

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

The Constitution Diagram of the Ruthenium-Rhenium System

E. M. SAVITSKII, M. A. TYLKINA and V. P. POLYAKOVA, *Zhur. Neorg. Khim.*, 1962, 7, (2), 439-441

Alloys of the system at intervals of 10 wt.% were prepared and examined by thermal analysis, microstructural and X-ray analysis, and hardness measurements. An uninterrupted series of solid solutions with melting points between those of Ru (2250°C) and Re (3170°C) was found. The maximum hardness in the cast and annealed states occurs in alloys with 60-70 wt.% Ru. Lattice parameters increase with increasing Re content.

A Study of the Ruthenium-Rhenium System

E. RUDY, B. KIEFFER and H. FRÖHLICH, *Z. Metallkunde*, 1962, 53, (2), 90-92

Sintered and arc-melted specimens were used in the investigation. Melting point determinations and X-ray, electrical conductivity, hardness and ductility measurements were made on a series of alloys. A continuous series of solid solutions was found. The hardness curve shows a maximum at about 40% Re. The cold-deformability of Re is decreased by Ru additions.

Research on the Alloys of Noble Metals with the More Electropositive Elements. V. Micrographic and X-Ray Examination of Some Magnesium-Iridium Alloys

R. FERRO, G. RAMBALDI and R. CAPELLI, *J. Less-Common Metals*, 1962, 4, (1), 16-23

Alloys in the range 0-75 wt.% Ir were studied by chemical analysis, specific gravity determination, micrographic and X-ray examination. Thermal analysis of alloys with up to 16 wt.% Ir was carried out. Results obtained indicate the existence of a eutectic point (3.2 at.% Ir and 615°C). The solid solution ζ -phase, corresponding to $Mg_{7.5}Ir$, and the δ -phase, corresponding to Mg_3Ir , were identified. A third phase ($Mg_4Ir?$) was detected. Crystal structure data for the ζ - and δ -phases are given.

Revision of the Phase Diagram for the Bi-Rh System

R. N. KUZ'MIN and N. N. ZHURAVLEV, *Soviet Phys. Cryst.*, 1961, 6, (2), 209-210 (Transl. of *Kristallografiya*, 1961, 6, (2), 269-271)

Thermal analysis showed that for the alloy containing 19.80 wt.% Rh the transition from

β - Bi_3Rh to α - Bi_2Rh occurs at 420°C. Needle-shaped crystals of β - Bi_3Rh were obtained by a casting method.

Crystal Structures of $ThRh_2$, $ThRu$ and $ThIr$

J. R. THOMSON, *Nature*, 1962, 194, (May 5), 465
 $ThRh_2$ (65 at.% Rh) was found to have a hexagonal crystal structure of the Ni_2In (B 8₂) type. $ThRu$ and $ThIr$ have orthorhombic crystal structures. Lattice parameters are given.

The Oxidation of a Work-Hardened and Recrystallised Tungsten-Platinum Alloy

R. F. VOITOVICH, *Metall. Ochr. Obrab. Met.*, 1961, (7), 47-48

It was found that in the temperature range 500-900°C a small addition of Pt to W sharply decreases the oxidation resistance of W. The oxidation resistance of a 1.5% Pt-W alloy is reduced by work-hardening, particularly at temperatures above 650°C.

Structures and Compositions of the Silicides of Ruthenium, Osmium, Rhodium and Iridium

L. N. FINNIE, *J. Less-Common Metals*, 1962, 4, (1), 24-34

The X-ray powder method was used to study the silicides of Ru, Os, Rh, and Ir stable at 1340°, 1350°, 1170° and 1340°C, respectively. The structure types and cell constants of previously reported $RuSi$ (FeSi-type) and $IrSi_3$ (Na_3As -type) and for the new phases $OsSi$ (CsCl-type) and $OsSi_2$ were determined. $OsSi$, $OsSi_2$ and $RhSi$ are stabilised by Al or oxygen. The phases $RuSi_{1.8 \pm 0.3}$, $OsSi_{1.8 \pm 0.3}$, $OsSi_{3.0 \pm 0.5}$, $RhSi_{0.7 \pm 0.1}$, $IrSi_{1.5 \pm 0.1}$, and $IrSi_{2.0 \pm 0.3}$ were also found.

Structures and Properties of Uranium-Fissium Alloys

S. T. ZEGLER and M. V. NEVITT, *U.S.A.E.C. Report ANL-6116*, Jul. 1961, 50 pp.

Synthetic U-Fs (Fs = Zr, Nb, Mo, Ru, Rh and Pd) alloys similar to those intended for the first core loading of the Experimental Breeder Reactor II were studied. Phase relations were shown to be similar to those in the U-Mo-Ru ternary system.

The Solid Solution of Mercury in Palladium

K. TERADA, *Acta Cryst.*, 1961, 14, (12), 1299
The lattice parameter of Pd in solid solutions containing up to 13.8 at.% Hg was determined. A body-centred tetragonal PdHg phase was obtained at concentrations above 13.8 at.% Hg.

The Palladium-Hydrogen System

J. G. ASTON and P. MITACEK, Abstracts of Papers, 10 M, Div. of Inorganic Chem., 141st Meeting, A.C.S., Washington, D.C., Mar. 1962

Heat capacity measurements were made on hydrogen absorbed in block Pd with 8, 4, 2 and approximately 1 Pd atom/mole H_2 , respectively. In the temperature range 15° to 150°K, the heat capacity per atom of hydrogen is independent of the composition. Either only a molecule such as PdH_4 exists in this region or only one of the two phases contains hydrogen and is of constant composition. Hysteresis occurs. Measurements of the energy of activation associated with diffusion showed two distinct processes with energies of activation of 4600 and 2900 cal, respectively. X-ray data on Pd-H and data on resistivity and rates of diffusion were reviewed.

