst consisting of Pt-Al<sub>2</sub>O<sub>3</sub> supported on porcelain rods. The average gas temperature on entering the catalyst chamber is 470° C and on leaving 753° C. The gases then pass through a heat recovery chamber before being discharged to the atmosphere at a temperature of 285° C. The gas flow rate is about 10,400 kg/hr.

#### The Catalytic Hydrogenation of Quinols

A. SIEGEL and H. BRÖLL-KECKEIS, *Monatsh.*, 1957, **88**, (5), 910-918

Free quinols on hydrogenation with Pd-BaSO<sub>4</sub>, and other Pd and Pt catalysts, give hydroaromatic compounds whereas quinol acetates give aromatic derivatives, e.g. 4-carbomethoxy-methyl-*p*-quinol on catalytic hydrogenation using Pd-BaSO<sub>4</sub> catalyst gives 4-carbomethoxymethylcyclohexanol-4-one, whereas its acetate derivative gives *p*-hydroxyphenylacetic acid.

#### Synthesis of Pseudoionone Homologues and Related Compounds

W. KIMEL, J. SURMATIC, J. WEBER, G. CHASE, N. SAX and A. OFNER, *J. Org. Chem.*, 1957, **22**, (12), 1611-1618

In the total synthesis of pseudoionone a key intermediate, 6-methyl-5-hepten-2-one, is formed by the reaction of acetone and acetylene, followed

by selective hydrogenation of the acetylenic alcohol using a Lindlar Pd catalyst and reaction of the product with diketene (*Platinum Metals Rev.*, 1957, **1**, (4), 119-120). Related ketones are prepared from this intermediate by effecting substitutions at carbon atoms 3, 4, 5 and 6 and are converted to the corresponding pseudoionones. The latter are precursors of a number of compounds of use in the essential oil industry.

## CATHODIC PROTECTION

#### Current Requirements for Cathodic Protection of Oil-Well Casing

E. W. HAYCOCK, *Corrosion*, 1957, **13**, (11), 767-773  
Methods at present used to indicate the minimum applied current required for complete cathodic protection are discussed and evaluated in terms of their scientific basis and their applicability to the protection of oil-well casing. Laboratory experiments are described in which cathodic protection currents are applied by means of Pt anodes to a series assembly of galvanic steel-Pt cells. Results of these experiments lead to a modification of the log current versus potential criterion of complete protection which is widely used at the present time. Experiments also indicate the amount of corrosion repressed as a function of the applied protection current. This is of considerable value when an economic balance is involved.

## GLASS TECHNOLOGY

#### Influence of Platinum Nucleation on Crystallisation of a Lithium Silicate Glass

G. E. RINDONE, *J. Amer. Ceram. Soc.*, 1958, **41**, (1), 41-42

The rate of crystallisation of Li<sub>2</sub>O·4SiO<sub>2</sub> glass at 650° C was greatly increased in the presence of 0.001 and 0.01% Pt. To render the glass completely opaque a 16 hr. heat-treatment is required if no Pt is present whereas in the presence of 0.001 and 0.01% Pt the time is reduced to 4 hr. and 45 min. respectively. The glass samples containing 0.01% Pt have a gray colour owing to the concentration of colloidal Pt. Nucleation by Pt results in smaller glass crystals with a more uniform distribution than when no Pt is present. The phase crystallising out is identified as primarily Li<sub>2</sub>O·2SiO<sub>2</sub>.

## ELECTRICAL ENGINEERING

#### The Effects of Dust and Force upon Certain Very Light Electrical Contacts

A. J. MADDOCK, C. C. FIELDING, J. H. BATCHELOR and A. H. JIGGINS, *Brit. J. Appl. Physics*, 1957, **8**, (12), 471-475

Pt-Au-Ag and Au contacts of the point-to-plane type in a low-current moving-coil relay were

investigated. Sets of about 80 contacts were used in order to obtain representative results. In testing the effect of dust on the contacts the voltage used was 3v, the current at make 200mA and the contact loading 1.8 mg. The contacts were enclosed in a dry-box and the dust concentration measured by an Owen's jet dust-counter. A linear relationship was found between the number of contact failures and the dust concentration, the failures increasing as the dust concentration rose.

