

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Constitution Diagrams of Alloys of Rhenium with Platinum Group Metals (Rhodium, Palladium, Iridium)

M. A. TYLKINA, I. A. TSYGANOVA and E. M. SAVITSKII, *Zhur. Neorg. Khim.*, 1962, 7, (8), 1917-1927

Constitution diagrams of the three systems were constructed after microscopic examination, thermal and X-ray analysis, and hardness measurements of a series of Rh-Re, Pd-Re and Ir-Re alloys. Diagrams of the peritectic type with two limited solid solutions were found in each case. There is no evidence of the formation of chemical compounds. The bigger the differences of the melting temperatures of Re and the Pt group metal, the lower is the temperature of the peritectic reaction and the greater the extent of the two-phase region. The physico-chemical properties of Re and the Pt metals and the relationships between them are discussed.

The Constitution Diagram of the Magnesium-Palladium System

E. M. SAVITSKII, V. F. TEREKHOVA and N. A. BIRUN, *Zhur. Neorg. Khim.*, 1962, 7, (10), 2367-2373

Various methods of physico-chemical analysis were used to construct the diagram. The system is characterised by the formation of the chemical compounds Mg_2Pd , Mg_4Pd , Mg_3Pd , Mg_5Pd_3 and $MgPd$. Mg_2Pd , Mg_4Pd and Mg_3Pd are formed by peritectic reactions at $700 \pm 10^\circ C$, $790 \pm 10^\circ C$ and $1130 \pm 10^\circ C$, respectively. Mg_2Pd_3 melts congruently at $1350 \pm 10^\circ C$ and $MgPd$ is formed from Mg_3Pd and Mg_2Pd_3 at $700 \pm 10^\circ C$. Eutectic reactions occur at $540 \pm 10^\circ C$ and ~ 27 wt.% Pd and at $1280 \pm 10^\circ C$ and $\sim 88-89$ wt.% Pd.

The Constitution Diagram of the System Molybdenum-Osmium

A. TAYLOR, N. J. DOYLE and B. J. KAGLE, *J. Less-Common Metals*, 1962, 4, (5), 436-450

X-ray diffraction and micrographic methods were used to examine alloys in the whole range of the system and the constitution diagram was constructed. The four single-phase fields observed are: (i) the b.c.c. α -Mo primary solid solution, (ii) the cubic intermediate β -phase based on Mo_3Os , (iii) the tetragonal σ -phase centred round Mo_2Os , and (iv) the terminal solid solution based on θ -Os. Lattice parameters were determined for α , β , σ and θ -phase alloys. The Mo-Os and W-Os systems are compared with alloys of Mo and W with other Pt metals.

On the Equilibrium Diagram of the System Bismuth-Rhodium

R. G. ROSS and W. HUME-ROTHERY, *J. Less-Common Metals*, 1962, 4, (5), 454-459

The equilibrium diagram was constructed by thermal analysis and X-ray examination of alloys with up to 50 at.% Rh. Only one modification of the compound Bi_4Rh was found, but two modifications of Bi_2Rh , with a transition temperature of $425^\circ C$, were identified. There was no evidence for the existence of Bi_3Rh . The NiAs-type structure of $BiRh$ was confirmed. Lattice spacings of $BiRh$ were measured up to $977^\circ C$.

Certain Alloys of Ruthenium with Molybdenum

G. A. GEACH, A. G. KNAPTON and A. A. WOOLF, *Powder Metallurgy in the Nuclear Age*, Plansee Proc., 1961, 750-758

Alloys over the full range of compositions were prepared by argon-arc melting and their cold working characteristics were studied. Maximum ductility was found with alloys containing 40-50 at.% Mo. The work-hardening, hot hardness and corrosion resistance of the 45 at.% Mo-Ru solid solution alloy were studied. The alloy may be cold-rolled or swaged, has good mechanical properties up to at least $1000^\circ C$, and is corroded only by alkaline oxidising solutions. A method for analysis of the alloy is given.

The Miscibility Gap in the System Silver-Iron-Palladium at 1000° , 1100° , and $1200^\circ C$

A. MUAN, *Trans. Met. Soc. A.I.M.E.*, 1962, 224, (5), 1080-1081

Phase relations in three isothermal sections (1000° , 1100° , $1200^\circ C$) were determined by studying 40 alloys within the Ag-Fe-Pd system by metallographic and X-ray methods. The miscibility gap originating along the Ag-Fe join of the isothermal sections decreases with increasing Pd content, but extends as far as ~ 75 wt.% Pd. All three sections show an area in which an alloy α of low Fe content is in equilibrium with an alloy β of low Ag content.

Tensile Properties of Refractory Metals at High Temperatures

C. A. BROOKES and B. HARRIS, *Powder Metallurgy in the Nuclear Age*, Plansee Proc., 1961, 712-722

Mechanical properties of Nb, Ta, W, Mo and Ir were measured in the range $0-2200^\circ C$ and their fracture mechanisms were studied. The variation of ultimate tensile strength, yield stress and percentage elongation as a function of temperature

for all the metals is shown in a series of graphs. Above 1000°C, Ir is stronger than Ta, Mo and Nb. Of the five metals, Ir is the most resistant to contamination in atmospheres containing oxygen and C.

Elevated-Temperature Properties of Rhodium, Iridium, and Ruthenium

R. W. DOUGLASS and R. I. JAFFEE, A.S.T.M. Preprint 65, 1962, 11 pp. (Paper presented at the 65th Annual Meeting of the A.S.T.M., June, 1962)

The tensile and short-time stress-rupture properties of Rh, Ir, and Ru were studied in vacuum in the temperature range 750°–1500°C. Rh, Ir and Ru have high strengths at high temperatures, Ir and Ru comparing favourably with W up to 1500°C. The tensile properties of Rh and Ru are affected by the testing atmosphere at 750° and 1000°C, respectively, and have higher strengths in vacuum than in air. The properties of Ir are unaffected by the atmosphere. Ir and Ru show intergranular failure over the testing temperature range.