The Solubility of Oxygen in Transition Metal Alloys

R. T. BRYANT, *J. Less-Common Metals*, 1962, 4, (1), 62-68

The solid solubility of oxygen in Nb, and alloys of Nb with Mo, Re, Ru, Zr and Ti was determined. The solubility in Nb is reduced by additions of Mo, Re, Ru, and Zr, but is increased by alloying with Ti.

Hall Effect in Palladium-Silver and Palladium-Copper Alloys

K. K. RAO, M. E. NICHOLSON and J. M. SIVERTSON, *Bull. Amer. Phys. Soc., Series II*, 1962, 7, (2), 116 (Abstract of paper presented at the Amer. Phys. Soc. Southwestern Meeting, Austin, Texas, Feb. 1962)

Hall coefficients were determined at 309°K. The Hall constants for alloys having C in solid solution were found to have lower numerical values than those for the alloys with no C. Results indicate that, for Pd-Ag and Pd-Cu up to about 60% noble metal, part of the Hall coefficients may be associated with the paramagnetism of the alloys.

Temperature Dependence of the Thermoelectric Power of the Pd-Ni Alloy System

A. I. SCHINDLER and E. W. KAMMER, *Bull. Amer. Phys. Soc., Series II*, 1962, 7, (3), 230 (Abstract of paper presented at the Amer. Phys. Soc. March Meeting, Baltimore, Mar. 1962)

The thermoelectric power (T.E.P.) of the alloy system was measured relative to pure Pd in the range 77° to 273°K. Measurements were also made at 4° and 20°K for several selected alloys. The isothermal variation of the relative T.E.P. as a function of composition shows a minimum around 50 at.% Pd. With increase of temperature the position of the minimum shifts to lower compositions. A distinct break in the T.E.P. appears to be related to the ferromagnetic-paramagnetic transition boundary. Only 10 at.% Ni-Pd and 17.2 at.% Ni-Pd have Curie temperatures within 77° to 273°K.

Superconductivity and Ferromagnetism of Chromium Alloys and Compounds

B. T. MATTHIAS, T. H. GEBALLE, E. CORENZWIT and G. W. HULL, *Bull. Amer. Phys. Soc., Series II*, 1962, 7, (3), 176 (Abstract of paper presented at the Amer. Phys. Soc. March Meeting, Baltimore, Mar. 1962)

It was found that Cr-Rh and Cr-Ir alloys become superconducting below 1°K. Cr-Ru alloys also become superconducting near 1°K. The transition temperature for 5% Cr-Ru is less than that of pure Ru.

Thermoelectricity at Low Temperatures. IX. The Transition Metals as Solute and Solvent

D. K. C. MACDONALD, W. B. PEARSON and I. M. TEMPLETON, *Proc. Roy. Soc., Series A*, 1962, 266, (1325), 161-184

Experiments were carried out on alloys of Au with Cr, Mn, Fe, Co, and Ni and alloys of Pt and Pd, separately, with Fe, Mn, Cu, and Sn in the temperature range 0.1°K to a few degrees K. Data are presented of the thermoelectric behaviour of these alloys and theories are proposed to account for the anomalous behaviour observed.

Interface Impedance and the Apparent Electrical Resistance of Palladium Hydrides in Aqueous Solutions

J. C. BARTON and F. A. LEWIS, *Trans. Faraday Soc.*, 1962, 58, (469), 103-109

Measurements of electrical resistance of hydrided Pd wires by a.c. methods in strongly acid solutions show even greater errors than d.c. measurements. It is possible to compensate for these errors by simulating the equivalent components of the electrolyte and interface impedance in the bridge balancing arm. The reduced resistance values obtained by a.c. measurements are related to the magnitude of co-conduction of the bridge current through the electrolyte.

The Rhodium-Chlorine System at High Temperature

W. E. BELL, M. TAGAMI and U. MERTEN, *J. Phys. Chem.*, 1962, 66, (3), 490-494

The system was studied over the temperature range 700° to 1500°C and over the chlorine pressure range 0.01 to 1.0 atm. Under these conditions solid $RhCl_3$ is the only stable condensed chloride. The dissociation pressure of $RhCl_3(s)$ reaches 1 atm at 970°C. $RhCl_2$ and $RhCl_3$ are the important gaseous species. Vapour pressure data for $RhCl_2$ and $RhCl_3$ are shown in a table.

Sorption and Magnetic Susceptibility Studies on Palladium-Nitric Oxide Systems

R. W. ZUEHLKE, *Diss. Abs.*, 1961, 22, 1432

The sorption of NO on finely divided Pd and Pd/SiO₂ gel was studied in the temperature range 195° to 308°K. On Pd, NO is first adsorbed by chemisorption which is followed by additional

physical adsorption and then by dimerisation of the physically adsorbed layer to N_2O_2 . The magnetic susceptibility steadily decreases as adsorption progresses. The sorption of NO on Pd/SiO₂ gel at room temperatures seems to proceed as a pseudo-chemisorption. The nature of the Pd layer is discussed.

Thermodynamic Properties of Palladium-Iron Alloys in the Temperature Range 1200–1460°C

E. AUKRUST and A. MUAN, *Acta Met.*, 1962, 10, (5), 555–560

Oxidation experiments were carried out on Pd-Fe alloy samples suspended in a thermal balance. The oxygen potential of the system was increased in small increments by adjusting the ratio of the CO₂/CO mixture surrounding the alloy. Weight increase of the sample indicated the start of oxidation of Fe in the alloys. The activity of Fe in the alloys was calculated.

