ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Thermal Diffusion in Platinum

S. C. HO, T. HEHENKAMP and H. B. HUNTINGTON, *J. Phys. Chem. Solids*, 1965, **26**, (2), 251–258

Observations of thermal diffusion of Pt in temperature gradients were clear and reproducible. Marker motion was 1 μ/d at about $1600°C$ in a $400°C$/m gradient. Heat of transport was 0.68 ± 0.09 eV, which is much larger than E_m-E_f, where E_m and E_f are migration and formation energy. This discrepancy is not yet explained.

Thermal Diffusivity at Incandescent Temperatures by a Modulated Electron Beam Technique

M. J. WHEELER, *Br. J. Appl. Phys.*, 1965, **16**, (3), 365–376

Pt at 1180–1750 °K has thermal diffusivity 0.223 ± 0.003 cm^2 sec $^{-1}$ and thermal conductivity $0.59 + (1.3 \pm 0.1)$ T $\times 10^{-4}$ W cm $^{-1}$ deg K^{-1}. Results were also obtained for Mo,Ta,W. The Lorenz functions were constant for each. Thin slabs of specimens were heated to incandescence by an electron beam, amplitude modulated to vary sinusoidally with time. The phase difference between the resulting temperature fluctuations of the slab gave the thermal diffusivity of the sample.

Thermoelectric Size Effect in Platinum

R. P. HUEBENER and R. E. GOVEDNIK, *Bull. Am. Phys. Soc.*, 1965, **10**, (3), 325, abs. BF2

The difference of thermoelectric power between thin Pt foils and 0.010 inch Pt wire was measured from 77 to 373°K and electrical resistance difference was measured at 4.2°K. The average electron mean free path in Pt at 296°K was $\bar{l}=(5.47 \pm 1.25)$. 10^{-7} cm and $\{\delta \ln \bar{l}/\delta E\}E_F=(4.5 \pm 2.5)$ eV^{-1}. The electrical conductivity associated with the d-band in Pt has the same order of magnitude as that of the s-band.

Deformation of Quenched Platinum

J. J. JACKSON, *Ibid.*, 337, abs. DE10

Deformation of quenched Pt specimens at temperatures from 4 to 600°K increases the dislocation density and may produce both lattice vacancies and interstitials. Annealing of these is not difficult.

Observations on the Precipitation Hardening of the 10 wt.% Gold-Platinum Alloy

G. REINACHER, *Z. Metallkunde*, 1965, **56**, (4), 216–221

Aging studies at 45, 500 and 600°C showed that at 600°C the aging behaviour depended on the furnace atmosphere. In air, precipitation occurred at points on the surface but in H_2 a front of discontinuous precipitation moved into the interior of the sample.

Solid Solution Strengthening in Iron-Nickel and Iron-Platinum Alloys

H. H. KRANZLEIN, M. S. BURTON and G. V. SMITH, *Trans. Met. Soc. A.I.M.E.*, 1965, **233**, (1), 64–70

Tests from $+25$ to $-196°C$ showed that the temperature dependence of yield stress is less in Fe alloys with up to 2 at.% Ni or Pt than in high-purity Fe. At room temperature, yield stress increased with alloy content but at $-78°C$ it first decreased with increasing alloy content. Current theories of solid-solution strengthening do not explain this.

Mössbauer Measurements of Fe^{57} Hyperfine Fields in Platinum-rich Pt-Fe Alloys near Pt$_3$Fe

C. W. KIMBALL, J. CRANGLE, D. PALAITH and R. PRESTON, *Bull. Am. Phys. Soc.*, 1965, **10**, (4), 471, abs. DF 7

Ordered 24.0, 26.7, 30.0 and 34.5% Fe-Pt alloys have magnetic ordering sensitive to Fe content. Mössbauer measurements of Fe^{57} showed one antiferromagnetic state at $T_N \sim 170°K$ and another growing at the first's expense as the Fe concentration rose. $H_1=288$ kOe at 24.0% Fe. H_2 was 30 kOe less at 26.7% Fe. At 30% Fe, H_2 dominated H_1. At 34.5% Fe the Mössbauer spectrum is complex.

On the Temperature Dependence of the Magnetic Properties and the Character of the Processes of Magnetisation of a CoPt Alloy

N. N. POTAPOV and A. G. RABIN'KIN, *Dokl. Akad. Nauk S.S.S.R.*, 1965, **160**, (3), 586–589

The magnetisation and demagnetisation of equiatomic CoPt alloys was studied at temperatures between 77 and 673°K. Isotherms show the decreasing magnetisation achieved at higher temperatures. The coercivity and magnetisation were higher for disordered than for ordered alloys.

Changes in the Crystal Structure and Magnetic Properties of a Co-Pt Alloy during the Ordering Process

A. G. RABIN'KIN, YU. D. TYAPKIN and K. M. YAMALEEV, *Fiz. Met. Metalloved.*, 1965, **19**, (3), 360–366

Single crystals of 51.3 at.% Pt-Co were studied

by X-rays during ordering while annealing at 600°C after quenching from 1000°C in water and after quenching at the 'critical' rate of 1.3 deg C/sec. Crystal structure changes were compared with changes in the magnetic properties.