The Mechanism of the Solubility of the Phases in the System Gold-Platinum

V. V. SANADZE, *Proc. Acad. Sci. U.S.S.R., Chem. Section*, 1961, **140**, (1–6), 889–892 (Transl. of *Doklady Akad. Nauk S.S.S.R.*, 1961, **140**, (1), 133–136)

Alloys containing 10 and 25 at.% Pt were studied by the method of successive quenchings. The mechanism of the solubility of the α_1 -solid solution, based on Pt, and the α_2 -solid solution, based on Au, is discussed in detail. It is concluded that Pt₃Au, PtAu and Au₃Pt are ordered states, not phases, arising on the course of the mutual solubility of the phases.

An Investigation of the Supercooling of Molten Metals

J. FEHLING and E. SCHEIL, *Z. Metallkunde*, 1962, **53**, (9), 593–600

The supercooling of molten Pd, Fe, Co, Ni, Cu, Au, Ag, Ge, and Ni-Pd, Ni-Cu and Ni-Au alloys was studied. The structures of the supercooled metals were investigated and the influence on their formation of low frequency vibrations and variations in the cooling rate was determined.

The "Invar" Properties of Iron-Palladium Alloys

K. JESSEN, *Ann. Physik*, 1962, **9**, (5/6), 313–315

Expansion measurements were made on Pd-Fe alloys containing 28–33 at.% Pd. The temperature range of lower thermal linear expansion, obtained by rapidly cooling the test specimens to 250°C, may be extended to 350°C by cold-working. Invar properties of the alloys are very unstable and disappear both as a result of heating and partially by cooling at low temperatures.

Magnetic Properties of a Chromium-Platinum Alloy with 30 At.% Chromium

A. J. P. MEYER and R. ASFELD, *Compt. rend.*, 1962, **254**, (25), 4266–4268

The alloy was obtained in the disordered state by quenching in H₂O from 1400°C and in the ordered state by annealing for 15 h at 950°C. A study was made, for both states, of the variation of magnetisation as a function of field, and of the paramagnetic behaviour below the ordering temperatures. The results are discussed briefly.

Electrical Resistivity and Thermoelectric Power of Palladium after Hydrogen Desorption

R. J. SMITH, A. I. SCHINDLER and E. W. KAMMER, *Phys. Rev.*, 1962, **127**, (1), 179–183

Resistance measurements were made between 4.2 and 300°K on Pd wires in the following conditions: unannealed, annealed, charged with hydrogen, and after hydrogen desorption. Thermoelectric power measurements were made between 77 and 273°K on specimens of Pd wire in the as drawn and annealed conditions and after hydrogen desorption. The desorbed samples showed an increase in the residual resistivity, a decrease in the value of dp/dT , and thermoelectric power values between those of annealed and cold-worked Pd. Experimental results are explained in terms of an observed expanded lattice.

The Effect of Iridium on the Mechanical and Electrical Properties of Palladium

A. A. RUDNITSKII and V. P. POLYAKOVA, *Zhur. Neorg. Khim.*, 1962, **7**, (10), 2361–2366

The properties of alloys with up to 30 wt.% Ir were studied. Results are given of various heat treatments on the hardness and strength of the alloys. All alloys with up to 25 wt.% Ir are easily cold-worked after quenching from 1400–1500°C without intermediate annealing. Measurements of electrical resistivity and its temperature coefficient confirmed that the solubility of Ir decreases from 30 wt.% above 1300°C to 10 wt.% and less below 700°C. Alloying with Ir increases the electrical resistivity of Pd and reduces its temperature coefficient.

Self-diffusion in Platinum

F. CATTANEO, E. GERMAGNOLI and F. GRASSO, *Phil. Mag.*, 1962, **7**, (Aug.), 1373–1383

Self-diffusion coefficients in Pt were obtained in the range 1250°–1725°C by measuring the decrease of activity at the surface of cylindrical specimens during diffusion.

The Effect of the State of the Surface on the Adsorption of Ions by Platinum

N. A. BALASCHOVA, *Electrochim. Acta*, 1962, **7**, (Sept./Oct.), 559–565

Radioactive tracers were used to study the effect of thermal and mechanical pretreatment and of

oxidation of a Pt surface on its adsorption of ions and on the kinetics of adsorption. The mechanism of the effect is explained in terms of the change in area of the real adsorbing surface and the penetration of ions into the Pt. It was found that oxygen adsorption is retarded by pre-adsorbed anions and *vice versa*.

A Study of the Mechanism of Carbon Monoxide Adsorption on Platinum by a New Electrochemical Procedure

S. GILMAN, Abstracts of Papers, 20T, Div. of Phys. Chem., 142nd Meeting, A.C.S., Atlantic City, N.J., Sept. 1962

The adsorption of CO from solution was studied as a function of the extent of surface coverage. From the information obtained, a lower limit was set on the rate of fast chemisorption of CO from solution and the nature of the CO-Pt bond was determined.

The Preparation and Properties of a Hydrous Ruthenium Oxide

C. J. KEATCHE and J. P. REDFERN, *J. Less-Common Metals*, 1962, 4, (5), 460-465

A method of preparing a compound with the empirical formula $\text{RuO}_2 \cdot \text{H}_2\text{O}$ is described. Results of a thermogravimetric study of the compound are given. Both the hydrous and the anhydrous material act as catalysts in the decomposition of 300 vol. H_2O_2 .

Xenon Hexafluoroplatinate (V) $\text{Xe}^+[\text{PtF}_6]^-$

N. BARTLETT, *Proc. Chem. Soc.*, 1962, (Jun.), 218

The formation of XePtF_6 , an orange-yellow solid, is reported. This charge-transfer compound is stable at room temperatures.