Surface Self-Diffusion and Surface Energy Measurements on Platinum by the Multiple Scratch Method

J. M. BLAKELY and H. MYKURA, *Acta Met.*, 1962, 10, (5), 565–572

Interference microscopy was used to observe the decay of sets of parallel scratches on Pt crystal surfaces during vacuum annealing at temperatures between 890° and 1310°C. Surface self-diffusion constants were evaluated from smoothing rates and surface energy was estimated.

The Corrosion Resistance and Mechanical Properties of Titanium-Molybdenum Alloys Containing Noble Metals

M. STERN and C. R. BISHOP, *A.S.M. Trans. Quarterly*, 1961, 54, (3), 286–298

Mo-Ti alloys with 0 to 35% Mo and with or without about 0.2% Pd were prepared both by consumable arc melting and induction melting in graphite. The corrosion resistance of these alloys in both oxidising and reducing media was evaluated in laboratory and field tests. Mechanical properties were also tested. Additions of 30 to 40% Mo to Ti increase its corrosion resistance in reducing media, but decrease its resistance in oxidising conditions. Additions of about 0.2% Pd to Mo-Ti alloys do not increase their corrosion resistance to oxidising media, but increase the resistance of alloys with 5 to 15% Mo in reducing environments. An alloy containing 15 to 20% Mo and 0.2% Pd has the most satisfactory combination of corrosion resistance and mechanical properties.

The Behaviour of Ruthenium Trichloride in Aqueous Solutions

F. PANTANI, *J. Less-Common Metals*, 1962, 4, (2), 116–123

The formation of hydroxy-complexes in aqueous

solutions and mixtures of chlorohydroxy- and chloro-complexes in the presence of alkali chloride and HCl were shown by argentometric and alkalimetric titrations. A reduction to Ru(II), a further reduction, and the catalytic discharge of H⁺ were recorded polarographically. The presence of Ru in the +4 valency state is indicated.

Ring Substitution Reactions of Metal-Cyclopentadienyls and Metal-Arenes

M. D. RAUSCH, Abstracts of Papers, 25 M, Div. of Inorganic Chem., 141st Meeting, A.C.S., Washington, D.C., Mar. 1962

Ring substitution reactions of ferrocene and other π -cyclopentadienyl derivatives of V, Cr, Mn, Ru, and Os have been shown. Similar reactions of several π -arene Cr compounds have also been observed. Oxidation, reduction, dehydration, addition, and rearrangement reactions of substituted metal-cyclopentadienyls are described.

Substitution and Exchange Reactions in Rhodium (I) and Iridium (I) Carbonyl Complexes

A. WOJCICKI, Abstracts of Papers, 32 M, Div. of Inorganic Chem., 141st Meeting, A.C.S., Washington, D.C., Mar. 1962

It was found that Rh(CO)₂(am)Cl and Ir(CO)₂(am)Cl (am = *p*-anisidine and *p*-toluidine) rapidly exchange with radiochloride ion at -35°C in C₂H₅OH and that their reaction with C₆H₅N to displace the co-ordinated Cl is extremely rapid at -80°C. CO exchange with Rh₂(CO)₄Cl₂, Rh(CO)₂(am)Cl, Rh(PPh₃)₂(CO)Cl, Rh(PPh₃)₂(CO)NCS, and Ir(CO)₂(am)Cl was also studied. Results indicate that carbonyls of Rh(I) and Ir(I) react at comparable rates.

Contact Potentials of Homologous Fatty Amines Adsorbed on Platinum

W. A. ZISMAN and K. W. BEWIG, Abstracts of Papers, 20-I, Div. of Colloid and Surface Chemistry, 141st Meeting, A.C.S., Washington, D.C., Mar. 1962

Monomolecular films of a homologous series of pure, primary fatty amines from C₄ to C₂₂ were adsorbed on pure polished Pt. The change in the contact p.d. between the Pt electrode and a reference electrode of Teflon-coated Au as a result of the adsorption of each monolayer was measured at 20°C and 50% R.H. The effects of homology, molecular packing, orientation, and solvent inclusion were studied.

Effect of Progressive Fluorination of a Fatty Acid on the Wettability of Its Adsorbed Monolayer

E. G. SHAFRIN and W. A. ZISMAN, Abstracts of Papers, 20-I, Div. of Colloid and Surface Chemistry, 141st Meeting, A.C.S., Washington, D.C., Mar. 1962

Films of a series of heptadecanoic acids with

perfluoroalkyl substitutions in 17-position of φ -ethyl, φ -propyl, φ -pentyl, and φ -heptyl groups were prepared by adsorption from the melt on Cr. Films of the φ -heptyl compound were also prepared on Pt, Ni, quartz, and soda-lime glass. Wettability tests showed that the metal substrates were less wettable than the siliceous surfaces. Differences in the wettability of terminally fluorinated aliphatic acids and analogous fully fluorinated acids were examined.

ELECTROCHEMISTRY

The Nature of Hydrogen Adsorption on Electrodes of the Platinum Metals

M. BREITER, *Electrochim. Acta*, 1962, 7, (Jan./Feb.), 25-38

Adsorption studies were carried out in 2.3M H_2SO_4 for Pt, Ir and Rh, and in various other solutions for Pt. With Pt and Ir electrodes, hydrogen is strongly bound at relatively positive potentials and weakly bound at relatively negative potentials. The strongly bound hydrogen is adsorbed as H atoms and it is suggested that the weakly bound hydrogen is similarly adsorbed. The influence of anions on the adsorption of hydrogen by Pt is discussed.

