

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

The Systems Palladium-Indium and Palladium-Tin

J. R. KNIGHT and D. W. RHYS, *J. Less-Common Metals*, 1959, 1, (4), 292-303

The constitution of the Pd-In and Pd-Sn systems was investigated by thermal analysis, metallographic and X-ray methods. In the Pd-In system, Pd₃In, Pd₂In, PdIn, Pd₂In₃ and PdIn₃ phases and in the Pd-Sn system, Pd₃Sn, Pd₂Sn, Pd₃Sn₂, PdSn, Pd₃Sn₄ and PdSn₂ phases were observed. The solid solubilities of In and Sn in Pd at the liquidus temperature were found to be 20-21 at.% and 17 at.% respectively, but Pd has a very low solid solubility in both In and Sn. Data for the hardness of Pd-In and Pd-Sn alloys are given. The resistivity of Pd-Sn solid solution alloys is compared with that of Pd-Ag and Pd-U alloys.

Studies on the Platinum-Base Alloys in the Pt-Mo System

H. NISHIMURA and H. KIMURA, *J. Jap. Inst. Metals*, 1959, 23, (11), 616-620 (English summary)

The maximum solubility of Mo in the α (Pt)-phase is 15% and the lattice parameter of the α -phase (f.c.c.) decreases with increased Mo content. α -phase alloys containing less than 6% Mo may be cold worked and their annealing temperature is above 1100°C. On heating above 1000°C, MoO₃ volatilises rapidly and the β -phase transforms into α -phase by oxidation in air. A preferred oxidation of Mo in the α -phase was observed on prolonged heating in air.

The Compound Bi₄Rh

R. G. ROSS and W. HUME-ROTHERY, *J. Less-Common Metals*, 1959, 1, (4), 304-308

High temperature X-ray experiments showed that only one form of Bi₄Rh exists at temperatures between 20° and 460°C. The temperature for the Bi₄Rh \rightleftharpoons Bi₂Rh peritectic horizontal was established as 460°C. The crystal structure of Bi₄Rh is body-centred cubic and the lattice spacing was determined as 14.9274 \pm 0.0002 Å at 20°C. A probable equilibrium diagram for Bi-rich Bi-Rh alloys is given.

Alloys of Silver with Ruthenium

A. A. RUDNITSKII and O. A. NOVIKOVA, *Russ. J. Inorg. Chem.*, 1959, 4, (7), 719-722 (Transl. of *Zhur. Neorg. Khim.*, 1959, 4, (7), 1596-1600)

Alloys rich in Ag were prepared and their con-

stitution was determined by thermal analysis and micrographic examination. The mechanical, electrical and thermoelectric properties of the alloys were examined. It was found that there is limited solubility in the liquid and solid states and that the alloys crystallise with the formation of a eutectic containing approximately 3 wt.% Ru at 920°C. Ru is not soluble in solid Ag. The hardness increases with increasing Ru content, reaching a maximum near the eutectic. Electrical resistivity of the alloys is lower than that of pure Ag, but does not depend on the Ru content. For alloys containing up to 3 wt.% Ru the thermoelectric properties are the same as for pure Ag. Alloys containing more than 3 wt.% Ru crystallise from a melt consisting of two layers.

Gold-Ruthenium Alloys

A. A. RUDNITSKII and O. A. NOVIKOVA, *Russ. J. Inorg. Chem.*, 1959, 4, (7), 722-724 (Transl. of *Zhur. Neorg. Khim.*, 1959, 4, (7), 1601-1605)

Au-rich alloys of the system were examined by thermal analysis and a study of their microstructure, mechanical and electrical properties. The phase diagram shows limited solubility in the liquid state up to about 1 wt.% Ru. The α -solid solution based on Au is formed by a peritectic reaction at 1066°C between the Ru-rich β -phase and the liquid phase rich in Au. The maximum solubility of Ru in Au decreases with decreasing temperature. Thermoelectric and electrical properties of Au are altered little by the addition of less than 1 wt.% Ru, but the temperature coefficient of resistance is lowered. The plasticity and tensile strength of Au are reduced by the addition of 0.5 wt.% Ru while the hardness is slightly increased.

Solid State Transformations in Alloys of Iron with Cobalt and Palladium

V. V. KUPRINA and A. T. GRIGOR'EV, *Russ. J. Inorg. Chem.*, 1959, 4, (7), 724-727 (Transl. of *Zhur. Neorg. Khim.*, 1959, 4, (7), 1606-1612)

Alloys corresponding to the ternary diagram parallel to the Fe-Co side containing 2, 5, 10, 20, 30, 40 and 50 at.% Pd were investigated by thermal analysis and examination of the microstructure of quenched and annealed alloys. The alloys studied undergo a polymorphic transformation between 700° and 900°C which is associated with the formation of a wide two-phase ($\alpha + \gamma$) region. This region contracts with increasing Pd content and increasing temperature. A three-phase ($\alpha + \gamma + \gamma_1$) region is formed with Fe-rich alloys. At about 2 at.% Pd the FeCo (α_1) region

penetrates into the ($\alpha + \gamma$) region and remains there up to about 46 at. % Pd. Ternary γ -solid solutions persist down to room temperature in Co-rich alloys and in those with more than 50 at. % Pd.

Effect of Atomic Ordering on Exchange Interaction in the Fe₃Pt Alloy

K. P. BELOV and Z. D. SIROTA, *Soviet Phys. JETP*, 1959, **36**, (9), (4), 752-754 (Transl. of *J. Expl. Theoret. Phys. (U.S.S.R.)*, 1959, **36**, (4), 1058-1062)

An Fe-Pt alloy containing 58 wt. % Pt was used in this investigation. The magnitude of the shift of the Curie point due to pressure and spontaneous deformation of the lattice is computed from data on the measurement of the temperature dependence of magnetostriction. It was found that these quantities decrease with atomic ordering in the alloy. Atomic ordering in the Fe₃Pt changes not only the magnitude of exchange interaction, but also the nature of its dependence on the interatomic distance.