The Molecular and Crystal Structure of $\text{Os}_3(\text{CO})_{12}$

E. R. COREY and L. F. DAHL, *Inorg. Chem.*, 1962, 1, (3), 521-526

The crystal and molecular structure of $\text{Os}_3(\text{CO})_{12}$, determined by X-ray diffraction, is described in detail.

Hydrido- and Related Organo-complexes of Transition Metals

J. CHATT, *Proc. Chem. Soc.*, 1962, (Oct.), 318-326

Recent developments in the study of the bonding of hydrogen to transition metals and of the properties of hydrogen as an anionic ligand are described. Numerous complexes of the Pt metals are discussed.

Vaporisation of Ruthenium and Osmium

M. B. PANISH and L. REIF, *J. Chem. Phys.*, 1962, 37, (1), 128-131

Vapour pressures were determined by the use of Knudsen effusion and Langmuir vaporisation techniques. The vapour pressure of Ru over the temperature range 2000°-2500°K is given by the

equation $\log p_{\text{mm}} = 10.81 - 33480/T$, and that of Os over the temperature range 2300°-2800°K by the equation $\log p_{\text{mm}} = 10.85 - 40950/T$. Heats of vaporisation found by third-law analyses of data are: Ru, $\Delta H_{298}^\circ = 154.9 \pm 1.3$ kcal/mole, and Os, $\Delta H_{298}^\circ = 187.4 \pm 0.9$ kcal/mole. Estimated boiling points are: Ru, 4350° ± 100°K and Os, 5300° ± 100°K.

The System Iridium-Oxygen

I. Measurements on the Volatile Oxide of Iridium

E. H. P. CORDFUNKE and G. MEYER, *Rec. Trav. Chim.*, 1962, 81, (6), 495-504 (In English)

A transportation method was used to obtain partial pressure measurements of a volatile oxide of Ir. The dependence of the partial pressure of this oxide on the oxygen pressure was determined. Results indicate that the formula of the volatile oxide is IrO_3 . The equilibria: $2\text{Ir}_{(s)} + 3\text{O}_2 \rightleftharpoons 2\text{IrO}_{3(g)}$ and $2\text{IrO}_{2(s)} + \text{O}_2 \rightleftharpoons 2\text{IrO}_{3(g)}$ were measured as a function of the temperature.

II. The Dissociation Pressure of IrO_2

Ibid., (8), 670-678

Results obtained in the determination of the dissociation pressure of IrO_2 are explained by the formation of the non-stoichiometric oxide IrO_{2-x} . The composition of the IrO_{2-x} phase in equilibrium with Ir was determined as a function of the temperature. For the three-phase equilibrium $\text{IrO}_{2-x} - \text{Ir} - \text{O}_2$, $\log p_{\text{O}_2} (\text{mm}) = -11780/T + 11.487$. For stoichiometric IrO_2 , $\Delta H_{298.16^\circ\text{K}} = -65.5 (\pm 1.5)$ kcal/mole.

The Adsorption and Diffusion of Electrolytic Hydrogen in Palladium

M. A. V. DEVANATHAN and Z. STACHURSKI, *Proc. Roy. Soc., Series A*, 1962, 270, (1340), 90-102

An electrolytic technique for the measurement of the instantaneous rate of permeation of electrolytic hydrogen through Pd membranes is described. It was found that the diffusion constant is independent of thickness in the range 0.0035 to 0.054 cm and the permeation is inversely proportional to thickness. For hydrogen-poor α -Pd the diffusion constant is $1.30 \pm 0.20 \times 10^{-7}$ cm² sec⁻¹ at room temperature. Errors arising from classical time-lag methods are discussed.

A Study of the Kinetics of Heating Palladium-Hydrogen Alloys by the Pulse Heating Method

V. M. KUL'GAVCHUK, *Zhur. Fiz. Khim.*, 1962, 36, (8), 1713-1716 (English summary)

Results are given of determinations of the energy consumption prior to melting, the resistance at the melting point and the jump in resistance on the pulse heating of pure Pd and Pd saturated with hydrogen ($\text{PdH}_{0.78}$). Heating was carried out with 1 μ sec electric current pulses at peak current densities of 2.4×10^7 A/cm². The melting point

of $\text{PdH}_{0.78}$ was calculated as 1123°C . The temperature coefficient of resistance of liquid Pd was estimated.

ELECTROCHEMISTRY

Recent Studies of the Action of Inorganic Inhibitors

G. H. CARTLEDGE, *Corrosion*, 1962, **18**, (9), 316t-322t

Recent work on the nature of the anodic process to be suppressed is discussed and the influence of adsorption and semiconducting surfaces on the kinetics of the dissolution reaction is shown. The action of corrosion inhibitors of the type XO_4^{n-} ($\text{X}=\text{P}$, Cr, Mo, W, Tc, or Os) is considered. Mechanisms involved in inhibitor action include oxidation-reduction processes, electrochemical polarisation, adsorption and ion exchange, and electrostatic polarisation. (41 references)

A Solid Electrolyte Fuel Cell

J. WEISSBART and R. RUKA, *J. Electrochem. Soc.*, 1962, **109**, (8), 723-726

A galvanic cell with a solid $(\text{ZrO}_2)_{0.88}(\text{CaO})_{0.12}$ electrolyte and two porous Pt electrodes is described. The cell acts as a simple oxygen concentration cell. Experimental data are given for the reaction of oxygen with hydrogen/ H_2O and $\text{CH}_4/\text{H}_2\text{O}$ mixtures. Experimental and theoretical open-circuit voltages for the hydrogen-oxygen reaction are in close agreement, and current-voltage curves show that the cell output is limited essentially by the resistance of the electrolyte. It is possible that such cells may be used as fuel cells with hydrocarbons as fuel and oxygen or air as oxidant.