A Study of the Electrochemical Properties of Powders

W. TOMASSI, *Electrochim. Acta*, 1962, 7, (Jan./Feb.), 91-99

Powder electrodes consisting of activated C or Pt black were found to have a potential lower than that of a Pt wire electrode in the same (Cl_2/Cl^-_{aq}) system. A cell which gave electrical work and could be charged and discharged, with the properties of an accumulator, was constructed. The powder electrodes may also be used in electrolytic gas evolution processes with a profitable lowering of the electrolysis potential. Gases evolved are adsorbed on the powder of the electrode. Results obtained in the electrolysis of 0.5 N HCl, 0.5 N H_2SO_4 , 25% KOH, 25% NaOH, and 5 N NaCl solutions are given.

An Investigation of Anion Adsorption with the Aid of Marked Ions

K. SCHWABE, *Electrochim. Acta*, 1962, 6, (1-4), 223-235

Adsorption on Pt, Ni, and Fe sheets and films was measured by means of $^{36}Cl^-$, $^{82}Br^-$, $^{36}ClO_4^-$, $^{35}SO_4^{2-}$, $H^{35}S^-$ and $^{14}CN^-$. A method was developed for the measurement of adsorption when the metal was in contact with the solution. It is thought that exchange between oxygen on the metal and the anion occurs. It was shown by autoradiography that adsorption occurs preferentially at the grain boundaries and increases with decreasing grain size. Results obtained in the investigation show that passivation may be considered as a competition between metal dissolution, coverage by a passivating oxide film, and exchange between the oxygen and anions.

Consideration of the Mechanism of the Electrode Process of the Chlorine Electrode on Carbon and Platinum Powders. Part I

W. TOMASSI, *Przemysl*, 1962, 41, (2), 62-64 (English summary)

Results are given of experiments using a Pt/C electrode in an aqueous solution containing chlorine and Cl^- ions. The phenomena observed during electrolysis are explained by a thermodynamic model. The reaction $2Ag(s) + 2HCl_{aq} \rightarrow 2AgCl(s) + H_2$ is used to illustrate the possibility of an easy spontaneous reversion of the course of some reactions.

Part II. Mechanism of the Electrode Process

Ibid., (3), 126-128

The mechanism of the electrode process of the chlorine on C and Pt powder is discussed. The parts played by three zones of the surface of the disintegrated phase is described.

The Phenomenon of the Decrease of Potential of Powder Electrodes in the Cl_2-Cl-H_2O System and Its Possible Interpretation

H. JANKOWSKA, W. TOMASSI, and D. KOCOT-BONCZAKOWA, *Electrochim. Acta*, 1962, 6, (1-4), 237-243

A study of powder electrodes in the Cl_2-Cl-H_2O system showed that the C and Pt powder electrodes have a smaller potential than a Pt wire dipping into the same system. This effect was not found with a SiO_2 gel electrode. An adsorption element consisting of a Pt wire electrode and a C powder electrode in contact with the Cl_2-Cl-H_2O system was developed. An interpretation of the observed phenomena is given.

Reduction Mechanism of Chemisorbed Oxygen on Platinum Electrodes by Molecular Hydrogen

M. W. BREITER, *J. Electrochem. Soc.*, 1962, 109, (5), 425-427

Experimental work was carried out to distinguish between chemical and electrochemical reduction of chemisorbed hydrogen on a smooth Pt wire electrode in 1N $HClO_4$ at 30°C. Reduction by molecular hydrogen at open circuit occurs at a much lower rate than the electrochemical reduction. The anodic current of hydrogen oxidation equals the cathodic electrochemical reduction current on the oxygen layer.

ELECTRODEPOSITION

Deposition of Several Platinum Metals from Molten Cyanide Electrolytes

R. N. RHODA, *Plating*, 1962, 49, (1), 69-71

A method is described for depositing hydrogen-free Pt, Ir, and Ru from molten NaCN or 53 wt.% NaCN-KCN electrolytes. The Pt metal to be deposited is dissolved in the electrolyte by passing a.c. between electrodes of this metal suspended

in the molten salt. The maximum thickness of sound deposits is 0.01 in. for Pt, 0.003 in. for Ir, and 0.0025 in. for Ru. Current densities are 0.3 to 3.0 amp/dm² for Pt, 1.4 to 5.1 amp/dm² for Ir, and 0.5 to 1.8 amp/dm² for Ru, with cathode current efficiencies of 65 to 98% for Pt²⁺, 9 to 20% for Ir³⁺ and 11 to 45% for Ru³⁺.

Palladium Plating

J. J. MILES, *A.T.E. Journal*, 1962, **18**, (1), 63-65

The electrodeposition of Pd from a bath based on sulphamate complexes of the metal and electroless deposition of Pd from a bath based on sulphamic acid solutions of Pd sulphamate complexes are discussed briefly. Properties of Pd electrodeposits and applications of both types of deposit in electrical engineering are described.

Noble Metal Electroplating for Electrical Engineering

A. KLEINLE and O. LOEBICH, *Galvanotechnik*, 1962, **53**, (2), 62-74

The properties and applications of electrodeposited Ag, Au, Pt, Pd, and Rh are discussed in detail. Among the many applications described are electrical contacts, printed circuits, semiconductors, electron tubes, high-frequency circuits, and platinised Ti anodes. Plating techniques, including those for electroless plating of Ru, Rh, Pd, and Pt, are also discussed. (10 references)

The Properties and Applications of Noble Metal Coatings in Engineering

H. W. DETTNER, *Galvanotechnik*, 1962, **53**, (2), 87-92

In this review the mechanical and corrosion properties of Ag, Au, Pt, Pd, and Rh coatings are described. Details are given of the electrical properties of Ag, Au, Pt, Rh, Pd, Os, and Ir. Applications of Ag and Au coatings in the electrical industry and of materials coated with the Pt metals are mentioned. (23 references)

CATALYSIS

Catalytic and Electron Spin Resonance Investigations of Supported Platinum Catalysts

C. NICOLAU and K.-H. SCHNABEL, *Nature*, 1962, **193**, (Mar. 3), 871-872

Pt/Al₂O₃, Pt/C/Al₂O₃, Pt/SiO₂, and Pt/C/SiO₂ catalysts were evaluated for activity in the C₉-dehydrocyclisation of *iso*-C₈H₁₈ and the production of 1, 1, 3-trimethylcyclopentane. Electron spin resonance spectra of these catalyst systems were investigated. The activity of the catalysts containing C is higher than that of those without C. It is suggested that a relationship exists between the free electrons recorded by means of the electron spin resonance method and the activity of the catalyst systems.