The Fabrication and Properties of Ruthenium

D. W. RHYS, *J. Less-Common Metals*, 1959, **1**, (4), 269-291

The physical properties and refining of Ru are outlined. Properties of Ru which affect its working and those of the worked metal prepared from sintered compacts are given in detail. Material used in the investigation was prepared by conventional processes though some extra purifying treatment was given. Four methods of powder preparation from RuCl₃ solution were used and compacts were pressed by steel die and plunger or by hydrostatic pressure. Sintering temperatures lay between 1450° and 2200°C and various atmospheres were used. Specimens were worked by pressing, hammering, swaging and rolling at temperatures up to 1800°C. Factors found to affect working properties include mode of powder preparation, purity and sintering conditions. The hardness and density of the sintered compacts and the worked material were measured. Directional properties developed during working were not removed by annealing. Crystallographic examination indicated that Ru deforms both by slip and by twinning. Machining of Ru proved impracticable. Ru melted in an argon-arc furnace was worked with difficulty. Single crystal Ru prepared by a floating zone electron bombardment technique was initially ductile, but work hardened rapidly and became polycrystalline and brittle on annealing. It is suggested that greater ductility may be obtained from material of higher purity.

Phosphides of the Platinum Metals

S. RUNDQVIST, *Nature*, 1960, **185**, (Jan. 2), 31-32
Crystallographic data for Ru₃P, RuP, RuP₂, OsP₂, Rh₂P, Ir₂P, RhP₃, PdP₃, IrP₃ and PtP₂

were obtained by studying X-ray powder photographs. Structural similarities with the phosphides of the Fe group metals were noted.

Oxide Complexes of the Platinum Metals

J. J. SCHEER, University of Leiden. Thesis presented May 1956, 76 pp. (English summary)

Oxide complexes of the alkali metals with Pt, Pd, Rh and Ir were prepared by heating a mixture of the alkali metal carbonate and the Pt metal in oxygen in crucibles made of fused MgO. Li₂RhO₃, Li₂PdO₃, Li₂IrO₃, Li₃IrO₄, Li₃PtO₃, Na₂IrO₃ and NaPtO₃ were found to be monoclinic, isomorphous with Li₃SnO₃, while Na₂Pt₃O₄ and NaPd₃O₄ are cubic. LiRhO₂ and NaRhO₂ are isomorphous with NaNiO₂ (monoclinic modification). The crystal structure of KRhO₂, Li₂PdO₂ and NaRhO₂ (high temperature modification) could not be resolved.

A Volatile Higher Chloride of Ruthenium

S. A. SHCHUKAREV, N. I. KOLBIN and A. N. RYABOV, *Russ. J. Inorg. Chem.*, 1959, **4**, (7), 763 (Transl. of *Zhur. Neorg. Khim.*, 1959, **4**, (7), 1692)

A higher chloride formed when RuCl₃ is heated in a current of chlorine is thought to be RuCl₄. Vapour pressure measurements support this theory.

The Crystal Structure of UPt₂

B. A. HATT and G. I. WILLIAMS, *Acta Cryst.*, 1959, **12**, (9), 655-657

The alloy was prepared by arc-melting stoichiometric proportions on a water-cooled Cu hearth under a purified argon atmosphere. By means of data obtained from powder and single-crystal photographs, the structure was determined. It was found that the structure is orthorhombic, space group A ma₂ with a=5.60, b=9.68 and c=4.12 Å. The similarity between this structure and that of UPt₃ is discussed.

Sorption of Hydrogen in an Aqueous Suspension of Palladium Catalyst During Shaking

F. NAGY and D. MOGER, *Acta Chim. Acad. Sci. Hung.*, 1959, **21**, (2), 159-167 (In German)

Hydrogen sorption, during shaking, in an aqueous suspension of Pd/BaSO₄ catalyst was investigated. It was found that there is a linear relationship between the quantity of sorbed gas at equilibrium and the changes in the concentration of the suspension. A kinetic equation is derived to describe the changes of sorption with time.

The Constitution of Manganese Base Alloys with Metals of the Second Transition Series

A. HELLAWELL, *J. Less-Common Metals*, 1959, **1**, (5), 343-347

Binary alloys of Mn with Y, Zr, Nb, Mo, Ru, Rh, Pd and Ag were prepared and examined by

thermal analysis and by microscopical and X-ray methods. The effect of the various solute metals upon the allotropic transformation temperatures was studied. Phase diagrams for the alloys (provisional in the cases of Y-Mn and Zr-Mn) are given.

Ordering in CoPt-FePt Alloys

J. C. WOOLLEY and B. BATES, *J. Less-Common Metals*, 1959, **1**, (5), 382-389

Six alloys were prepared covering the range from CoPt to FePt in increments of 10 at.% Fe with a constant 50 at.% Pt content. Lattice parameter values were determined for both the ordered and disordered states. The disordered phase of FePt could not be obtained. For alloys of less than 25 at.% Fe (less than 50 mol.% FePt), X-ray techniques were used to determine the ordering temperatures and types of ordering reaction occurring at various temperatures. Possible values of percentage disregistry between the ordered and disordered structures of the low Fe % alloys were calculated. The possibility of producing hard magnetic materials from these alloys is discussed.