Anodic Protection of Austenitic Stainless Steels in Sulphuric Acid-Chloride Media

S. J. ACELLO and N. D. GREENE, *Corrosion*, 1962, **18**, (8), 286t-290t

Studies on the anodic protection of Types 304 and 310 stainless steels showed that stress-corrosion cracking of 18Cr-8Ni stainless steel in 10 N H_2SO_4 plus 0.5 N NaCl may be prevented by maintaining the metal in the passive region by impressed anodic currents. A Pt wire auxiliary electrode was used. The stress-corrosion cracking is potential-dependent and is initiated in the active state. Chloride solutions up to 0.1 N do not greatly affect the passive or transpassive dissolution behaviour of the steels in H_2SO_4 .

Passivating Effect of Chemisorbed Oxygen on the Anodic Oxidation of Molecular Hydrogen at Platinum

M. W. BREITER, *Electrochim. Acta*, 1962, **7**, (Sept./Oct.), 601-611

The oxygen coverage of a smooth Pt wire electrode was determined by cathodic charging curves at

different potentials under the conditions of periodic, low-speed, potentiostatic current/potential curves in 1N HClO_4 , with hydrogen or argon stirring, between +0.6V and +1.5V. It was shown that most of the passivation is caused by a small oxygen coverage. (33 references)

Use of a Precious Metal Anode in the Electrowinning of High-Purity Chromium from a Fluoride Bath

J. A. WHITTAKER, *J. Electrochem. Soc.*, 1962, **109**, (10), 986-987

The use of a Pd anode instead of a 7% Sn-Pb anode in the production of electrolytic Cr resulted in a decrease in efficiency of the CrO_3 bath and an increase in the bath resistance. These disadvantages may be overcome by saturating the bath with PbCrO_4 and by preforming PbO_2 anodically on the Pd anode.

Halogen Electrodes on Carbon and Platinum Powders

W. TOMASSI and M. JANIKOWNA, *Przemysl Chem.*, 1962, **41**, (8), 449-451 (English summary).

It was found in an investigation of the behaviour of C and Pt powder electrodes in the chlorine, bromine and iodine electrode systems that only the iodine electrode always reached the state of equilibrium. A relationship was established between the deviation of the stationary state from the equilibrium state and the value of the dissociation energy of halogen molecules, as well as the ability of the powder to adsorb these molecules.

Overvoltage and the Hydrogen Content of Palladium Cathodes

J. C. BARTON and F. A. LEWIS, *Z. Phys. Chem. (Frankfurt)*, 1962, **33**, (1-4), 99-110 (In English)

The relative electrical resistance, R/R_0 (where R_0 = the initial resistance of hydrogen-free Pd), and electrode potentials of hydrided Pd wires were measured at 25°C during and after cathodisation in hydrogen-saturated HCl. The wires had received various pre-activation treatments. It was shown that for current densities $< 0.1 \text{ A/cm}^2$, the rate at which hydrogen molecules can diffuse from the electrode surface controls the component of the overvoltage of static, catalytically active electrodes, itself a function of their hydrogen content.

The Role of Surface Films in the Kinetics of Oxygen Evolution at Palladium-Gold Alloy Electrodes

J. J. MACDONALD and B. E. CONWAY, *Proc. Roy. Soc., Series A*, 1962, **269**, (1338), 419-440

Anodic oxygen evolution was studied on Pd, Au, and Pd-Au alloys containing 21, 35.1, 40, 45.1, 60 and 75 at.% Pd in ultra-pure H_2SO_4 and KOH solutions. In KOH, with Au and the Au-rich alloys, a transition region in the current-potential relation was observed which probably corresponds

to a limiting high coverage of the active surface with adsorbed reaction intermediates and to the onset of passive behaviour. Results obtained in H_2SO_4 indicate that the discharge process involves H_2O rather than OH^- ions.

LABORATORY APPARATUS AND TECHNIQUE

Susceptor Elements for High Temperature Induction Heating

S. HASKO and H. S. PARKER, *Bull. Amer. Ceram. Soc.*, 1962, **41**, (7), 467-469

The design and fabrication of susceptors produced from Ir and W powders, and sheet W, Ta, Mo, and 20% Rh-Pt, are described. Advantages and disadvantages of crucible, ring-type and sandwich-type susceptors used for heating small specimens *in vacuo*, and in oxidising, inert, and reducing atmospheres, are discussed. Temperatures up to 2300°C in air and >2600°C in helium were attained with Ir and W susceptors, respectively

METAL WORKING

A New Brazing Alloy for Age-Hardenable Super Alloys

J. F. BARKER, P. R. MOBLEY and T. K. REDDEN, *Welding J. (Research Suppl.)*, 1962, **41**, (9), 409S-412S

J-8600 alloy containing 33% Cr, 24% Pd, 4% Si, balance Ni has been developed for brazing super alloys such as René 41. The brazing alloy shows good wetting and flow properties without eroding or embrittling the base metal when used on René 41 *in vacuo* at 2150°F. J-8600 alloy has high temperature strength comparable to that of other brazing alloys and has been used successfully in prototype jet engines.

CATALYSIS

Catalytic Decomposition of Acid Hydrogen Peroxide Solutions on Platinum, Iridium, Palladium and Gold Surfaces

G. BIANCHI, F. MAZZA and T. MUSSINI, *Electrochim. Acta*, 1962, **7**, (Jul./Aug.), 457-473

The decomposition of H_2O_2 (10^{-4} to 10^{-1} M) was studied in 0.5 M H_2SO_4 and M HCl solutions at 25°C using Pt, Ir, Pd and Au disc electrodes as catalysts. It was found that in H_2SO_4 solution, Pt, Ir and Pd catalyse the reaction, but Au is inactive; in HCl solution, none of these metals is catalytically active. The catalytic activity is found only when the metal surface is covered with a film of oxide, and is prevented by the formation of complexes. The reaction mechanism is explained.