Specific Heat of 0.5% Solutions of Cr, Mn, Fe, Ni in Platinum

Studies in the range 1.6–7°K showed that the specific heats of Cr, Mn, and Fe in Pt at 1.6–6°K obey the formula $C = \gamma T + \alpha T^3 + A/T^2$. The big increase in the specific heats compared to that of pure Pt is due to localised factors at the impurity centres.

The Magnetic Moment of Ni, Co, Mn, Fe, Cr, Gd Dissolved in Platinum

The temperature dependence of paramagnetic susceptibility of 0.5 at.% solid solutions of Ni,Co, Fe,Mn,Cr, and Gd in Pt was studied at 20–300°K. The magnetic moments of the alloying atoms, calculated by the Curie-Weiss formula, are P_{Co}, 5.8; P_{Fe}, 6.7; P_{Mn}, 5.7; P_{Cr}, 5.6; P_{Gd}, 6.8μ_B. Results are discussed in the light of existing theory on localised composition.

Electrical Conductivity of Dilute Solutions of Transition Metals in Platinum

The "residual" resistance of 0.5% solutions of the $3d$ transition metals and some of the $4d$ group in Pt is not uniformly related to the impurity. Of the $3d$ metals, Ti has the greatest "residual" resistance; Zr has the most of the $4d$ metals. Results are related to localized state theory.

Constitution of the Boron-Platinum System

X-ray diffraction, thermal analysis and metallographic tests of the Pt-B system indicated eutectics at ~42 at.% B, 920°C and at ~28 at.% B, 795°C. Peritectic reactions occurred at 890°C and at 825°C. Pt_3B_2 formed directly from the melt at 940°C. The eutectoid reaction $Pt_3B_2 \rightarrow Pt_2B + B$ occurred at 600–650°C. Compounds detected were Pt_3B_2, Pt_2B and Pt_3B.

Dislocation Mechanisms in the Growth of Palladium Crystals

Pd metal whisker crystals grow at ~0.02 cm/sec in irrational crystallographic directions around dislocation intersections at whisker tips by catalytic decomposition of Pd_xCl_y to Pd and Cl_2, while lateral growth is retarded by a thin film of liquid $PdCl_2$. Nucleation probably occurs at bubbles in the film over dislocation intersections with the massive substrate surface. Dislocations provide growth steps on whisker tips and climb helical paths. Changes in direction occur but the whisker remains straight as systematic helical climb is inhibited or helical growth is suppressed by simultaneous operation of many dislocations.

A Mass Spectrometric Study of the Vaporisation of Palladium

The average heat of sublimation of Pd from relative vapour pressure measurements, using a Knudsen-cell effusion source and mass spectrometer detector, was $H_{298} = 91.2 \pm 0.9$ kcal/mole. Other molecular species were not observed.

Neutron Diffraction Study of Temperature-dependent Properties of Palladium Containing Absorbed Hydrogen

Structures of single-phase β-PdH have space groups R$\bar{3}$m and Fm3m below and above 55°K, respectively. Partial migration of H atoms from octahedral to tetrahedral sites in the f.c.c. Pd lattice causes the low-temperature structure. The r.m.s. vibrational amplitude of the H atoms is approximately 0.25 Å at 293°K, 0.17 Å at 4.2°K. Transfer of H atoms between lattice sites causes anomalies in temperature dependence of electrical resistivity and in heat capacity.

Heat Capacity and Spontaneous Heat Flux in H-Pd alloys

Dynamic measurements of β-phase H-Pd alloys at 1.2–4.2°K gave γ values about 1/4–1/7 those of pure Pd but Debye θ's were only slightly different, thus supporting the view that electrons from dissolved H_2 enter the d band of the alloy. Heat flux depended on alloy composition, temperature and thermal history. It decreased with time at constant temperature but was restored after annealing at N_2 or room temperature. Heat fluxes were about 2–5 μW/g of dissolved H_2 but their source was not established.

Absorption Isotherms and Diffusion Constants of Hydrogen in the α-Phase of the Hydrogen/Palladium System

The average isoteric heat for the reaction $H_2 + x$ H: y Pd → (x + 2) H: y Pd is −5875 ± 150 cal/mole H_2 from H/Pd=0 to 0.014. Data were obtained at 0–90°C from changes of electrode potential and resistivity of Pd wires during absorption from H_2-stirred solutions. Uniform

H$_2$ absorption required slow absorption with the absorption rate $\propto$ Cp$_{H_2}$ in solution. High absorption rates were also studied. Diffusion constants were obtained at 0–50°C and the effect of H/Pd on them was considered.

The Palladium-Hydrogen System

H. BRODOWSKY, *Z. Phys. Chem. (Frankfurt)*, 1965, **44**, (3-4), 129–142

The solubility of H$_2$ in Pd is explained by the dissociation of 4 atoms into protons and electrons. Deviations from ideal behaviour occur when electron bands of the metal are filled or when protons cause local expansion and tension of the lattice by thermal motion. The tendency of protons to associate is proportional to the chemical potential of dissolved H$_2$. D$_2$ behaves similarly to H$_2$ but its association energy is less because of its smaller amplitude of vibration.

Hydrogen in Palladium/Silver Alloys

H. BRODOWSKY and E. POESCHEL, *Ibid.*, 143–159

Absorption isotherms are given for H$_2$ in 10, 20, 30, and 40 wt.% Ag-Pd alloys at 30–148°C, 0.01–760 Torr on Cu powder by gas volumetric measurements. Deviations from ideal behaviour are discussed. The effect of Ag additions is to alter the energy required to expand the lattice to admit H$_2$.