The Effect of Plastic Deformation on the Resistivity of Copper-Palladium Alloys

E. KLOKHOLM and B. HYATT, *Trans. Met. Soc. A.I.M.E.*, 1959, **215**, (5), 792-794

Wires in the range 9.6-29 at.% Pd were annealed at 600°C and quenched in an ice bath. The wires were deformed in tension in a tensile tester and after each increment of plastic strain, the load was reduced to zero and the resistivity measured. The relative change in resistivity as a function of plastic strain is illustrated graphically. A continuous decrease in resistivity with increasing tensile strain was observed. This effect increases with increasing Pd content until about 12.5 at.% Pd, decreases until about 20.9 at.% Pd, and then again increases. In addition to the usual increase in resistivity caused by plastic deformation, there must be a simultaneous mechanism which produces a net resistivity decrease in alloys in this range. It is assumed that the anomalous decrease in resistivity, compared with results for brass and Cu₃Au, is due to the decrease in short-range order after cold work.

The Constitution of Zirconium-Palladium Alloys

K. ANDERKO, *Z. Metallkunde*, 1959, **50**, (12), 681-686

The phase diagram of the Zr-Pd system in the range 0-50 at.% Pd was established by thermal, micrographic, resistometric and X-ray analysis. In the range 50-100 at.% Pd, the system was examined less thoroughly. The intermediate phases Zr₂Pd, ZrPd, ZrPd₂ and ZrPd₃ were observed. The solubility of Pd in α -Zr is less than 0.1 at.%, while in β -Zr it reaches 11.5 at.%.

The Influence of Palladium on the High-Temperature Water Corrosion of Zirconium

H.-W. SCHLEICHER, *Z. Metallkunde*, 1959, **50**, (12), 687-690

Small additions of Pd and coupling with Pd improve the corrosion resistance of Zr in high-temperature water and steam. Methods of testing are described and results are discussed with regard to possible mechanisms.

ELECTROCHEMISTRY

Action of the XO₄ⁿ⁻ Inhibitors

G. H. CARTLEDGE, *Corrosion*, 1959, **15**, (9), 37-40
Results of experiments on the effect of CrO₄²⁻, MoO₄²⁻, WO₄²⁻, TiO₄⁻ and OsO₄ upon the corrosion of Fe and steel are summarised. The competitive and reversible nature of the surface state has been shown by measurements of electrode potentials in inhibited solutions and the effect of foreign electrolytes upon these potentials. In the case of OsO₄, passivation is so complete that an Fe electrode indicates the thermodynamic potential of the Os^{IV}-Os^{VIII} couple. Oxygen is believed to build films on specimens in inhibited, aerated solutions without the use of HNO₃ or anodic polarisation. The effect of adsorbed particles on the kinetics of electrode processes at metal-solution interfaces is discussed.

Studies on the Alternating Current Electrolysis. IV. The Attack on Bright Platinum Electrodes Caused by Alternating Current Electrolysis in Aqueous Solutions of Various pH

S. SHIBATA, *J. Chem. Soc. Japan (Pure Chem. Section)*, 1959, **80**, (5), 453-456
0.1N H₂SO₄, acetate buffer (pH 5), borax buffer (pH 10) and 0.1N NaOH solutions were used in this investigation. In hydrogen-saturated solutions, the minimum value E_c of the cathodic polarisation in each cycle was found to depend on the pH of the electrolyte, but not on the current density. Maximum value E_a of the anodic polarisation increased with current density and finally reached the oxygen evolution potential. Electrode attack began at a value E_a^o, where E_a^o is a constant anodic potential characteristic for the pH of the solutions. E_a^o coincides with the equilibrium potential of the PtO-PtO₂ couple. It is concluded that electrode attack is caused by repeated oxidation and reduction of the Pt.

A Study of the Zinc-Noble Metal Couple in Alkaline Solutions

T. P. DIRSKE and E. G. VRIELAND, *J. Electrochem. Soc.*, 1959, **106**, (12), 997-999

Thin metal strips of Zn coupled with one of the metals Ni, Ag, Cu, Pt and Pb were immersed in 35% KOH solution at room temperature. Coatings of Zn or a Zn-rich alloy were formed

on Ag, Cu, Pb and Pt, but not on Ni. The conditions under which the coating is formed were studied and it was found that Zn is deposited on Cu, Ag, Pb and Pt when these metals are coupled with Zn in strong KOH solutions containing dissolved ZnO. Several possible mechanisms for the process are discussed. It is suggested that the coating results from the reduction of the dissolved Zn species by atomic hydrogen. The persistence of the coating depends on the ability of the Zn atoms to fit into the lattice of the noble metal.

Overvoltage and Diffusion through Iron and Palladium

J. N. ANDREWS and A. R. UBBELOHDE, *Proc. Roy. Soc.*, 1959, **253**, (1272), 6-15

High-dispersion X-ray methods were used to measure the lattice parameters of Fe and Pd cathodes before, during and after the entry of electrolytic hydrogen into the lattice. For Fe, no expansion of the lattice greater than 0.0002 Å could be observed during diffusion and no preferred crystallographic planes for the evolution of molecular hydrogen were observed. Blisters formed across the faces of single-crystal Fe cathodes indicated that diffusion of hydrogen occurs through the crystal grains. For Pd, an expansion of 0.0170-0.0002 Å was observed during actual electrolysis. There was a reversion to a less-expanded lattice of Pd hydride after electrolysis ceased. No preferred planes for hydrogen evolution were indicated.

ELECTRODEPOSITION

Electroplating Metal Contacts on Germanium and Silicon

D. R. TURNER, *J. Electrochem. Soc.*, 1959, **106**, (9), 786-790

Pt, Rh, Au, Ag, Cr, Co, Ni, Cu, Zn, Cd, In, Sn, Sb, Te, Pb, and Bi have been successfully plated on to Ge, mostly by the use of a jet plating technique. All the metals except Sb gave rectifying contacts on *n*-type Ge and ohmic contacts on *p*-type Ge; Sb contacts behave in the opposite manner. Cu, Au, Ni, In, Sn and Zn were plated on to Si. Oxide films and chemical residues on the Ge may be removed by cathodic reduction prior to plating. In the case of Si, the oxide layer was reduced by HF and alkaline solutions.