### The Variation with Current and Inductance of Metal Transfer between Contacts of Palladium and Silver

R. I. B. COOPER and J. RIDDLSTONE, *Inst. Elect. Eng. Monograph No. 272*, Dec. 1957, 6 pp.

Transfer between Pd and Ag contacts was measured in 6v D.C. circuits and work on Pd was extended to 12 and 24v circuits. In 6v circuits experiments were carried out with break currents of up to 6.5A for Pd and up to 14.5A for Ag and inductances from 0.07-77  $\mu$ H. Except for inductances <0.1  $\mu$ H the transfer for Ag is several times greater than for Pd. Photographic records were obtained of the surface damage caused by a single switching at about 6A and 0.07 and 4.5 $\mu$ H. The behaviour of Pd in 12v circuits is similar to that at 6v, but at 24v considerable cathodic erosion appears at quite low inductances for currents above 2.4A. This is due to the mean arc voltage for the contacts lying between 12 and 24v. The general nature of transfer in Pd contacts is similar to that for Pt, but in the case of Ag neither residual nor reversed short arc transfer was demonstrated.

### Metal Migration in Electrical Contacts

G. ZIELASEK, *Arch. Elektrotech. (Berlin)*, 1957, **43**, (4), 249-275

In Pt and Pd contacts metal transfer depends primarily on the Thomson effect whereas in Cu, Ag and Au the principal causes are tunnel effects and heat conduction. Variations in the physical properties of the contact materials can cause large divergencies between transfer values, as has been found experimentally. With Cu, Ag and Au the loss of material from the anode is dependent on current (I) and I<sup>2</sup>, with a contribution from a factor I<sup>3</sup> at high currents (20-100A) due to the Thomson effect. With Pd and Pt the transfer is dependent on I<sup>3</sup> over the whole current range. These two possible mechanisms help to explain the previous discrepancies between the nearly quadratic current dependencies obtained experimentally and the theoretical I<sup>3</sup>-proportionality. Material loss in Pd and Pt, controlled by the Thomson effect, is independent of voltage. For Cu, Ag and Au it increases with the square of the voltage and is greater for slowly separating contacts. Theoretical and experimental results are in good agreement.

## ELECTRONICS AND TELECOMMUNICATIONS

### Principles of Very Low Power Electrochemical Control Devices

R. M. HURD and R. N. LANE, *J. Electrochem. Soc.*, 1957, **104**, (12), 727-730

A new technology utilising electrochemical phenomena has been developed from which it is possible to design detection and control devices with power consumption 100-1000 times smaller than that of transistors. A detector for acoustic energy, using Pt gauze electrodes in KI + I<sub>2</sub> solution, operates on 10  $\mu$ W in the quiescent state, delivering 300-500 $\mu$ W when fully excited. Development work to date has been limited to low frequencies—0-200 c.p.s.

## TEMPERATURE MEASUREMENT

### Temperature Measurement of Liquid Steel by Immersion Thermocouples

M. M. EPSTEIN, *Metallurg.*, 1957, (No. 2), 11-14 (In Russian)

Tests made at the Kuznetskii Metallurgical Combine have led to new developments in the construction of Pt/Rh-Pt thermocouples. Systems of temperature measurement of liquid steel in open-hearth and electric furnaces are described.

### A Method for the Continuous Measurement of Liquid Steel Temperature in the Ladle

R. KATAKURA, H. MIWA and Y. WADA, *Sumitomo Metals*, 1957, **9**, (Jan.), 13-20 (In Japanese)

An immersion thermocouple sheathed with fused alumina and protected by alumina cement and a steel tube is used for the continuous measurement of liquid steel temperatures in ladles of various sizes. The temperature difference between the ladle and the trough during casting is only 6° C. This method can therefore be used to investigate ladle cooling of steel and to control the casting operation.

### Thermoelectric Measurement of Open-Hearth Furnace Roof Temperatures

H. J. KIRSCHNING, E. HOCHSTRATE and H. RODRIAN, *Arch. Eisenhüttenwesen*, 1957, **28**, (10), 611-614 (Transl. in *Iron Coal Trades Rev.*, 1958, **176**, (Jan. 3), 42-44)

Roof-temperature control has recently gained in importance because the increased furnace temperatures used require more accurate control measures. Indirect measurement by means of optical pyrometers is now standard practice, but has several disadvantages. Thermocouples could be used if effective shielding were devised. Various types of shielding were therefore tested in two German steel plant furnaces with acidic and basic roof-linings respectively. A 6%