Magnetic Properties of Pd Metal and Pd-Rh and Pd-Ag Alloys Containing Co and Fe Atoms

T. TAKAHASHI and M. SHIMIZU, *J. Phys. Soc. Japan*, 1965, **20**, (1), 26–35

Assuming that the Co and Fe atoms have localised magnetic moments and are distributed at random, an analysis by the itinerant model of 4d – electrons gives the spin quantum numbers as 1 and 3/2 for Co and Fe, respectively, in the alloys. The composition dependence of the magnetic moment and the Curie termperature, and the temperature dependence of paramagnetic susceptibility of the alloys were calculated.

On the Problem of the Existence of Antiferromagnetism in Fe-Pd Alloys with Invar Characteristics

H. FUJIMORI and H. SAITO, *Ibid.*, (2), 293–294

30 at.% Pd-Fe alloy has magnetic moment μ similar to that of the 35 at.% Ni-Fe alloy, which has Invar characteristics. Its magnetic state can be described as a mixture of ferro- and antiferromagnetic.

Effect of Small Additions of Fe on the Hall Coefficient of Pd

A. I. SCHINDLER and D. J. GILLESPIE, *Bull. Am. Phys. Soc.*, 1965, **10**, (3), 326, abs. BF8

Hall coefficients of Pd and of 0.09, 0.13 and 0.29 at.% Fe-Pd alloys were measured at 2–4.2°K and at 45–77°K. At 77°K all were field-independent

but, at about 4-K, those of Pd increased with magnetic field while those of the alloys decreased with increasing field. Hall coefficients at 4 and 77°K increased with Fe content.

Constitution and Magnetic and Electrical Properties of Palladium Tellurides (PdTe-PdTe$_2$)

A. KJEKSHUS and W. B. PEARSON, *Canad. J. Phys.*, 1965, **43**, (3), 439–449

X-ray studies of the PdTe-PdTe$_2$ region confirmed that a continuous solid solution exists at high temperatures, and that narrow PdTe and PdTe$_2$ homogeneity regions exist at low temperatures. PdTe is nonstoichiometric below 500°C. Magnetic susceptibility, electrical resistivity, thermoelectric power, and superconducting transition temperatures were measured but no very satisfactory results were obtained for the superconducting transition temperature of PdTe and for the conductivity and thermoelectric power of PdTe$_2$, in the (001) direction.

Investigations in the Palladium-Mercury System

G. JANGG and W. GRÖLL, *Z. Metallkunde*, 1965, **56**, (4), 232–234

The phase diagram and solubility curve of the Pd-Hg system were studied by vapour pressure measurements, by X-rays and thermal analysis, and the compounds PdHg$_4$, Pd$_2$Hg$_5$ and PdHg were found, of which the two latter have narrow ranges of homogeneity. Peritectic reactions occur at 90 and 238°C. Heats of formation of Pd$_2$Hg$_5$ and PdHg are −55.8 kcal/mol and −22.5 kcal/mol.

Thermomagnetic Measurements on Iridium-Manganese and Rhodium-Manganese Alloys

K. KUSSMAN, K. MÜLLER and M. WUTTIG, *Z. Metallkunde*, 1965, **56**, (4), 228–231

β-phases of Ir-Mn and Rh-Mn alloys are ferromagnetic. Field strengths were measured. The temperature dependence of magnetisation of Rh-Mn alloy shows hysteresis behaviour between +300 and −200°C. Magnetisation varies considerably with the pretreatment of the alloy. The other phases are paramagnetic.

Superconductivity in Binary Alloy Systems of the Rare Earths and of Thorium with Pt-Group Metals

T. H. GEBALLE, B. T. MATTHIAS, V. B. COMPTON, E. CORENZWIT, G. W. HULL and L. D. LONGINOTTI, *Phys. Rev.*, 1965, **137**, (1A), A119–A127

All binary systems of Sc, Y, La, Ce, Lu, and Th with Co, Rh, Ir, Pd, and Pt contain at least one superconducting phase, except Sc-Pt and Ce-Rh. Transition temperatures of analogous compounds indicate that pure Rh should become superconducting above 10 mdeg, pure Pt much lower. Superconducting properties of all compounds tested are tabulated.

Superconductivity in Cr_3Si-Type Ternary Phases with Niobium and Group VIII Metals

S. T. ZEGLER, *Ibid.*, (5A), A1438–A1440

Cr_3Si-type alloys of general composition $Nb_3Rh_{1-x}B_x$, where B is Co, Ru, Pd, Os, Ir, Pt, or Au were investigated down to 1.7°K. All metals substituted for Rh in Nb_3Rh increase cell volume and decrease the superconductivity transition temperature, except Pt and Au, which increase the transition temperature, but not above that of Nb_3Pt or Nb_3Au. Transition temperature increases as the valence electron-atom ratio rises from 6 to 6.5 but decreases with larger cell volume.