LABORATORY APPARATUS AND TECHNIQUE

Determination of Boric Oxide in Glass by Pyrohydrolysis Separation

J. P. WILLIAMS, E. E. CAMPBELL and T. S. MAGLIOCCA, *Anal. Chem.*, 1959, **31**, (9), 1560-1563

B₂O₃ in many glasses may be separated by a reaction in which steam is passed over a mixture

of the sample, U₃O₈ and Na₂SiO₃·9H₂O at 1300-1350°C. The mixture in a Pt-lined Alundum boat, is placed in a Pt pyrolysis tube 1 in. o.d. and 17 in. long contained in a 10% Rh-Pt wound combustion furnace. The temperature of the interior of the reactor tube is measured by a 10% Rh-Pt thermocouple. A Pt condenser tube 0.25 in. o.d. and 18 in. long is welded at right-angles to the closed end of the reactor tube and is surrounded by a glass water-cooling jacket. The B₂O₃ content of the distillate is determined by mannitol-NaOH titration. The effects of sample size and composition, catalyst, temperature and distillation rate are discussed.

Electrical Ignition in the Schöniger Oxygen Flask Method

A. J. MARTIN and H. DEVERAUX, *Anal. Chem.*, 1959, **31**, (11), 1932

Thermally unstable materials for C-determination may be ignited by electrical means instead of hand ignition. An adapter consisting of a Pt wire mesh basket for the sample connected to a Pt ignition filament is described. The procedure for the use of the adapter is given.

Leak Detection

W. STECKELMACHER, *Nucl. Eng.*, 1959, **4**, (43), 450-453

Vacuum test and positive pressure methods of leak detection are described. Among the vacuum test instruments is the Pd barrier detector which employs hydrogen as the search gas and a hot ionisation gauge as the sensing element. The Pd disc, acting as anode, is heated by electron bombardment from an indirectly heated cathode. In exceptional cases, leaks of the order of 10⁻⁵ lusecs may be detected.

Investigations on the Working of a Palladium-Pirani Gauge

P. K. DUTT and S. K. MUKHERJEE, *Z. Angew. Phys.*, 1959, **11**, (12), 470-474 (In English)

Physical principles involved in the use of the gauge for leak detection are discussed. Experiments showed that for different background pressures in a vacuum system a "threshold" hydrogen pressure exists for transmission through Pd. Dependence of hydrogen flow rate through Pd on hydrogen pressure was studied. Pirani gauge conversion factors for hydrogen and deuterium gases were found to be not even approximately constant over the Pirani range of readings.

Gas Chromatography with Hydrogen and Deuterium

C. O. THOMAS and H. A. SMITH, *J. Phys. Chem.*, 1959, **63**, (3), 427-432

A fixed phase of Pd on quartz was used in the partial separation of a hydrogen-deuterium mixture.

Improved Apparatus for Rapid Measurement of Viscosity of Glass at High Temperatures

R. L. TIEDE, *J. Amer. Ceram. Soc.*, 1959, **42**, (11), 537-541

A viscometer for making rapid measurements in the range 6.5 to 13,000 poises has been developed. In the furnace, an insulated Pt-alloy tube serves as both resistance-heating element and glass container. Eight fins are welded on to the outside of the tube in order to obtain a uniformly heated section. A Pt-alloy spindle containing a thermocouple is immersed in the molten glass during the testing period. The viscometer mounting, temperature controller and operating procedure are described. About 15 min per point are required to establish a viscosity/temperature curve and precision is good.

CATALYSIS

Absorption of Hydrogen and Catalytic Activity of Palladium-Silver Alloys

M. KOWAKA, *J. Jap. Inst. Metals*, 1959, **23**, (11), 655-658 (In English)

A study of the kinetics of hydrogen absorption and hydrogen-C₂H₄ combination was carried out in the temperature range 0°-400°C. Ribbons of Pd and Pd-Ag alloys were used as catalysts, the pressure of the gases used was 10 cm Hg, and change in pressure was measured at constant volume. Pretreatment by hydrogen poisons a Pd catalyst, but has little or an opposite effect on the Pd-Ag alloys. The energy of activation for the combination reaction remains constant and a discontinuous increase occurs at about 60 at.% Ag. The activity of the reaction rises to a maximum at about 35 at.% Ag, decreases with increasing Ag content, and falls to zero at about 65 at.% Ag. A similar behaviour was found in the absorption of hydrogen. It appears that there is a close correlation between hydrogen diffusion and catalysis.

The Combination of Hydrogen and Oxygen on Palladium-Silver Alloys

M. KOWAKA, *J. Jap. Inst. Metals*, 1959, **23**, (11), 659-662 (In English)

Kinetic measurements for the combination reaction were made in the presence of ribbons of Pd, Ag, and their alloys in the temperature range 80°-450°C. Pressure changes were measured at constant volume. For pure Pd there is an induction period at the start of the reaction, but for pure Ag the decrease in pressure is a linear function of time. Pretreatment by oxygen raised the reaction rate for Pd, but had little effect for Ag. The apparent activation energy of the reaction remains constant until 60 at.% Ag when it increases with increasing Ag content. The activity of a series of alloys has a maximum at

30 at.% Ag. The significance of the results is discussed.