Reaction of Sodium Borohydride with Platinum Metal Salts in the Presence of Decolourising Carbon - A Supported Platinum Catalyst of Markedly Enhanced Activity for Hydrogenations

H. C. BROWN and C. A. BROWN, *J. Amer. Chem. Soc.*, 1962, **84**, (14), 2827

A method of preparing *in situ* Ru/C, Rh/C, Pd/C, Os/C, Ir/C, and Pt/C catalysts is described. In the hydrogenation of 1-octene, the activities of Rh/C, Pd/C and Pt/C are greater than those of the corresponding unsupported metals; however, the activities of Ru, Os and Ir are decreased by the presence of the C support. The rate of hydrogenation of several unsaturated hydrocarbons over the Pt/C catalyst is 200 to 400% greater than that observed with an unsupported Pt catalyst.

Hydrogenation of Nitroaromatics in the Presence of the New Platinum Metal and Carbon-Supported Platinum Metal Catalysts

H. C. BROWN and K. SIVASANKARAN, *Ibid.*, 2828

Unsupported and C-supported Ru, Rh, Pd, Os, Ir and Pt catalysts were prepared *in situ* and evaluated for the hydrogenation of $C_6H_5NO_2$. Results showed that both supported and unsupported Pd and Pt are the most active catalysts for the reaction. The catalysts prepared *in situ* are almost twice as active as commercial Pd/C and Pt/C. A number of nitroaromatics were converted to the corresponding amines using the new Pt/C catalyst.

The Surface Chemistry of Ethylene on Alumina and Platinum/Alumina

V. KEVORKIAN, J. L. CARTER and P. J. LUCCHESI, Abstracts of Papers, 10-1, Div. of Colloid and Surface Chem., 142nd Meeting, A.C.S., Atlantic City, N.J., Sept. 1962

The surface chemistry, adsorption kinetics, and energetics of C_2H_4 on Al_2O_3 and Pt/ Al_2O_3 were studied at 250°C in a differential isothermal microcalorimeter and infra-red spectrometer. Adsorption heats on both catalysts change from exothermic to endothermic with increasing coverage because of extensive surface reactions. Infra-red analysis indicates that on Al_2O_3 the chemisorbed ethyl group ($S-C_2H_5$) appears first, and the sideways-held form ($S-CH_2-CH_2-S$) appears second. Over Pt/ Al_2O_3 , both forms appear at the onset of adsorption. C_2H_4 self-hydrogenates on Pt/ Al_2O_3 .

Deuterium Tracer Studies of the Mechanism of Homogeneous Catalytic Hydrogenation

J. HALPERN and B. R. JAMES, Abstracts of Papers, 23N, Div. of Inorg. Chem., 142nd Meeting, A.C.S., Atlantic City, N.J., Sept. 1962

A study of the isotopic exchange of deuterium with aqueous solutions of $RuCl_3$ suggested that the principal exchange path involves the heterolytic splitting of deuterium by the catalyst, i.e.,

$\text{Ru}^{\text{III}} + \text{D}_2 \rightleftharpoons \text{Ru}^{\text{III}}\text{D}^- + \text{D}^+$. Other reactions studied include (i) the isotopic exchange between deuterium and H_2O , catalysed by Ru(II)-olefin complexes and (ii) RuCl₂-catalysed homogeneous hydrogenation of fumaric acid to succinic acid. The mechanism of reaction (ii) is discussed.

Reductions with Ruthenium Catalyst

III. Hydrogenation of Nuclear Substituted Anilines

M. FREIFELDER and G. R. STONE, Abstracts of Papers, 8-O, Div. of Medicinal Chem., 142nd Meeting, A.C.S., Atlantic City, N.J., Sept. 1962. The effect of nuclear substituents on conversion of the benzene ring to the cyclic structure was studied. In addition, the effect of the Ru catalyst on groups that may undergo hydrogenolysis under the reaction conditions (90°C and 70 atm pressure) was investigated. N-Methylaniline and ethyl N-phenylglycinate were hydrogenated to compare the effects of mono- and di-substitution.

On the Mechanism of Thermal Decomposition of Nitrous Oxide at a Platinum Filament

N. R. MURTY, *Naturwiss.*, 1962, **49**, (19), 447-448. The thermal decomposition of N_2O at a Pt filament at 970°C followed an apparent zero order rate. During the course of the reaction the Joshi effect, $\pm \Delta i$, was studied. The mechanism proposed for the reaction involves the chemisorption of oxygen and the formation on the catalyst surface of a labile electrogenative radical due to the interaction of the chemisorbed atomic oxygen on the Pt surface and nitrogen in the gas phase.

Decomposition of *n*-Propane and *n*-Butane on Clean Rhodium Foils

R. W. ROBERTS, *J. Phys. Chem.*, 1962, **66**, (9), 1742-1743

The decomposition reactions were carried out at 27° and 100°C on Rh films about 50 Å thick deposited by pulse evaporation on the inside of a Pyrex sphere. It was found that both *n*-C₃H₈ and *n*-C₄H₁₀ decompose in these conditions to give lower hydrocarbons and an adsorbed hydrocarbon residue. The primary reaction product for both saturated hydrocarbons is CH₄. Adsorbed gases reduce the activity of the Rh films.

The Effect of Adsorbed Oxygen on the Catalytic Activity of Platinum and Platinum-Gold Alloys in the Conversion of Para-Hydrogen

D. MENZEL and L. RIEKERT, *Z. Elektrochem.*, 1962, **66**, (5), 432-439

The conversion reaction was studied at temperatures in the range 170-500°K with Pt and 5, 10 and 20 at. % Au-Pt alloy catalysts, and at >800°K with 75 and 90 at. % Au-Pt catalysts. The dependence of the reaction rate on the pretreatment of the catalysts with oxygen and hydrogen was investigated. Pretreatment of the 5, 10 and 20 at. %

Au-Pt alloys had less effect on their catalytic activity than on that of Pt. The lower activity of the 75 and 90 at. % Au-Pt alloys and of pure Au could not be measured accurately.