Chemisorption Studies on Supported Platinum

H. L. GRUBER, *J. Phys. Chem.*, 1962, **66**, (1), 48-64

The adsorption of hydrogen, oxygen and CO on γ -Al₂O₃ and on 1.1% Pt/ γ -Al₂O₃ reforming catalysts was investigated. Hydrogen adsorption was used to determine the Pt surface area of the catalysts, which were prepared by impregnation. Heat treatment of the catalysts at 500°C results in a decrease of Pt dispersion. The amounts of hydrogen and oxygen adsorbed by the catalysts in different steps of oxidation-reduction cycles were measured. A mechanism for the oxidation-reduction cycle is proposed. Studies of CO adsorption showed that it depends on the degree of Pt dispersion and the nature of the support and that the Pt is present as a discontinuous monolayer or as small crystallites.

Catalysis of Fuel Cell Electrode Reactions

R. B. ROZELLE, *Diss. Abs.*, 1961, **22**, (6), 1842

The catalytic activity of Group VIII and Ib metals in fuel cell anode reactions was investigated. Group VIII noble metal catalysts produce theoretical or near theoretical potentials for the hydrogen electrode in aqueous NaOH electrolyte. Group Ib metal catalysts produce much lower potentials for this electrode. Similar results are obtained with CO, C₂H₄, C₂H₂, and C₃H₈ electrodes.

Platinum (II) Catalysed Reaction of Silicon Hydrides with Olefins as an Example of Co-ordination Catalysis

A. J. CHALK and J. F. HARROD, Abstracts of Papers, 25M, Div. of Inorganic Chem., 141st Meeting, A.C.S., Washington, D.C., Mar. 1962

The activation of chemical bonds by certain metal ions and the effects of the retention of the resulting species in the co-ordination sphere of the metal ion are discussed. The reactions of silicon hydrides with olefins are compared with other co-ordination catalyses. It was found that Pt(II) olefin complexes are simple homogeneous catalysts for the addition of \equiv Si-H to olefins and it is proposed that a Pt(II) olefin hydride complex is a reaction intermediate. When the olefin is replaced by a similar but less reactive π acceptor ligand, a hydride may be isolated.

The Stability of Hydrocracking Catalysts

C. G. MYERS, W. E. GARWOOD, B. W. ROPE, R. L. WADLINGER and W. P. HAWTHORNE, Abstracts of Papers, 6Q, Div. of Petroleum Chem., 141st Meeting, A.C.S., Washington, D.C., Mar. 1962

Pt and Co-MoO₃ catalysts were compared for stability in cycles of gas oil hydrocracking and oxidative regeneration at conditions causing declining activity and product value. Acid sites appear to be rate-controlling with Pt catalysts, while with Co-MoO₃ catalysts hydrogenation-dehydrogenation activity appears to be rate-

controlling. The reduction in the surface area of the catalysts during operation was studied.

Some Recent Advances in Hydrocracking

A. VOORHIES and W. M. SMITH, Abstracts of Papers, 6Q, Div. of Petroleum Chem., 141st Meeting, A.C.S., Washington, D.C., Mar. 1962

The performance of a new unspecified noble metal-containing hydrocracking catalyst is described. This catalyst is more resistant to the deactivating effects of naturally occurring feed N compounds than catalysts previously used for hydrocracking. It is shown that the catalyst may be used at 1500 p.s.i. when feed N content is as high as 1000–2000 p.p.m.

Mechanisms of Homogeneous Catalytic Hydrogenation and Related Processes

J. HALPERN, Abstracts of Papers, 10Q, Div. of Petroleum Chem., 141st Meeting, A.C.S., Washington, D.C., Mar. 1962

Recent studies on the mechanisms of homogeneous catalytic hydrogenation are described. The function of a Ru(II) chloride catalyst in the hydrogenation of some olefinic compounds is discussed. Other related reactions which involve (i) activation of the C=C bond through π -complexing and (ii) addition across the C=C bond by rearrangement of the π -bonded complex to an α -bonded one, are considered.

Selective Catalytic Hydrogenation of Acetylenes

N. A. DOBSON, G. EGLINTON, M. KRISHNAMURTI, R. A. RAPHAEL and R. G. WILLIS, *Tetrahedron*, 1961, **16**, (1–4), 16–24

A 10% Pd/C catalyst was used in the study of the stepwise catalytic hydrogenation of undeca-1,7-diyne. Protection of the ethynyl group during hydrogenation was achieved by conversion into the corresponding 1-bromoacetylene. The partial catalytic reduction of several acetylenic hydrocarbons using Pd/CaCO₃, Pd/BaSO₄ and Pd/C catalysts was found to produce substantial amounts of *trans*-ethylenes. Stereomutation of *cis*- to *trans*-ethylenes occurred. The extent of the stereomutation depends on the quantity of catalyst used and on its origin.