Metallic Salts as Promoters in Hydrogenation with Platinum Oxide Catalysts

E. B. MAXTED and S. AKHTAR, *J. Chem. Soc.*, 1959, (Nov.), 3130-3133

The effect of adding small amounts of various metallic chlorides to liquid-phase hydrogenation systems in the presence of a PtO₂ catalyst was investigated. It was found that for the hydrogenation of CH₃(CH₂)₃CHO, SnCl₂ was the most effective promoter tested. The variation of the promotion effect with temperature was examined; in both promoted and unpromoted systems the hydrogenation rate for CH₃(CH₂)₃CHO passes through a maximum at 25°C. The use of SnCl₂ in the hydrogenation of CH₃COCH₃, C₆H₅CH·CHCOOC₂H₅ and cyclohexene was also studied. If the addition of the promoter is made before the reduction of the PtO₂ to metal, an increase in the hydrogenation rate up to over ten times its unpromoted value is obtained. It is suggested that retardation by the promoter of the autocatalytic reduction of PtO₂ prolongs the period during which highly active nascent Pt is produced.

The Mechanism of Hydrogenation of Benzoquinone on Skeleton Nickel, Platinum, and Pd/CaCO₃

N. M. POPOVA and D. V. SOKOLSKY, *Zhur. Fiz. Khim.*, 1959, **33**, (11), 2573-2578 (English summary)

The hydrogenation reaction was investigated in order to determine the stability of the contacts and the reaction mechanism. The surrounding medium and temperature have a definite effect on the rate and order of the process. It is shown that the activity of Pt or Pd/CaCO₃ is not reduced in quinone hydrogenation, but that of the Ni decreases as a result of poisoning. The activity of partially poisoned skeleton Ni is dependent on the amount of hydrogen sorbed in it. The reaction mechanism is discussed in the light of the donor-acceptor theory of catalysis.

Kinetics of the Decomposition of Ammonia on Platinum at Low Pressures

L. O. APEL'BAUM and M. I. TEMKIN, *Zhur. Fiz. Khim.*, 1959, **33**, (12), 2697-2705

Experiments were carried out at pressures of the order of 10⁻³ mm Hg. In the temperature range 900-1350°C, the decomposition rate is proportional to the NH₃ pressure, the reaction is not retarded by its products, and the activation energy is 5100 cal. In the range 490°-560°C, the decomposition is retarded by hydrogen, its rate being proportional to (p_{NH₃}²/p_{H₂}³), where n varies from 0.73 to 1 with increase in hydrogen pressure, and the activation energy is 49300 cal (for n=0.73). The rate-controlling step in the

low temperature range is the desorption of nitrogen, while in the high temperature range it is the decomposition of NH_3 molecules on their impact at the surface. In the high temperature range, the rate of nitrogen formation approaches that in the oxidation of NH_3 .

The Catalytic Properties of Osmium Tetroxide

L. J. CSÁNYI, *Acta Chim. Acad. Sci. Hung.*, 1959, **21**, (1), 35-39 (In German, English summary)

OsO_4 may be used as an effective general oxidising catalyst in both acidic and alkaline media. In an acidic medium, the redox pair Os(VIII)-Os(IV) is responsible for the catalysis, while in an alkaline medium, the redox pair Os(VIII)-Os(VI) is responsible. OsO_4 promotes oxidation reactions carried out with H_2O_2 and its derivatives and catalyses the electroreduction of H_2O_2 . This catalysis is neutral and, in a very slightly acid medium, may be interpreted by the formation of peroxy-osmic acid. Induction reactions observed in the system $\text{H}_2\text{O}_2\text{-OsO}_4$ are similarly promoted by the catalytic effect of OsO_4 .

Structure and the Action of the $\gamma\text{-Al}_2\text{O}_3/\text{Pd}$ Catalyst

A. KRAUSE, *Roczniki Chem.*, 1959, **33**, (2), 533-535 (German summary) (*Chem. Abs.*, 1959, **53**, (22), 21101f)

The reaction mechanism for the hydrogenation of C_6H_6 is used to illustrate the mutual interaction of $\gamma\text{-Al}_2\text{O}_3$, Pd and hydrogen. Electrons are thought to oscillate between Pd and the radical $\text{O}=\text{Al}$ — even in the absence of hydrogen. This may explain the decrease in magnetic susceptibility of metallic Pd adsorbed on the surface of Al_2O_3 .

Decarboxylation of Oxaloacetic Acid by Silk Fibroin-Palladium Catalysts

Y. FUJII, *J. Biochem. (Japan)*, 1959, **46**, (8), 1069-1075

Three types of silk fibroin-Pd catalyst, (i) silk fibroin- PdCl_2 complex, (ii) its reduction product, and (iii) *p*-nitrosodiethylaniline-treated (i), have been found to catalyse active decarboxylation of oxaloacetic acid to pyruvic acid at 30°C and pH 5. The most effective catalyst is (iii). An interpretation of the experimental results in terms of modes of linkage between Pd and silk fibroin is discussed. Some characteristics of the catalysed decarboxylation reaction are given.

Osmium and Ruthenium Tetroxide-Catalysed Oxidations of Pyrene

F. C. OBERENDER and J. A. DIXON, *J. Org. Chem.*, 1959, **24**, (9), 1226-1229

The oxidation of pyrene was investigated as a possible route to the synthesis of sterically hindered 4,5-dialkylphenanthrenes. Oxidation systems used were $\text{OsO}_4\text{-H}_2\text{O}_2$, $\text{OsO}_4\text{-NaIO}_4$ and

$\text{RuO}_2\text{-NaIO}_4$. The $\text{OsO}_4\text{-NaIO}_4$ system produced pyrene-4,5-quinone and the lactol of 4-formylphenanthrene-5-carboxylic acid by exclusive 4,5-bond oxidation. From the $\text{OsO}_4\text{-H}_2\text{O}_2$ oxidation, only pyrene-4,5-quinone could be identified. Oxidation by the $\text{RuO}_2\text{-NaIO}_4$ system occurred at the atoms of greatest electron density as well as at the 4,5-bond. Yields of the 4,5-quinone and lactol from the $\text{OsO}_4\text{-NaIO}_4$ oxidation were 23% and 24% respectively.