CHEMICAL COMPOUNDS

Pyridine N-Oxide-Carbonyl-Dichloroplatinum (II) Complexes

W. H. CLEMENT and H. ORCHIN, *J. Organomet. Chem.*, 1965, **3**, (1), 98–99

CO reacts rapidly with ethylene-pyridine N-oxide-platinum (II) complexes and replaces the C_2H_4 ligand to form the carbonyl complexes. This is a simple route to Pt carbonyls at room temperature.

Nucleophilic Constants and Substrate Discrimination Factors for Substitution Reactions of Platinum (II) Complexes

U. BELLUCO, L. CATTALINI, F. BASOLO, R. G. PEARSON and A. TURCO, *J. Am. Chem. Soc.*, 1965, **87**, (2), 241–246

Reaction kinetics for substitutions of 6 Pt complexes of *trans*-[PtL₂Cl₂]-type with 18 nucleophilic reagents showed that log $k_y = Sn_{Pt} + \log k_s$, where n_{Pt} is nucleophilic reactivity constant of each reagent based on *trans*-[Pt(py)₂Cl₂] as standard. k_y is second-order rate constant for nucleophile Y, S is nucleophilic discrimination factor, k_s is "intrinsic" reactivity measure equal to first-order rate constant for reaction in which solvent is nucleophile. When k_s is low, S is high, and vice versa. Strong π-bonding in *cis* position causes low k_s, high S.

Structure of and Bonding in [(C₃H₅) PdCl]₂

W. E. OBERHANSLI and F. DAHL, *J. Organomet. Chem.*, 1965, **3**, (1), 43–54

Yellow monoclinic crystals of [(C₃H₅)PdCl]₂ have a $=7.46 \pm 0.02$ Å, b $= 7.43 \pm 0.02$ Å, c $= 8.61 \pm 0.02$ Å, $\beta = 93.6 \pm 0.01°$. Related organometallic complexes are compared.

New Double Oxide of Palladium and Rhodium

A. U. SEYBOLT, *Trans. Met. Soc. A.I.M.E.*, 1965, **233**, (1), 248

An oxide, which appeared as a subscale during O_2 equilibrations with 5 at.% Rh-Pd, has hexagonal lattice with $a_0 = 5.22$ Å, c -6.0 Å and may be $(Pd_xRh_{1-x})_3O$, where $x = 0.4 \pm 0.1$.

Ternary Oxides of the Transition Metals. IV. Alkaline-earth-iridium (IV) Oxides: Crystal Structure of $CaIrO_3$

F. RODI and D. BABEL, *Z. anorg. allgem. Chem.*, 1965, **336**, (1-2), 17–23

The two modifications of $CaIrO_3$ are hexagonal (a $= 5.44_1$, c $= 6.39_2$ Å), which forms IrO_2 and $CaCO_3$ on heating, and orthorhombic (a $= 3.14_5$, b $= 9.85_5$, c $= 7.29_3$ Å), which forms as single crystals from a melt of the components in $CaCl_2$. X-ray data on these structures are discussed.

Oxygen Chemisorption on Ruthenium Dioxide

J. T. SOMMERFELD and G. PARRAVANO, *J. Phys. Chem.*, 1965, **69**, (1), 102–115

Adsorption and desorption data for O_2 on RuO_2 at 100–385°C and low pressures enabled the nature of the RuO_2 surface to O_2 adsorption to be characterised by an exponential distribution of adsorption equilibrium functions. Activation energies were determined. Adsorbed species were both mobile and dissociated.

The Crystal Structure of Barium Ruthenium Oxide and Related Compounds

P. C. DONOHUE, L. KATZ and R. WARD, *Inorg. Chem.*, 1965, **4**, (3), 306–310

$BaRuO_3$ has complex oxide structure based on close-packed stacking of close-packed BaO_3 layers and a rhombohedral lattice. Ru ions occupy octahedral sites. The octahedra are in strings of three sharing faces; the strings are linked by corner sharing. Intermetallic bonding is suggested by face sharing giving a Ru-Ru-Ru arrangement with 2.55 Å interionic separation. $BaIrO_3$ and $BaPtO_3$ are probably similar.

Electrical Properties of Some Compounds Having the Pyrite or Marcasite Structure

W. D. JOHNSTON, R. C. MILLER and D. H. DAMON, *J. Less-Common Metals*, 1965, **8**, (4), 272–287

Measurements of electrical resistivity and Seebeck coefficient were made on pyrite and marcasite compounds, among them $OsSb_2$, $RhSb_2$, $RuSe_2$, $OsTe_2$, PtP_2, $PtAs_2$, $PtSb_2$, and α-$PtBi_2$. The compounds are classified as metals if the total number of valence electrons in the molecule is 21 and as semiconductors if the number is 20 or less.

ELECTROCHEMISTRY

Electrochemical Characterisation of the Surface Composition of Heterogeneous Platinum-Gold Alloys

M. W. BREITER, *J. Phys. Chem.*, 1965, **69**, (3), 901–904

Periodic voltammetric current-voltage curves for O_2-layer formation and reduction on heterogeneous two-phase Pt-Au alloys in 1 N H_2SO_4

at 30°C are an approximate addition of the respective pure metal curves. The Pt-rich α_1-phase behaves electrochemically like Pt; the Au-rich α_2-phase like Au. Surface composition is characterised by two parameters from a least-squares fit from the experimental data.