Effects of Temperature and Catalyst Variation upon the Stereochemistry of Hydrogenation of Disubstituted Benzenes

R. D. SCHUETZ and L. R. CASWELL, *J. Org. Chem.*, 1962, **27**, (2), 486–489

The hydrogenation of the three xylenes was carried out on Adams' (PtO₂) and Raney Ni catalysts. With PtO₂ catalyst the yields of *trans*-dimethylcyclohexanes obtained from the xylenes were in the order *para* > *meta* > *ortho*, while with Raney Ni they were in the order *meta* > *ortho* > *para*. Hydrogenation of diethyl phthalate on PtO₂ failed to give a *trans* product, but on

Raney Ni significant amounts were obtained. For all xylenes, increase of temperature resulted in increased yield of *trans* isomers, but increased pressure had little effect. The amount of catalytic isomerisation of *cis* isomers was insufficient to account for the amounts of *trans* products of hydrogenation, and it is concluded that the *trans* products are formed during hydrogenation.

The Erdölwerke Frisia Refinery at Emden

J. H. SCHEWE, *Erdöl u. Kohle*, 1962, **15**, (1), 11–14
The layout and operation of this refinery are described. Principal units are the 30,000 b/d crude oil distillation plant, the naphtha desulphuriser, the 4000 b/d catalytic reformer, and the LPG recovery plant.

Activation of Metal Hydrogenation Catalysts by Irradiation

D. GRAHAM, *J. Phys. Chem.*, 1962, **66**, (3), 510–511
The activity of 30% Ni/Filter-Cel, 5% Pd/C and 1% Pt/C catalysts was measured after high-energy irradiation. Both the Ni and Pd catalysts showed increased activity after 2 meV β - and X-irradiation although the activity decreased again with time. The Pt catalyst was not affected by radiation at the 2 meV level, but its activity increased after 3 meV irradiation. It appears that active centres are both created and destroyed by irradiation. The energy required for forming new active centres and the stability of these centres vary directly with the temperature required for atomic diffusion in the catalyst metal surface. This temperature is a function of the metal's melting point.

Mechanism of Oxidation, Hydrogenation and Electrochemical Combustion on Solid Catalysts. VII. Problems of Chemisorption. Mechanisms of the Origin of the Hydrogen and Oxygen Electrode Potentials on Platinised Platinum

O. K. DAVTYAN and E. G. MISYUK, *Zhur. Fiz. Khim.*, 1962, **36**, (4), 673–680 (English summary)

Changes in potential arising from the electrochemical deposition of oxygen or hydrogen on the surface of platinised Pt electrodes, or from their removal, are explained by assuming migration of chemisorbed atoms. Atoms from active centres migrate to the less active or inactive centres in the case of deposition of gas, and *vice versa* in the case of removal of gas. The migrational processes tend towards dynamic equilibrium with time. It was shown that active centres for hydrogen and oxygen on Pt are energetically inhomogeneous.

Olefin Oxidation with Palladium Chloride Catalysts

J. SMIDT, W. HAFNER, R. JIRA, R. SIEBER, J. SEDLMEIER and A. SABEL, *Angew. Chem.*, 1962, **74**, (3), 93–128

The mechanism of the oxidation process, with

particular reference to the oxidation of C_2H_4 to CH_3CHO is discussed in detail. A commercial process for the manufacture of CH_3CHO employing a $PdCl_2-CuCl_2$ catalyst solution is described.

Enrichment of Heavy Water by High-Pressure Exchange Between Hydrogen and an Aqueous Catalyst Suspension. Part II. Construction and Operation of a Pilot-Scale Experimental Plant

S. WALTER, E. NITSCHKE, C. BODE, E. W. BECKER, R. P. HÜBENER, R. W. KESSLER and U. SCHINDEWOLF, *Chem.-Ing.-Techn.*, 1962, **34**, (1), 7-10

The principles of operating this dual-temperature exchange process using an aqueous suspension of 0.1% Pt/C as catalyst are discussed. The construction and operation of the pilot-plant are described. Results of an 86-day experiment show the technical feasibility of the process and justify earlier estimates of its economics.

Part III. Influence of Specific Exchange Efficiency by Additives

E. W. BECKER, R. W. KESSLER and R. P. HÜBENER, *Chem.-Ing.-Techn.*, 1962, **34**, (2), 105-108

The effect of additions to the liquid phase of various acid, neutral and basic inorganic materials and of surface-active organic materials was studied. Additions of nitrogen, CH_4 , H_2S and CO were also made to the gas phase. The results obtained are discussed with reference to the deleterious effects which may be produced by impurities present in the process materials.

The Effect of Oxygen on the Catalytic Activity of Platinum Films in Hydrogen Isotope Exchange

G. K. BORESKOV and A. A. VASILEVICH, *Kinetika i Kataliz*, 1961, **2**, (5), 679-683

The poisoning effect of oxygen on the adsorption of hydrogen by Pt films, on the exchange of adsorbed tritium with molecular hydrogen, and on the exchange in molecular hydrogen was studied. With increased adsorption of oxygen, hydrogen absorption decreases. The presence of small amounts of oxygen has no marked effect on the adsorptive and catalytic properties of the films. The adsorption of hydrogen and velocity of isotope exchange on sites not occupied by oxygen are not affected by the presence of considerable quantities of oxygen.

The Poisoning of Platinum/Alumina Catalysts Containing Different Amounts of Metal, Investigated by Means of Thiophene-S³⁵

KH. M. MINACHEV, D. A. KONDRAT'EV and P. I. SLYUNYAEV, *Kinetika i Kataliz*, 1961, **2**, (5), 690-693

The distribution of S on catalysts containing 0.05 to 10.0% Pt as a result of the passage over them of a mixture of 98% cyclohexane and 2% thiophene was investigated. The experimental temperature and hydrogen pressure were 450°C

and 20 atm, respectively. The regeneration of the poisoned catalyst by the passage of pure cyclohexane was also investigated.