The Reaction between Hydrogen and Nitrous Oxide on Gold-Platinum Alloys

G.-M. SCHWAB and H. KNESER, *Z. Phys. Chem. (Frankfurt)*, 1959, **22**, (5/6), 359-376

The kinetics of the reaction $\text{H}_2 + \text{N}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{N}_2$ were investigated using Pt, Au, 20% Pt-Au and 95% Pt-Au as catalysts. The theory of the reaction mechanisms is discussed in detail.

Studies of Mixed Hydrogenation Adsorption Catalysts. II. Investigation into the Activity of Mixed Pd-Ag Catalysts Adsorbed on SiO_2 with Respect to the Order of Adsorption of Pd and Ag

A. A. ALCHUDZHIAN and M. A. MANTIKYAN, *Zhur. Fiz. Khim.*, 1959, **33**, (8), 1691-1694 (English summary)

The activity of Pd-Ag/ SiO_2 catalysts was studied with relation to the order of adsorption and reduction of Pd and Ag as salts on SiO_2 . It was found that when Ag is adsorbed first, activity increases with increasing Ag (and constant Pd) content to a maximum and then decreases. A similar maximum is obtained with simultaneous adsorption of Ag and Pd. Zero activity results when Pd is adsorbed first. It is suggested that in the latter case Ag concentration on the Pd surface is always high, electronic interaction between Ag and Pd increases and the catalyst becomes inactive.

Organic Deuterium Compounds. II. Some Deuterated Tetrahydrofurans

E. R. BISSELL and M. FINGER, *J. Org. Chem.*, 1959, **24**, (9), 1259-1261

The synthesis and some of the physical properties of tetrahydrofuran-2,2,5,5- d_4 , tetrahydrofuran-3,3,4,4- d_4 , tetrahydrofuran-2,3,4,5- d_4 and tetrahydrofuran- d_8 are reported. Tetrahydrofuran-2,3,4,5- d_4 was prepared by reduction in an atmosphere of deuterium in the presence of a 5% Rh/ Al_2O_3 catalyst.

Competitive Hydrogenation of Acetylenic Compounds

T. FUKUDA, *Bull. Chem. Soc. Japan*, 1959, **32**, (12), 1299-1302

The properties of Pd/ CaCO_3 as a catalyst for the hydrogenation of phenylacetylene and propargyl alcohol were studied. It was shown that

partial hydrogenation was not possible in the presence of quinoline and that the catalytic properties are affected by the adsorption of 1,4-butynediol, phenylacetylene and propargyl alcohol.

Catalytic Activation of Molecular Hydrogen in Solution by Chlororhodate (III) Complexes

J. F. HARROD and J. HALPERN, *Canad. J. Chem.*, 1959, **37**, (11), 1933-1935

RhCl_3 in an aqueous HCl solution activates molecular hydrogen homogeneously. The catalysed reduction of FeCl_3 was studied to determine the kinetics which were found to be of the form $-d[\text{H}_2]/dt = k[\text{H}_2][\text{Rh(III)}]$. The slight dependence on the HCl concentration and the effects of added electrolytes follow much the same pattern as found for Pd(II) and are attributed to variations in the solubility of hydrogen. It is suggested that the major catalytic contribution is due to the RhCl_4^- species.

The Carbon Monoxide Exchange of Iron Carbonyls

A. N. WEBB and J. J. MITCHELL, *J. Phys. Chem.*, 1959, **63**, (11), 1878-1885

Exchange reactions were carried out at 0°C and progress was followed by using C^{14} , initially present in the gas phase, as a tracer. Solid Fe carbonyls apparently exchange CO without a catalyst, but a catalyst is required for exchange with $\text{Fe}(\text{CO})_5$ at 25°C or below. Catalysts for the exchange in ascending order of activity are Fe_2O_3 , Al_2O_3 , Fe, Cu, Fe_3O_4 , Ni and Pt. The exchange reaction is halted by covering the catalyst surface with more than a monolayer of Fe carbonyl. A mechanism for the reaction is proposed.

Recovering Refinery Waste Heat by Catalytic Oxidation

D. S. FRASER, *Petroleum*, 1960, **23**, (1), 15-16

The principles and economics of the operation of Oxycat heat recovery units using a Pt/ Al_2O_3 catalyst are discussed. The operating process is described.

Properties of Metal-Oxide Catalysts for Gasoline Reforming. V. Some Peculiarities of Catalytic and Physical Properties of Palladium Catalysts

KH. M. MINACHEV, M. A. RYASHENTSEVA and A. M. RUBINSHTEIN, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1959, (5), 819-825 (*Chem. Abs.*, 1959, **53**, (22), 22855b)

Three Pd catalysts, (i) Pd/ Al_2O_3 , (ii) Pd/ Al_2O_3 pretreated with HF and (iii) as (ii) but given an aftertreatment with HF, were tested. Only (ii) showed signs of sintering in gasoline reforming. The catalysts contained only crystalline Pd and $\gamma\text{-Al}_2\text{O}_3$. The temperature coefficient of the reaction rate with (iii) was appreciably greater

than with the others and explains its high activity in gasoline reforming. The high stability and activity of this catalyst is ascribed to the presence of Pd sulphide.