Rh-Pt/30% Rh-Pt thermocouple was used and the materials selected for shield tubes were BeO, spinel, ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. These tubes were protected by a Cr-Ni steel tube in the acidic-roofed furnace, but this was unnecessary with the basic type. The life-time of the shields in operation at a temperature of ~1700° C is as follows (in numbers of melts): BeO over 100, ZrO<sub>2</sub> 18-20, Al<sub>2</sub>O<sub>3</sub> 18-20, spinel ~14. The life of the thermocouple was 300 melts. The best

shield material is obviously BeO although ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> could also be used. Spinel is not suitable. A disadvantage in using Al<sub>2</sub>O<sub>3</sub> is that carbon contamination (observed in all cases) leads to the formation of an Al carbide with a melting point of only 1400° C. Carbides of Zr and Be which may be formed have melting points of 3500° and 2100° C respectively. The estimated cost of temperature control by this method is less than that using optical pyrometers.

## NEW PATENTS

### Glutamic Acid Derivatives

INTERNATIONAL MINERALS & CHEMICAL CORP.  
*British Patent 786,226*

A platinum, palladium or rhodium catalyst is used in the treatment of N-carboallyloxy-L-glutamine to remove the carboallyloxy group.

### Preparation of Metal Gluconates

CHAS. PFIZER & CO. INC. *British Patent 786,288*

A metal gluconate is prepared by contacting an aqueous glucose solution (concentration at least 20% by weight) containing a noble metal catalyst with oxygen at not above 55°C and at a pH maintained at between 8 and 11, the pH used at any given temperature being chosen so as to minimise decomposition. The catalyst consists of palladium-on-charcoal or palladium-on-alumina.

### Hydrogenation of Organic Nitro Compounds

E. I. DU PONT DE NEMOURS & CO. *British Patent 786,407*

In the catalytic hydrogenation of organic nitro compounds to the amine product with the use of a noble metal, i.e. platinum or palladium catalyst supported on an inert carrier, e.g. carbon, diatomaceous earth or silica, an increased rate of hydrogenation is obtained by mixing with the catalyst an oleophilic carbon having an oil absorption factor of at least 200.

### Production of Tetracycline

AMERICAN CYANAMID CO. *British Patent 787,056*

Tetracycline is made by reacting hydrogen with chlortetracycline in the presence of a palladium hydroxide catalyst. The palladium hydroxide may be used alone or supported on a porous carrier, e.g. activated carbon or activated alumina.

### Gasoline Reforming Catalyst

W. R. GRACE & CO. *British Patent 787,275*

An alumina base reforming catalyst is made by simultaneously incorporating silica and fluorine values with a porous gamma-type alumina base by impregnating the base with silicon tetrafluoride or fluosilicic acid in sufficient amount to form a final catalyst containing 0.03-3 wt.% of silica and 0.1-8 wt.% of fluorine and mixing in

an aqueous solution of a water-soluble platinum compound in sufficient amount to give 0.1-2 wt.% of platinum. The platinum compound which is preferably chloroplatinic acid is then reduced to the metal.

### Removing Impurities from Platinum

UNIVERSAL OIL PRODUCTS CO. *British Patent 787,296*

An aqueous solution of an acid containing platinum as part of a complex anion and also containing a cation impurity is purified by contacting the solution with a solid cation exchange material, transferring the impurity to this material by a cation exchange reaction and separately recovering the purified solution of the platinum. The platinum may be present as chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>).

### Regeneration of Catalysts

LAPORTE CHEMICALS LTD. *British Patent 787,340*

A supported palladium catalyst, after becoming deactivated in use for the manufacture of hydrogen peroxide, is reactivated by treatment with a solution of sodium hydroxide.

### Catalytic Conversion of Hydrocarbons

UNIVERSAL OIL PRODUCTS CO. *British Patent 787,539*

A platinum-alumina-combined halogen catalyst (*British Patent 657,565*) or a platinum-alumina-silica catalyst containing 0.2-2 gm of platinum per 100 cc of catalyst (*U.S. Patent 2,478,916*) is used in a process for the catalytic reforming of gasoline hydrocarbons.

### Platinum-Alumina Catalyst

STANDARD OIL CO. *British Patent 787,755*

An alumina-supported platinum catalyst is made by adding an alkaline substance, e.g. ammonia or a water-soluble amine to peptised alumina, e.g. an alumina hydrosol, in sufficient amount to raise the pH to 8.5 to 12, maintaining this condition for over 1 hour, separating solid hydrous alumina from the resulting slurry, drying to a volatiles content below 50% by weight wet basis,