Hydrogen Adsorption on Heterogeneous Platinum-Gold Alloys in Sulphuric Acid Solution

Ibid., Trans. Faraday Soc., 1965, **61**, (4), 749–754

Electrochemical studies of H_2 adsorption on 5–70 at.% Au-Pt alloys in $1\ N\ H_2SO_4$ at 30°C by slow-speed voltammetric current-potential curves showed that H_2 adsorption occurs only on the Pt-rich phase to an extent determined by the amount of this phase on the surface.

On the Activity of Electrolytically Mixed Precipitates of Platinum and Ruthenium in the Electrooxidation of Methanol

O. A. PETRII, *Dokl. Akad. Nauk S.S.S.R.*, 1965, **160**, (4), 871–874

Electrode charging curves for platinised Pt, for 9:1 Pt:Ru precipitate and for Ru were plotted and also polarisation and electrooxidation curves for CH_3OH at these electrodes in $1\ N\ H_2SO_4$ and $1\ N$ KOH solutions. Electrooxidation at the mixed precipitate proceeded with greater kinetic regularity than at platinised Pt.

Cathodic Reduction of Oxygen on Smooth Platinum in Acid Solutions

G. BIANCHI and T. MUSSINI, *Electrochim. Acta*, 1965, **10**, (4), 445–455

H_2O_2 is formed at cathode potentials ≤ 680mV (nhe) on smooth Pt in 0.5 M H_2SO_4 whereas the initial rest-potential is 960mV. Current efficiencies for H_2O_2 formation depend on cathode potential and duration of electrolysis.

Electrochemical Oxidation of Hydrocarbons on a Platinum Electrode

R. KH. BURSHTEIN, V. S. TYURIN and A. G. PSHENICHNIKOV, *Dokl. Akad. Nauk S.S.S.R.*, 1965, **160**, (3), 629–632

Oxidation tests were carried out with C_2H_6 and C_2H_4 on Pt electrodes in $1\ N\ H_2SO_4$ and $1\ N$ KOH solutions at 21 and 97°C. Charging curves were drawn and the mechanism of the process was investigated.

The Platinum-on-Carbon Catalyst System for Hydrogen Anodes. I. Characterisation of the Catalyst and Support. II. Chemical Requirements of the Carbon Surface

L. J. HILLENBRAND and J. W. LACKSONEN, *J. Electrochem. Soc.*, 1965, **112**, (3), 245–249, 249–252

Active electrodes containing 50m²/g Pt/C were most effective when Pt occupied the outer layers of C. The Pt appeared to be 40–50 Å crystallites.

High activity from 3% Pt/C electrodes depended on proper choice of C, on control of electrode preparation, and on chemical factors. Good H_2 anodes were prepared containing 1 mg Pt per cm² electrode. E.S.R. measurements indicated Pt-C interaction. Activity decreased almost to zero when, before application of Pt, the C was cleaned in N_2 at 1000°C but full activity was restored by CO_2 treatment at 1000°C.

ELECTRODEPOSITION AND SURFACE COATINGS

Palladium Black Coating

L. MISSEL, *Metal Finishing*, 1965, **63**, (1), 51

High emittance calorimeters for monitoring radiant: convected energy ratio of rocket exhaust gases at rocket-bases have Pd black surfaces applied over Zn-plated Cu by a dip method. Details of the procedure are given. Emittance exceeds 0.90 at 0.2–20 microns after 4–6 h baking at 400°F. This is less than for Pt black on Be, but Be is toxic. The coating has lower resistance to heat deterioration.

Dropwise Condensation on Hydrophobic Metal and Metal Sulphide Surfaces

R. A. ERB and E. THELEN, *Abs. Papers, 149th Meeting, Am. Chem. Soc.*, 1965, 6U–16

Ag, Au, Rh and Pd are not wetted by pure steam under continuous condensing conditions. These coatings on Fe and Cu-alloys, sometimes previously coated by a diffusion-barrier material, produced dropwise condensation of steam above 100°C for many thousand hours without organic promoters. The mechanism is applicable to distillation of sea water.

Solderable Evaporated Metal Films

J. L. VOSSEN, *Electrochem. Technol*, 1965, **3**, (1–2), 56–57

75 at.% Au-Pd was evaporated on glass and ceramic substrates on which Cr had been deposited to improve the adhesion of the noble metal layer. The high O_2-activity of Pd improved adhesion whilst the solderability of Au allowed wires to be attached to the surface.

LABORATORY APPARATUS AND TECHNIQUE

Chemisorption Detector for Hydrogen

M. M. EISENHARDT and S. A. HOENIG, *Rev. Sci. Instrum.*, 1965, **36**, (1), 66–68

A device effective in the range 10^{-5}–10^{-8} Torr depends on the change in work function of a Pd filament exposed to H_2. O_2 inhibited electron emission strongly and N_2 weakly. However, such H_2-O_2 mixtures are seldom encountered and the effect of N_2 is not serious until $\alpha = P_{N_2}/P_{H_2}$ is large.

CATALYSIS

Production of High Octane Number Petrol and of Aromatics by Catalytic Reforming of Naphtha

F. ESCHARD, J. GUILLEMAT and H. LAUNE, *Rev. Inst. Fr. Pétrole*, 1964, **19**, (12), 1391–1405

The Institut Francais du Pétrole has developed a process for reforming naphtha to produce high-octane gasoline and petrochemical intermediates, using plant which includes Pt catalysts, supported on halogen-promoted Al_2O_3 or on SiO_2-Al_2O_3. Pt content varies from 0.3 to 0.8%.