Physical Properties of Solid Catalysts. III. Electroconductometric Studies of the Platinum-Alumina Catalyst Applied in the Platforming Process and Determination of Semi-Conductivity in Platinum Oxide

I. V. NICOLESCU and A. POPESCU, *Acad. rep. populare Romine, Studii cercetari chim.*, 1959, **7**, 49-60 (*Chem. Abs.*, 1959, **53**, (22), 21102b)

The combined influence of both the support and the active component was studied. A direct relationship of electrical conductivity to electronic structure of the solid and to its catalytic properties is considered. Results are given for $\gamma\text{-Al}_2\text{O}_3$, PtO, PtO/ Al_2O_3 and Pt/ Al_2O_3 operating under various conditions of temperature and atmosphere. PtO behaves as an *n*-type semiconductor in the temperature range $200^\circ\text{-}500^\circ\text{C}$. At low temperatures, Al_2O_3 and 10.8% PtO/ Al_2O_3 appear as weak *p*-type semiconductors and as *n*-type at high temperatures. 1.08% PtO/ Al_2O_3 behaves as a weak *n*-type semiconductor, whereas 1% Pt/ Al_2O_3 acts as a weak *p*-type.

The Products of Up-Grading Heavy Gasoline from German Crude Oil in a Platforming Plant

H. PIETSCH and B. FRITZ, *Erdöl u. Kohle*, 1959, **12**, (9), 712-717

The operation of a German refinery is described. It consists of a Unifining unit, a Platforming unit and a plant for utilising the by-product gases. Advantages of the use of the reforming process for the production of high octane gasoline and the utilisation of other products in the chemical industry are emphasised. The future use of hydrogen for isomerisation processes with Pt catalysts is an important development.

Preparation of Toluene Concentrates from Petroleum Fractions by Low-Temperature Dehydrogenation over Platinised Carbon

N. I. SHUIKIN, KH. M. MINACHEV, I. L. GARANIN, S. S. NOVIKOV and N. F. KONONOV, *J. Appl. Chem. U.S.S.R.*, 1958, **31**, (11), 1757-1759 (Transl. of *Zhur. Priklad. Khim.*, 1958, **31**, (11), 1765-1767)

Results of experiments on the production of $\text{C}_6\text{H}_5\text{CH}_3$ concentrates in a pilot unit are given. $\text{C}_6\text{H}_5\text{CH}_3$ was subsequently isolated from the concentrate by azeotropic distillation with CH_3OH . A 4% Pt/C catalyst has high activity and stability in the aromatisation of the 98-112° fraction of gasoline from Il'skij petroleum. The yield was 23-30% of the catalyst. Aromatisation of the 98-112° fraction of Khadyzhensk petroleum, not treated to remove S compounds, yielded

concentrates containing 25-40% $C_6H_5CH_3$, and the catalyst remained active for more than 58 days. Trials showed that 98-112° fractions containing S compounds may be used providing the time of the catalyst run is reduced.

Up-Grading of Straight-Run Gasolines by Low-Temperature Dehydrogenation over Platinised Carbon

N. I. SHULKIN, KH. M. MINACHEV, S. S. NOVIKOV, N. F. KONONOV and I. L. GARANIN, *J. Appl. Chem. U.S.S.R.*, 1958, **31**, (11), 1717-1723 (Transl. of *Zhur. Priklad. Khim.*, 1958, **31**, (11), 1732-1738)

Pilot-plant aromatisation of Surakhany gasoline has been achieved at 300°C using a 4% Pt/C catalyst. The preparation of the catalyst is described in detail and the pilot-plant process is outlined. The octane number of the gasoline obtained was 95.5. Laboratory tests of 2% Pt/C and 4% Pt/C showed that both catalysts were of high activity and stability. Results of the pilot-plant process show that aromatisation continued at almost the same level for 700 hours.

CATHODIC PROTECTION

Some Platinum Anode Designs for Cathodic Protection of Active Ships

H. S. PREISER and B. H. TYTELL, *Corrosion*, 1959, **15**, (11), 56-60

The development of Pt-clad anodes and their holders is described. Design criteria for hull-mounted anodes are enumerated. Sea-water tests carried out in the laboratory and in Boston harbour established current-voltage relationships for various Pt anode forms. A Pt-clad Ta disc produced the best ratio in both cases. In the harbour tests, it gave 2 amps per impressed volt, while the other anodes gave 1.3 amps per impressed volt. In the laboratory tests, the ratios obtained were 3.2, 3.1, 2.6, 2.2 and 2.1 amps per volt for the Pt-clad Ta disc, wire gauze, 48-in. and 36-in. wire spirals, and a flat Pt disc, respectively.

The Permanent Anode in Impressed-Current Cathodic Protection Systems—Part 2

C. A. CURTIS, *Corrosion Technol.*, 1959, **6**, (11), 333-334 and 342

The properties, use and limitations of Pb, platinised Pb and platinised Ti are described. The fundamental principles of connection are given.

GLASS TECHNOLOGY

Glass-Metal and Metal-Ceramic Wettability

Y. GODRON, *Silicates Indust.*, 1959, **24**, (11), 539-549

Definitions of various surface phenomena and methods of measuring them are given. Results

of wetting angle measurements by the author and other workers at glass-metal and metal-ceramic contacts are shown. The metals used as surfaces were Cu, Ag, Ni, Pd, Pt, Au, Fe, Ti, Mo, W, Ta, Rh-Pt, Pd-Pt and Ir-Pt. Si, Ni and Fe were used to form drops on surfaces of refractory oxides of Al, Zr, Mg, Be, Ti and Th and on carbides. Experiments were carried out in N, He, H, O, air and in a vacuum. A suggested explanation of the results obtained is given in terms of a metal-oxygen bond and the phenomenon of coalescence (12 references).