Dehydrogenation of Normal Alcohols

W. ZABLOTNY and M. I. SMIRNOW, *Przemysl Chem.*, 1962, **41**, (7), 386-388 (English summary)

A spiral of Ni-Cr wire covered with Pt was used as the catalyst in the dehydrogenation of ethyl, *n*-propyl, *n*-butyl and *n*-amyl alcohols. Reaction constants and activation energies were computed from experimental results. Gas analysis of the reaction products showed that dehydration of the alcohols and thermal decomposition of the aldehydes obtained occurred to only a small extent.

Comparison of Hydrogen Isotope Exchange, Para-Hydrogen Conversion and Oxyhydrogen Gas Combustion in Aqueous Suspensions of Noble Metal/Activated Charcoal Catalysts

U. SCHINDEWOLF, M. KENAWY and E. G. MAHADEVAN, *Z. Elektrochem.*, 1962, **66**, (5), 406-412

Aqueous suspensions of Pt/C and Pd/C were used as catalysts for the isotope exchange between hydrogen and water, para-hydrogen conversion, and oxyhydrogen gas combustion at pressures < 1 atm and at room temperature. A study of the reaction processes leads to the assumptions that the three reactions are initiated by the catalytic activation of hydrogen and that the chemisorption of hydrogen is proportional to the pressure.

Palladium-Catalysed Decarbonylation of *trans*- α -Substituted Cinnamaldehydes

N. E. HOFFMAN, A. T. KANAKKANATT and R. F. SCHNEIDER, *J. Org. Chem.*, 1962, **27**, (7), 2687-2689

A 10% Pd/C catalyst was used in the decarbonylation of several *trans*- α -substituted cinnamaldehydes. It was found that *cis*-olefins predominate if the product is distilled rapidly after formation, but that *trans*-olefins result from isomerisation of the *cis*-olefins if the product is distilled only after decarbonylation is complete.

Palladium - Catalysed Hydrogenation of Pyridines

G. N. WALKER, *J. Org. Chem.*, 1962, **27**, (8), 2966-2967

It has been found that 10% Pd/C may be used as a catalyst for the reduction of pyridines to the corresponding piperidines at reaction temperatures and pressures of 70-80°C and 3-4 atm, respectively. Compounds closely related to known central stimulants have been produced.

Hydrogenation-Hydrogenolysis Studies of Symmetrically Substituted 1, 4-Acetylenic Glycols

R. J. TEDESCHI, *J. Org. Chem.*, 1962, **27**, (7), 2398-2402

Hydrogenation of the 1, 4-acetylenic glycols was

carried out at 55–85°C and 30–55 p.s.i. using a 5% Pd/C catalyst. The addition of small amounts of base such as KOH, NaOH, or $(\text{CH}_3\text{CH}_2)_3\text{N}$ before hydrogenation was found to inhibit hydrogenolysis side reactions, and high yields of olefinic and saturated diols were obtained. A route for the hydrogenolysis is given.

Selective Hydrogenation of Methyl Oleate Ozonolysis Products by Palladium in Pyridine-Methanol Solvent

E. H. PRYDE, D. E. ANDERS, H. M. TEETER and J. C. COWAN, *J. Org. Chem.*, 1962, 27, (9), 3055–3059

The presence of $\text{C}_6\text{H}_5\text{N}$ improved the yield of methyl azelaaldehyde when the ozonolysis products were hydrogenated over a Pd/C catalyst at room temperature and 1 atm. $\text{C}_6\text{H}_5\text{N}$ poisoned the catalyst for hydrogenation of olefinic unsaturation. Unused methyl oleate could be recovered.

Stereochemistry and the Mechanism of Hydrogenation of Cyclo-alkenes. IV. 4-tert-Butyl-1-methylcyclohexene and 4-tert-Butyl-1-methylenecyclohexane on Platinum Oxide and a Palladium Catalyst

S. SIEGEL and B. DMUCHOVSKY, *J. Amer. Chem. Soc.*, 1962, 84, (16), 3132–3136

The hydrogenation reactions were carried out in CH_3COOH using PtO_2 , 5% $\text{Pt}/\text{Al}_2\text{O}_3$ and 5% $\text{Pd}/\text{Al}_2\text{O}_3$ catalysts. It was found that the ratio of the saturated stereoisomers obtained with reduced PtO_2 catalyst is a function of the pressure of hydrogen. The extent of isomerisation of the alkene varies with the catalyst used and occurs in the order: $\text{Pd}/\text{Al}_2\text{O}_3 > \text{Pt}/\text{Al}_2\text{O}_3 > \text{PtO}_2$. It is assumed that with a Pd catalyst the rate-limiting surface reaction occurs at a later stage than with a Pt catalyst.

The Stereochemistry of the Hydrogenation of the Isomeric Xylenes and p-tert-Butyltoluene over a Platinum Catalyst

S. SIEGEL, G. V. SMITH, B. DMUCHOVSKY, D. DUBBELL and W. HALPERN, *J. Amer. Chem. Soc.*, 1962, 84, (16), 3136–3139

Hydrogenation over reduced PtO_2 in CH_3COOH at 25°C produced a mixture of *cis*- and *trans*-dialkylcyclohexanes. The *cis/trans* ratio is a function of the structure of the substrate and the pressure of hydrogen. Comparison of the experimental results with the stereochemistry of the hydrogenation of the related cycloalkenes suggests that the latter are intermediates in the reduction of the aromatic cycle.

Oxidation of Ethylene to Acetaldehyde by the Direct Oxidation Process

G. BERGER and R. MITTAG, *Erdöl u. Kohle*, 1962, 15, (9), 699–702

Technical details are given of the one-cycle and two-cycle processes for the production of

CH_3CHO in which a $\text{PdCl}_2/\text{CuCl}_2$ oxidation catalyst is used. The yield and quality of the CH_3CHO obtained is described.

Ethylene Enters a New Field

H. C. BOZEMAN, *Oil & Gas J.*, 1962, 60, (42), 216–221

The Celanese Chemical Co.'s plant at Bay City, Texas, is described. CH_3CHO is produced by the direct oxidation of C_2H_4 , using a PdCl_2 catalyst, in the two-stage Wacker process. CH_3CHO is used as the raw material for the production of 2-ethyl hexanol and *n*-butanol.