Alteration of the Properties of Platinum-on-Alumina Reforming Catalysts during Continuous Operation

G. N. MASLYANSKII, N. R. BURSIAN and V. V. SHINIKIN, *Khim. i Tekhnol., Topliv i Masel*, 1965, (1), 2–6

Continuous operation of Pt/Al_2O_3 reforming catalysts leads to increased metallic content, especially of Fe, to reduced halide content, particularly of F and Cl, and to decreased effective area of the catalysts. These changes reduce the activity for isomerisation and dehydrogenation. There is also deterioration of the activity and selectivity of reforming.

The Use of Platinum Catalysts at High Pressures

W. THIELEBEULE and G. HEY, *Chem. Tech.*, 1965, **17**, (2), 87–90

The amount of hydrocracking observed, when Pt/Al_2O_3-SiO_2 and Pt/Al_2O_3-F petroleum refining catalysts were tested for the upgrading of petroleum, reached a maximum of 100 kg.cm.$^{-2}$ The quality of the products depended on the amount of conversion.

Textural Study of Catalysts by Gas Adsorption. II. Platinum-Alumina Catalysts

J. E. GERMAIN, M. OSTYN and J.-P. BEAUFILS, *J. Chim. phys.*, 1965, **62**, (1), 32–36

Total metal area, and pore distribution, of 2–7% Pt/Al_2O_3 were measured by gravimetric measurements of N_2 and H_2 adsorption. Textural variations due to the methods of preparation, the heat treatment, and the Pt content were studied during the catalytic aromatisation of trimethyl-1,1,3-cyclohexane but no simple relation between catalytic activity and texture was found despite Pt crystallites being generally constant at 25Å.

The Dispersion of Platinum on Silica Gel from X-ray Data and the Chemisorption of Hydrogen

E. S. ZHMUG', V. S. BORONIN and O. M. POLTORAK, *Zh. Fiz. Khim.*, 1965, **39**, (3), 809–811

X-ray tests on Pt dispersion in platinised SiO_2 containing 0–7.2% Pt and in 5.5% Pt/SiO_2, with SiO_2 additions ranging from 0 to 100%, con-firmed H_2 chemisorption data and related Pt dispersion to the conditions of Pt/SiO_2 production.

Stereochemistry and the Mechanism of Catalytic Hydrogenation of Cycloalkenes. VI. The Isomerisation of 1,2-Dimethylcycloalkenes as a Route to Both *cis*- and *trans*-1,2-Dimethylcycloalkanes

S. SIEGEL, P. A. THOMAS and J. T. HOLT, *J. Catalysis*, 1965, **4**, (1), 73–76

Hydrogenation of 1,2-dimethylcyclohexene and of 1,2-dimethylcyclopentene over reduced PtO_2 is accompanied by isomerisation to the corresponding 2,3-dimethylcycloalkenes, which are reduced more rapidly to a mixture of *cis*- and *trans*-1,2-dimethylcycloalkenes, whose ratio appears independent of the fraction of the original cycloalkene which has reacted. Most of the *trans* isomers arises from reduction of 2,3-dimethyl-cycloalkenes but some appears to be formed directly from the 1,2-dimethylcycloalkenes.

Catalytic Conversions of 1,1-Dimethyldicyclohexyl and 1-Methyl-1-phenylcyclohexane on Platinum Catalysts in Conditions of High Temperature and Pressure of Hydrogen

S. I. KHROMOV, D. CHULTEM and E. S. BALENKOVA, *Vest. Moskov. Univ., Ser. II, Khim.*, 1965, (1), 51–55

Conversions of almost 100% are achieved on 1% Pd/C and 1% Pd/Al_2O_3 at 20 atm, 460°C; nearly as much at 1 atm, 460°C. Products are tabulated in each case and also for conversions at 1 atm, 320°C.

Conversion of Homologues of Tetrahydrofuran on Palladium-on-Carbon

N. I. SHUIKIN, R. A. KARAKHANOV and I. IBRAKHIMOV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1965, (1), 165–167

Conversions over Pd/C at 300–400°C showed up to 80% isomerisation to aliphatic ketones and also dehydrogenation to the furan homologues. Conversions exceeding 90% occurred for 2,2-dialkyltetrahydrofurans converted to isoparaffinic hydrocarbons.

Homogeneous Catalysis by Noble Metal Salts. I. The Homogeneous Isomerisation of Olefins by Palladium Compounds

G. C. BOND and M. HELLIER, *J. Catalysis*, 1965, **4**, (1), 1–5

$PdCl_2$ and its bis(benzonitrile) and bis(acetonitrile) complexes catalysed isomerisation of *n*-pentenes at 1 atm, 70°C in C_6H_6 solution, ethyl acetate and methyl ethyl ketone but in the absence of solvents at 40°C the reactions were much slower. *cis*-2-Pentane had an induction period and isomerised more slowly than 1-pentene. The ratio of *cis*-2-pentene/*trans*-2-pentene formed from 1-pentene exceeded the equilibrium ratio. Possible mechanisms are discussed briefly.