The Relationship between Wettability by Glass Melts and the Electrochemical Properties of Noble Metal Alloys

A. DIETZEL and M. COENEN, *Glastechn. Ber.*, 1959, **32**, (9), 357-361

The angle of contact of molten soda-lime glass on foil of Pt-Rh alloys of various compositions, a Pt-Au and a Pt-Be alloy was chosen as an index of wettability. A relationship was established between wettability by glass melts at temperatures between 800° and 1100°C and the metal electrode potential in 1N H_2SO_4 , the anode overpotential at room temperature and the damping of mechanical vibrations. Since the overvoltage vanishes at the temperature at which oxygen atoms may diffuse through the lattice, it is concluded that the overvoltage at room temperature represents a measure of the capacity for diffusion at higher temperatures. For Pt-Rh and Pt-Au alloys, for which a relationship between oxygen-overvoltage and wetting angle exists, the wetting is determined by the diffusion of oxygen atoms through the metal lattice and by the oxygen atoms produced at the metal surface. For Pt-Be alloys another wetting mechanism, the formation of BeO, is assumed. A hindering of the diffusion of atomic oxygen leads to oxygen overvoltage.

ELECTRICAL ENGINEERING

The Formation of Increasingly Resistant Layers of Organic Origin on Electrical Contacts

I. DIETRICH and M. HONRATH-BARKHAUSEN, *Z. Angew. Phys.*, 1959, **11**, (10), 399-403

To study the formation of these layers, which were traced to the decomposition of organic substances on the contact spot, naphthalene with C^{14} was used as indicator. It showed that the black layers are formed by making currentless contact with only the Pt metals and their high percentage alloys and by making contact during the passage of current with all noble metals including Cu. Adsorption experiments which were undertaken to explain the effect showed no preferred naphthalene adsorption on the Pt metals.

ELECTRONICS AND TELECOMMUNICATIONS

The Solion Integrator

L. WILSON, *Elect. Manufacturing*, 1960, **65**, (1), 156
The design and operating principles of this precision electrochemical cell are described.

Housed in glass, it contains four small Pt electrodes and a KI/I₂ solution. The integrator anode and cathode constitute the covers of a small cylindrical volume for storing electrical information in the form of ions. The integrator may be stored for many years and produces 1 to several thousand μ amp as a true-time integrated function of an electrical input.

NEW PATENTS

Measurement of Dissolved Oxygen

CAMBRIDGE INSTRUMENT CO. LTD. *British Patent* 818,732

The invention concerns apparatus for the measurement of dissolved oxygen in a liquid which includes a scrubbing tower in which a gaseous stream, inert with oxygen gas, is contacted with an oxygen-containing liquid, the oxygen being absorbed by the stream, and an electrochemical cell for measuring the concentration of the oxygen. The cell contains an anode comprising platinum wire coated with platinum black. A small furnace containing a palladised asbestos catalyst may be used for checking the zero of the apparatus.

Production of Methylol Aminoalkanes

DEUTSCHE GOLD-UND SILBER-SCHNEIDANSTALT.
British Patent 818,764

A hydrogenation catalyst comprising activated nickel together with a platinum group metal is used in a process for production of methylol aminoalkanes by reacting a nitroalkane with formaldehyde in an alkaline medium and hydrogenating the methylol nitroalkane formed with hydrogen.

Production of Saturated Chlorohydrocarbons

BADISCHE ANILIN & SODA FABRIK A.G. *British Patent* 819,420

A catalyst composed of a platinum group metal or compound thereof is used in a process for producing saturated chlorinated hydrocarbons from olefinic, cyclo-olefinic or alkenyl-aromatic hydrocarbons by adding on chlorine to these substances in the presence of the catalyst at temperatures up to 300°C. Palladium chloride on alumina is the preferred catalyst.

Reaction of Silanic Hydrogen-bonded Compounds with Unsaturated Compounds

UNION CARBIDE CORP. *British Patent* 822,830

A catalyst composed of platinum on a support of 99.99% gamma alumina is used in a process for producing organo-silicon compounds by reacting at elevated temperature and pressure and in the presence of the catalyst an unsaturated organic compound with a silane of given general formula.

High Temperature Measuring Apparatus

DEUTSCHE GOLD-UND SILBER-SCHNEIDANSTALT.
British Patent 822,916

Apparatus for measuring high temperatures, e.g. 1500°–2000°C includes a thermocouple, one limb of which consists of iridium or tungsten or molybdenum and the other limb of an iridium-rhenium alloy, a housing of gas-impermeable non-metallic temperature-resisting material surrounding the thermocouple. The first limb may, if desired, also consist of an iridium-rhenium alloy.

Catalyst Manufacture

UNIVERSAL OIL PRODUCTS CO. *British Patent* 822,998

A catalyst is made by vaporising aluminium chloride or bromide on to a prepared composite of a refractory oxide and a platinum group metal, preferably platinum, with subsequent heating at above 300°C until substantially all uncombined chloride or bromide has been removed.

Catalytic Cracking of Methyl Isopropenyl Ketone Dimer

THE DOW CHEMICAL CO. *British Patent* 822,999

A platinum group metal, preferably palladium, catalyst is used in a process for converting methyl isopropenyl ketone dimer to methyl isopropenyl ketone monomer by heating the dimer at 196°–600°C in the presence of the catalyst.

Isomerisation of Hydrocarbons

UNIVERSAL OIL PRODUCTS CO. *British Patent* 823,010

An isomerisable hydrocarbon is subjected to the isomerising action of a catalyst composed of alumina, 2–5% by wt. combined fluorine, less than 0.075% by wt. chlorine and from 0.01–2.0% by wt. of a platinum group metal, preferably platinum. Numerous examples are given.

Reforming of Petroleum Naphthas

ESSO RESEARCH & ENGINEERING CO. *British Patent* 823,320

A component for gasoline blends is prepared by catalytically reforming a naphtha in the presence of hydrogen and a platinum catalyst at 100–300