Different Catalytic Activities of Platinum and Palladium in Cyclohexene and Cyclohexadiene Conversions

V. M. GRYAZNOV, V. D. YAGODOVSKII, E. A. SAVEL'eva and V. I. SHIMULIS, *Kinetika i Kataliz*, 1962, **3**, (1), 99-102

Films of Pt and Pd prepared in the same way differed greatly in their catalytic properties. In the conversion of cyclohexene and cyclohexadiene-1,3 dehydrogenation predominated when the Pt catalyst was used, and redistribution of hydrogen occurred when the Pd catalyst was used. The difference in catalyst activity is attributed to the ability of Pd to absorb much greater quantities of hydrogen than does Pt.

Liquid-Phase Catalytic Oxidation of Organic Compounds on Noble Metals. III. Oxidation of Ethylene Glycol to Glyoxal

I. I. IOFFE, N. V. KLIMOVA and A. G. MAKEEV, *Kinetika i Kataliz*, 1962, **3**, (1), 107-110

Up to 15% conversion of ethylene glycol to glyoxal was obtained with the use of supported Pt or Pt-Pd catalysts in the liquid-phase. In addition glycolic acid, glycolaldehyde, $HCOOH$, and CH_2O were formed. The solubility of various catalyst supports in the reaction conditions was investigated. C and Al_2O_3 are the most stable supports in the given process.

Isomerisation of n-Pentane on Platinum/Alumina Catalysts

J. MARÉCHAL, R. CAHEN and H. DEBUS, *Rev. Inst. Franç. Pétrole*, 1961, **16**, (11), 1299-1306

The investigation was carried out in a fixed-bed flow system. A study of the influence of pressure, hydrogen-to-hydrocarbon ratio, C_5H_{12} and hydrogen flow showed that the reaction is first order with respect to the $n-C_5H_{12}$ mole fraction. Pressure has no influence in the range 5 to 50 kg/cm². The influence on the catalyst activity of the presence of a chloride in the feed and of the addition of Al fluorides to the catalyst was studied. Increasing Pt content of the catalyst up to about 0.5% Pt raises its activity.

Reduction of Aromatic Nitro-Compounds by Sodium Borohydride Catalysed by Palladised Charcoal

T. NEILSON, H. C. S. WOOD and A. G. WYLIE, *J. Chem. Soc.*, 1962, (Jan.), 371-372

Very pure amines have been obtained from a number of nitro-compounds by this reduction method. A 10% Pd/C catalyst was used and the reductions were carried out at room temperature in alkaline solution or in aqueous CH_3OH . The rate of reduction was shown to be roughly proportional to the amount of catalyst used.

Steroids and Related Natural Products IX. Selective Osmium Tetroxide Oxidation of Olefins

G. R. PETTIT and B. GREEN, *J. Org. Chem.*, 1961, **26**, (11), 4673-4675

A glycol is obtained from α -apoloobetulin by treatment of the olefin with OsO_4 in $\text{C}_6\text{H}_5\text{N}$ solution followed by H_2S . 3 - isopropyl - A - norlanost - 3(5)-ene treated with $\text{OsO}_4/\text{C}_6\text{H}_5\text{N}$ and sodium bisulphite yields a diketone, while a glycol is obtained by treatment of the olefin with $\text{OsO}_4/\text{C}_6\text{H}_6$ and H_2S .

Patterns of Behaviour in Catalysis by Metals

G. C. BOND, G. WEBB, P. B. WELLS and J. M. WINTERBOTTOM, *J. Catalysis*, 1962, **1**, (1), 74-84

Relative advantages of supported metals, metal powders and evaporated metal films as hydrogenation catalysts are discussed. A literature survey shows that certain properties of metal catalysts are characteristic of the metal and not of its physical form. Two such features of Group VIII metals are (i) the degree of selectivity shown in the hydrogenation of multiply unsaturated hydrocarbons and (ii) the degree of olefin isomerisation and exchange during hydrogenation. Results are reported of new work using $\alpha\text{-Al}_2\text{O}_3$ -supported Ru, Rh, Pd, Os, Ir and Pt catalysts in the hydrogenation of unsaturated hydrocarbons. Ru, Rh, and Pd give substantial isomerisation and exchange, in contrast to the behaviour of Os, Ir, and Pt. These differences in behaviour are used to explain the selectivity sequence of the metals in the hydrogenation of acetylenes and diolefins which has been reported previously and confirmed in this work.

The Determination of the Free-Metal Surface Area of Palladium Catalysts

J. J. F. SCHOLTEN and A. VAN MONTFOORT, *J. Catalysis*, 1962, **1**, (1), 85-95

Two methods described for determining the free-metal surface area of supported Pd catalysts are based on the chemisorption of CO at room temperature. Catalysts examined were Pd black, Pd sponge, Pd/ $\alpha\text{-Al}_2\text{O}_3$, Pd/C and Pd/kieselguhr. In some cases results are compared with those obtained by other techniques and good agreement is shown. The dispersion of Pd on the supports is discussed.

The Catalytic Dehydrogenation of Dihydrofurans

N. I. SHUIKIN, I. F. BEL'SKII and R. A. KARAKHANOV, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1962, (1), 138-142

The dehydrogenation of 2-methyl-4, 5-dihydrofuran on Ru/C, Rh/C, Os/C and Ir/C catalysts was investigated at 200° and 300°C. The first reaction in these conditions is dehydrogenation to α -methylfuran. Hydrogen which is separated either hydrogenates the original dihydromethyl-

furan to tetrahydromethylfuran or promotes the hydrogenolysis of α -methylfuran to methylpropyl ketone. The latter compound may also be formed by the isomerisation of tetrahydromethylfuran.