Hydrazine as a Reducing Agent for Organic Compounds (Catalytic Hydrazine Reductions)

A. FURST, R. C. BERLO and S. HOOTON, *Chem. Rev.*, 1965, **65**, (1), 51–68

Complete reductions of aromatic and heterocyclic nitro compounds are reviewed. Pt metal catalysts used in many of the reactions include Pt, Pd, Pd/C, Ru/C, Ru/Ca, Pd/CaCO$_3$, Pd/SrCO$_3$. (183 references).

Homogeneous Catalysis. II. The Mechanism of the Hydrosilation of Olefins Catalysed by Group VIII Metal Complexes

A. J. CHALK and J. F. HARROD, *J. Am. Chem. Soc.*, 1965, **87**, (1), 16–21

Relative importance of hydrosilation and iso-merisation of olefins by Pt(II) and Rh(I) olefin complexes depends on the silane used. Alkyl-phosphine complexes of Pt(II) reacted with trialkylsilanes to produce the corresponding Pt(II) hydride. No stable Pt-Si bonds were noticed but a phosphine complex of Ir(I) decomposed several Si hydrides, retaining both Si and hydride fragments in its coordination sphere.

Hydride Intermediates in Homogeneous Hydrogenation Reaction of Olefins and Acetylenes Using Rhodium Catalysts

J. F. YOUNG, J. A. OSBORN, F. H. JARDINE and G. WILKINSON, *Chem. Commun.*, 1965, (7), 131–132

The connection has been demonstrated between the taking up of H$_2$ by tris(triphenyl-phosphine) chlororhodium(I) and homogeneous hydrogenation. The compound is a very efficient catalyst for the reduction of double and triple bond compounds when in 5×10^{-3}M concentration in C$_2$H$_5$OH-C$_6$H$_6$ solution at 25°C, $\leqslant 1$ atm.

Homogeneous Catalytic Hydrogenation and Hydroformylation of Acetylenic Compounds

F. H. JARDINE, J. A. OSBORN, G. WILKINSON and J. F. YOUNG, *Chem. & Ind.*, 1965, (13), 560

Alkynes as well as alkenes may be catalytically hydrogenated to alkanes, using Rh complexes. Hex-1-yne, (~2M), was reduced to *n*-hexane at 20°C, <1 atm in C$_2$H$_5$OH-C$_6$H$_6$ solution of (Ph$_3$P)$_3$ RhCl, (~5 × 10^{-3}M). In the presence of 1:4 mixture of H and CO at 110°C, 120 atm, it was catalytically hydroformylated to give a 15% yield of *n*-heptaldehyde and 2-methyl-hexaldehyde.

Adsorption and Catalytic Reactions on Evaporated Metal Films. XI. Adsorption and Interaction of Hydrogen and Oxygen on Rhodium

V. PONEC, Z. KNOR and S. ČERNÝ, *Coll. Czech. Chem. Commun.*, 1965, 30, (1), 208–216

H$_2$ and O$_2$ adsorption on Rh films were measured and the changes in electrical resistance occurring at the same time. The order of catalytic activity of metal films is Pd,Rh > Ni > Mo.

On the Catalytic Properties of Iridium Compounds in Aqueous Solutions

S. I. GINSBURG and M. I. YUZ'KO, *Zh. Neorg. Khim.*, 1965, **10**, (4), 823–828

A series of Ir complexes catalyses the reaction of strong oxidising agents with H$_2$O, by which is formed atomic O. The rate of reaction of Ce(SO$_4$)$_2$ with H$_2$O is first order in the presence of low concentrations of Ir(III) sulphate but at higher concentrations the rate decreases and the catalytic process tapers off. The catalytic properties are not possessed by the Ir(IV) sulphate complexes but by ions of hydrated Ir(III). Secondary hydrolysis products are inactive and decrease the rate but at low catalyst concentrations these products are only present in minute amounts.

Oxidation of Ammonia over a Supported Ruthenium Catalyst

T. J. SCHRIBER, *Diss. Abs.*, 1964, **25**, (6), 3459–3460

NH$_3$ was oxidised over 0.5 wt.% Ru/Al$_2$O$_3$ at 246–345°C, 2.3–3.7 atm, forming N$_2$, N$_2$O and H$_2$O. Rates of formation of N$_2$ and N$_2$O depended on P$_{NH_3}$, P$_{O_2}$ and P$_{H_2O}$. Increasing P$_{H_2O}$ inhibited both rates, increasing P$_{O_2}$ promoted both rates, and increasing P$_{NH_3}$ favoured N$_2$O formation, as did higher temperature.

FUEL CELLS

Notes on a Study of Fuel Cell Hydrocarbon Electrodes

R. THACKER and D. D. BUMP, *Electrochem. Technol.*, 1965, **3**, (1–2), 9–12

Pt, Pd and Ag supported on carbon discs were used as electrodes in studying the rest potential and polarisation of C$_2$H$_6$, C$_2$H$_4$, C$_3$H$_8$, C$_3$H$_6$ and *n*-C$_4$H$_{10}$ in 35% KOH solution at 80°C, 1 atm and at 150°C, 20 atm. C$_2$H$_4$ showed the best polarisation behaviour. The order of catalytic activity was Pt > Pd ≫ Ag.