The Kinetics of the Oxidation of Cyclohexene by Palladium Salts in Aqueous Solutions

M. N. VARGAFIUK, I. I. MOISEEV and YA. K. SYRKIN, *Proc. Acad. Sci. U.S.S.R., Phys. Chem. Section*, 1961, 139, (1–6), 634–636 (Transl. of *Doklady Akad. Nauk S.S.S.R.*, 1961, 139, (6), 3196–3199)

The oxidation reaction was studied in the temperature range 7.0° to 30.3°C in the presence of *p*-benzoquinone which oxidised the metallic Pd formed from the PdCl_2 catalyst. Confirmation of an earlier assumption that the reaction proceeds through the formation of a π -complex is provided by the results of the kinetic study.

The Reactions of Olefins with Aqueous Solutions of Palladium Salts

W. HAFNER, R. JIRA, J. SEDLMEIER and J. SMIDT, *Chem. Ber.*, 1962, 95, (7), 1575–1581

Experimental work was carried out to investigate the mechanism of the reactions. The effects of acids and complex ligands upon the course of the reaction were traced to the different polarisation of the unsaturated compounds in the respective Pd complexes. Solutions of K_2PdCl_4 were used in the oxidation of propylene and hept-1-ene.

A Method for the Reactivation of Noble Metal Catalysts

H. KÖGLER and S. QUECK, *Chem. Techn.*, 1962, 14, (9), 541–545

The method described for reactivating spent $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts involves treatment with a solution of NH_4Cl and NH_4NO_3 followed by heat treatment in an oxidising medium. It appears that spent catalysts may be successfully reactivated several times by this method.

Catalytic Oxidation of Automotive Exhausts

W. A. CANNON and C. E. WELLING, *Ind. Eng. Chem. (Product Res. & Dev.)*, 1962, 1, (3), 152–156

A laboratory method for evaluating catalysts for the oxidation of simulated exhaust gas mixtures is described in detail. Catalysts found to be satisfactory for complete oxidation of simulated exhausts from unleaded gasolines include Mn-Cu oxides, Cu chromite, $\text{Ag}_2\text{O}-\text{BaO}_2$, promoted Fe_2O_3 , CuO , V_2O_5 , and supported Pt and Pd. Phase changes and decreased activity of Mn-Cu

oxides, $\text{Ag}_2\text{O}-\text{BaO}_3$, and Cu-promoted Fe_2O_3 on heating to 760°C for 16 h indicate that these catalysts may be unsuitable under actual operating conditions.

Mechanism of the Transformations of Cyclohexene and 1, 3-Cyclohexadiene on Platinum Films

V. M. GRYAZNOV and V. I. SHIMULIS, *Proc. Acad. Sci. U.S.S.R., Chem. Section*, 1961, **139**, (1-6), 749-752 (Transl. of *Doklady Akad. Nauk S.S.S.R.*, 1961, **139**, (4), 870-873)

Experimental results show that both cyclohexene and 1, 3-cyclohexadiene exhibit simultaneous hydrogenation and dehydrogenation on Pt films at 20°C . At low pressures the dehydrogenation predominates, but as the hydrogen accumulates, the hydrogenation rate increases. The mechanism of the reactions is discussed.

Refining-Petrochemical Centre

G. L. FARRAR, *Oil & Gas J.*, 1962, **60**, (27), 100-104

The layout and operation of the El Paso Natural Gas Products-Rexall Drug & Chemical installations at Odessa, Texas, are described. Among the many units are a Platformer operated for the production of aromatic hydrocarbons and a motor-fuel Platformer.

The Refining Hydrogenation and Catalytic Reforming Plant of Homs Refinery (Syria)

Z. KOPELENT, *Chem. Techn.*, 1962, **14**, (8), 451-456

The operation of this refinery, which went on stream in 1959, is described in detail. The refinery comprises two main units, a hydrogenation plant and a catalytic reforming plant in which a Pt catalyst is used.

An Improved Platinum Catalyst for Hydrogenation of an Olefin

R. W. BOTT, C. EABORN, E. R. A. PEELING and D. E. WEBSTER, *Proc. Chem. Soc.*, 1962, (Oct.), 337

The catalyst was prepared by adding 0.01 m mole H_2PtCl_6 in 95% aq. $\text{C}_2\text{H}_5\text{OH}$ to a solution of 0.1 m mole tribenzylsilane in 95% aq. $\text{C}_2\text{H}_5\text{OH}$ at 70°C . In the hydrogenation of oct-1-ene at 30°C this catalyst was found to be more active than Adams' (PtO_2) catalyst or Brown and Brown's catalyst (*J. Amer. Chem. Soc.*, 1962, **84**, (8), 1493-1495). However, it is less active than Adams' catalyst in the hydrogenation of C_6H_6 , Trichloro-, triethyl-, tri-*n*-butyl-, and triphenylsilane were also used to reduce H_2PtCl_6 with the formation of catalysts of similar activity to the one described.

Particle Size Determination of Supported Catalytic Metals: Platinum on Silica Gel

C. R. ADAMS, H. A. BENESI, R. M. CURTIS and R. G. MEISENHEIMER, *J. Catalysis*, 1962, **1**, (4), 336-344

Results are given of particle size determinations of

a Pt/ SiO_2 gel catalyst which were obtained by using electron microscope, X-ray diffraction, and adsorption techniques. All three methods give comparable results. Applications and limitations of the methods are discussed.