CATHODIC PROTECTION

Platinum in Anodes. Cathodic Protection Applications. Part 1

G. W. WALKIDEN, *Corrosion Technol.*, 1962, **9**, (1), 14-16

The design and performance of various types of supported Pt anodes are discussed. Among the anodes described are a ring of Pt-Pd foil supported by a reinforced plastic holder, a Pt-clad Ag trailing anode, and platinised Ti or Ta anodes. The advantages of the use of Pt-Pd alloys and platinised Ti or Ta over other anode materials are stressed. (17 references)

Part 2

Ibid., 1962, **9**, (2), 38-40, 44

The applications of platinised Ti anodes in the cathodic protection of small ships, boats and a jetty are described. A coating of Pt 0.0001 in. thick obtained electrolytically is usually employed. The loss of Pt due to corrosion of the anodes in chloride-containing solutions, and the effects of the geometry of the anode and a.c. ripple on corrosion of the anode are discussed. Pt/Pb bielectrodes in which Pt micro-electrodes are inserted in Pb anodes and their use in sea water or 0.1 M to 1.3 M NaCl solutions are described. (22 references)

Cathodic Protection—Something Old—Something New

G. G. PAGE, *Corrosion Technol.*, 1962, **9**, (4), 89-93, 112

The development of cathodic protection methods is described. Facts necessary for the assessment of a corrosion problem and the possible application are outlined. Future trends in cathodic protection are discussed.

ELECTRICAL ENGINEERING

Surface Films on Precious Metal Contacts

H. C. ANGUS, *Brit. J. Appl. Phys.*, 1962, **13**, (2), 58-63

Surfaces of Pt, Pd, Rh, Ir, and Ru were examined and compared with a Au reference surface. The Pt metals were in the wrought, electrodeposited, melted or sintered forms. Variation of contact resistance with loading (1 mg to 5000 mg) was studied and the results are interpreted in terms of film behaviour. Reproducible contact resistances may be obtained at loads of <1 g corresponding to film thicknesses of the order of 5 Å. Abrasion

causes surface deterioration at light loads. Fractured sintered compacts have the most stable surfaces, but cold-formed and electrodeposited surfaces deteriorate only slowly if abrasion is minimised.

Properties and Behaviour of Precious Metal Electrodeposits for Electrical Contacts

H. C. ANGUS, *Trans. Inst. Metal Finishing*, 1962, **39**, (1), 20-28

Au, Rh, and Pd contact coatings electrodeposited from conventional electrolytes have been examined. The importance in the performance of the contacts of the thickness, hardness, and electrical resistivity of the deposits is discussed. Results of exposure tests under various conditions show that porosity of the coating has a significant effect on the behaviour of the contacts. Effects of mechanical wear during service are also discussed. Suitable deposit thicknesses are suggested for each metal.

ELECTRONICS AND TELECOMMUNICATIONS

The Solion

K. JOACHIM, *Elektronik*, 1962, **11**, (1), 7-11

The electrochemical principles underlying the operation of the solion are discussed. This electrochemical control cell consists basically of Pt electrodes in a KI/I₂ solution. Devices which incorporate the solion include electrochemical diodes, flow- and pressure meters, integrators, multipliers, and electrokinetic pressure generators. The simplicity of construction of the

solion and low current requirements are emphasised.

TEMPERATURE MEASUREMENT

Progress in Platinum Resistance Thermometry

C. R. BARBER and J. A. HALL, *Brit. J. Appl. Phys.*, 1962, **13**, (4), 147-154

The history of the development of Pt resistance thermometry is discussed. Various thermometers designed for the measurement of temperatures in the ranges -183° to 630°C and 630° to 1063°C , and below -183°C are described. Improvements in accuracy have been achieved by refinements in and new methods of measurement and by better reproducibility of fixed calibration points. Methods of measurement based on the potentiometer, the Wheatstone bridge and the Kelvin double bridge are outlined. The role of the Pt resistance thermometer in the International Practical Scale of Temperature is discussed and the extension of its use for measurements up to 1063°C and down to 20°K is predicted. (34 references)

An Improved Resistance Thermometer Bridge

ANON., *Nat. Bur. Stds. Tech. News Bull.*, 1962, **46**, (2), 8-10

A modified Mueller bridge for use with a Pt resistance thermometer is described. The addition of a lower resistance decade has increased maximum measurement definition to $1\ \mu\text{ohm}$. The range of the instrument is 0 to 422 ohms.

NEW PATENTS

Semiconductors

WESTINGHOUSE ELECTRIC CORP. *British Patent* 888,829

A junction is formed in a silicon carbide single crystal by applying to a crystal of one conductivity type an alloy comprising palladium and/or rhodium and a doping impurity for converting a region of the crystal into a different conductivity type so that a junction between the region and the remainder of the crystal is produced. The alloy consists of 78.5-99.5% platinum, palladium and/or rhodium, and 10-0.5% lead, tin and/or bismuth.

Electrochemical Detectors

UNION CARBIDE CORP. *British Patent* 888,915

A detecting electrode comprising a strip of platinum having a number of bosses on both sides is used in an electrochemical detector device.

Catalysts

THE DISTILLERS CO. LTD. *British Patent* 888,999

A catalyst for selective hydrogenation of an acetylenically unsaturated compound to the corresponding ethylenically unsaturated compound is made by contacting a platinum group metal, supported on a carrier, with a solution of a lead compound in an organic solvent. Palladium on calcium carbonate, or on charcoal, or on barium sulphate may be used.

Electrode Structures

IMPERIAL CHEMICAL INDUSTRIES LTD. *British Patent* 889,147

An electrode structure consists of an anodically polarisable metal (titanium, titanium-base alloy, niobium, tantalum or alloy of titanium with niobium and/or tantalum), to the surface of which is secured a platinum group metal in reticulate