A New High-performance Fuel Cell Employing Conducting-porous-Teflon Electrodes and Liquid Electrolytes

L. W. NIEDRACH and H. R. ALFORD, *J. Electrochem. Soc.*, 1965, **112**, (2), 117–124

Conducting porous electrodes of 5–10 mil thickness developed from Pt black and Teflon on Ni screens have good strength, conductivity, and wetting characteristics. They were tested in fuel cells with 6*N* KOH and 5*N* H$_2$SO$_4$ electrolytes at ambient temperature. O$_2$ and air were oxidants for H$_2$. Hydrocarbons and CH$_3$OH were suitable fuels. An acid electrolyte, air oxidant cell produced 176 mA/cm^2 and alkaline cells produced 263 and 88 mA/cm^2 for over 5 months.

CHEMICAL TECHNOLOGY

Spinneret Makers Enjoy Fibres Surge. Are Pushed by Economic and Technological Factors Likely to Continue Unabated for Some Time

Chem. Engng. News., 1965, **43**, (5), 34–36

Spinneret alloys commonly used for rayon production are 70% Au-Pt, 10% Rh-Pt, 49% Au-1% Rh-Pt. Fibre production depends on the precision with which the holes are made; 0.0001 inch tolerance for diameter, perfect shape, sharp-edged. Special shapes are used for special fibres.

Influence of Deformation and Tempering Temperature on the Electrochemical Corrosion of Titanium and the Titanium Alloy with 0.2% Palladium

N. D. TOMASHOV and YU. M. IVANOV, *Zashchita Met.*, 1965, **1**, (1), 36–41

Cold-rolled Ti and 0.2% Pd-Ti sheets corrode less than annealed sheets. The rate of corrosion decreases as the deformation from rolling increases.

Investigation of the Protective Action Mechanism of Palladium in Corrosion-resistant Titanium-Palladium Alloys by Radiochemical Methods

N. D. TOMASHOV, M. N. SHCHULEPNIKOV and YU. M. IVANOV, *Ibid.*, 122–123

As surface corrosion commences, there is an accumulation there of Pd which passivates the surface and which leads to Pd additions of 0.1–0.2% to Ti being sufficient.

Technological Properties and Corrosion Behaviour of a Titanium Alloy with 0.2% Palladium

K. RUDINGER, *Werkstoffe u. Korrosion*, 1965, **16**, (2), 109–115

Tests on welded and non-welded samples of 0.2% Pd-Ti and of Ti showed that their technological, physical and processing properties are similar. Alloy and metal have the same corrosion-resistance under oxidising conditions but 0.2% Pd-Ti is superior under reducing conditions.

ELECTRICAL ENGINEERING

Electrical Contact Materials in Low Current Technology

W. H. ABBOTT and H. R. OGDEN, *Battelle Tech. Rev.*, 1965, **14**, (3), 17–22

A survey of contact types, causes of failure, and contact design. Au, Pt metal and precious metal alloy contacts are particularly useful. Their properties and difficulties in use for electronics applications are described.

TEMPERATURE MEASUREMENT

Pressure Dependence of the emf of Thermo-couples to 1300°C and 50 kbar

R. E. HANNEMAN and H. M. STRONG, *J. Appl. Phys.*, 1965, **36**, (2), 523–528

Relative temperature corrections accurate to $\pm 1°C$ due to pressure are given for Pt:10% Rh-Pt, Pt:13% Rh-Pt, Chromel-Alumel, and iron-constantan thermocouples as functions of temperature and pressure. They exceed 40° in some cases. Absolute corrections ΔT were also studied and are proportional to pressure at a given temperature. ΔT can exceed 50° for Pt:10% Rh-Pt at 50 kbar, $T > 1300°C$.

A New Method for the Computation of Temperature in Platinum Resistance Thermometry

J. L. HALES and E. F. G. HERINGTON, *J. Sci. Instrum.*, 1965, **42**, (4), 203–209

Temperatures on the International Practical Scale of Temperature of 1948 between – 182.97 and +630.5°C can be calculated from the resistance of a Pt thermometer using the equation $t = t_{Pt} + \delta_{Pt}(t_{Pt}-100)t_{Pt}.10^{-4}$, where δ_{Pt} depends on the Pt temperature t_{Pt} and on the thermometer constants δ and β. A master table of δ_{Pt} as a function of t_{Pt} is given for a thermometer with $\delta = 1.492$, $\beta = 0.110$ and tables can be derived for other values of δ and β. Using such tables and a desk calculator, temperature errors should not exceed 3×10^{-4} deg C.

NEW PATENTS

METALS AND ALLOYS

Production of Ultra Pure Hydrogen

JOHNSON, MATTHEY & CO. LTD.
British Patent 982,509

Ultra-pure H_2 is produced from a gas or gaseous mixture by passing it through a diffusion cell, at 50–400 p.s.i.g. and 600–1000°F, consisting of a ceramic tube impregnated with an Ag-Pd alloy.

Resistor Compositions

E. I. DU PONT DE NEMOURS & CO.
British Patent 982,789

An electrical resistor comprises a solid ceramic base and a conductive resistor composition applied on it and consisting of 20–49 wt.% glass frit matrix and 51–80 wt.% 0.5–50 μ particle size Pd and Ag, taken in a 55:45 to 45:55 ratio by wt., the said Pd containing 0.1–1 wt.% combined oxygen.