The Catalytic Properties of Borides of Platinum Group Metals

B. D. POLKOVNIKOV, A. A. BALANDIN and A. M. TABER, *Doklady Akad. Nauk S.S.S.R.*, 1962, **145**, (4), 809-811

Borides of Pd, Pt, and Rh were prepared and their catalytic activity in the liquid-phase hydrogenation of various unsaturated organic compounds was compared with that of Pd black, Pt black, and Rh black. Hydrogenations were carried out at 20°C in CH_3OH . The boride catalysts showed greater activity and stability than the corresponding "black" catalysts in the reactions reported. The activity of the boride catalysts was found to be in the order: Pd-B > Pt-B > Rh-B.

CATHODIC PROTECTION

The Use of Platinised Titanium in a New Form for Marine Cathodic Protection Installations

ANON., *Corrosion Prevention & Control*, 1962, **9**, (10), 51-54

Two forms of strip anode are described and their advantages are pointed out. One type consists of a Ti strip platinised on the side exposed to the seawater and located in a plastic backing. The second type is a $\frac{1}{2}$ in. diameter Cu-cored platinised Ti rod sheathed with perforated PVC.

CHEMICAL TECHNOLOGY

On the Use of Palladium Osmosis Tubes

R. W. CROMPTON and M. T. ELFORD, *J. Sci. Instr.*, 1962, **39**, (9), 480-481

Precautions to be observed in the use of Pd diffusion (osmosis) tubes for the purification of hydrogen are discussed. Cracking of the tubes due to the α - to β -phase transition when Pd is heated or cooled in hydrogen, leaking of the seal between the tube and the vacuum system, and reduction of the diffusion rate during operation are avoided by adopting these precautions. The advantages of using Ag-Pd diffusion tubes are mentioned.

ELECTRICAL ENGINEERING

Improving Reliability of Microcircuit Connectors

J. R. ANDERSON and J. B. SAUNDERS, *Electro-Technol.*, 1962, **70**, (4), 74-78

The use of monolayer boundary lubricants to

reduce friction and wear between contact metals is discussed. Data are given for the coefficient of friction, wear track width and contact resistance of several unlubricated metal pairs (Au on Pd, Pt on Pd, Au on Au, Pt on Au, Au on Rh, Pt on Rh, and Pt on Ag) for loads of 2-50 g. Octadecylamine hydrochloride, octadecylamine, stearic acid, and iodide films were evaluated as lubricants for various noble metal pairs.

TEMPERATURE MEASUREMENT

Precision Method of Measurement for Testing the Thermal-E.M.F. Temperature Dependence of Platinum - Rhodium : Platinum Thermocouples by Comparison with a Standard Thermocouple

W. HEYNE, *Feingerätetechn.*, 1962, **11**, (9), 400-402
A method of measurement suitable for use with noble metal thermocouples is described and contrasted with the conventional method. It is claimed that the new method of comparison of similar thermocouple limbs is the quicker and more accurate of the two.

Effect of Thermal Neutron Irradiation on Thermocouples and Resistance Thermometers

C. W. ROSS, *A.I.E.E. Trans., Part 1, Communications & Electronics*, 1962, (July), 192-196

The results are given of a study of the effect of

transmutations due to neutron adsorption on the accuracy of Pt:10% Rh-Pt thermocouples and of Cu, Pt and Ni resistance thermometers. It was found that the thermal e.m.f. of a Pt:10% Rh-Pt thermocouple is decreased by thermal neutron irradiation, largely as a result of the transmutation of Rh. Increases in resistance of Cu, Pt and Ni due to transmutations are in the order: Cu>Pt> Ni. Methods for estimating the resulting errors in temperature measurement are given.

Thermoelectric Instability of Some Noble Metal Thermocouples at High Temperatures

B. E. WALKER, C. T. EWING and R. R. MILLER, U.S. Naval Research Laboratory Report NRL 5792, June 1962, 19 pp.

The thermoelectric instabilities of Al₂O₃-sheathed individual thermoelements and thermocouples of Pt, Rh, Ir, 50% Ir-Rh, and some Rh-Pt alloys were studied in the temperature range 1000°-1700°C in argon and in air. Compositional changes in the thermal gradient zone of the thermocouple material are the main cause of instability. Fe originating in the Al₂O₃ sheathing tubes is the main contaminant of Rh-Pt thermocouples and the resulting instability is greater in argon than in air. Internal changes are the main cause of instability of pure Rh, Ir, and 50% Ir-Rh thermoelements; Ir and 50% Ir-Rh have excellent resistance to Fe contamination. In argon, stability of Rh-Pt thermocouples is increased by increasing the wire size, but in air it is independent of wire size.

NEW PATENTS

Cathodic Protection of Ships

H. S. PREISER *British Patent* 902,667

An anodic assembly for use in cathodic protection of a ship's hull consists of a rod of platinum or of copper, or a silver-copper alloy, coated with platinum or palladium connected to an insulated cable so that the rod can trail behind the ship.

Production of Aromatic Nitriles

CALIFORNIA RESEARCH CORP. *British Patent* 902,880

Aromatic nitriles are made by contacting in the vapour phase an alkyl substituted aromatic hydrocarbon (7-15 carbon atoms per molecule) with ammonia and air at 300°-650°C in the presence of a composite catalyst consisting of at least 1% of a heavy metal oxide, e.g. vanadium pentoxide and at least 0.01% by wt. of platinum.

Hydrocarbon Conversion Catalyst

STANDARD OIL CO. *British Patent* 903,773

A reforming catalyst is made by impregnating an

alumina and/or silica support with compounds of germanium and of platinum and heating the support at over 800°F (900°-1800°F) to form a solid solution comprising germanium and platinum and containing at least 5% each of germanium and platinum, the finished catalyst containing 0.1-10% by wt. of the solid solution.

Reduction of Pyridine and Salts thereof

ABBOTT LABORATORIES *British Patent* 904,117

Piperidine or a salt thereof is made by hydrogenating pyridine or a salt thereof in the presence of rhodium (0.05-2% by wt. based on wt. of starting material) at a pressure below 125 p.s.i. and a temperature between room temperature and 150°C.

Hydrogenation of Aromatic Hydrocarbons

UNIVERSAL OIL PRODUCTS CO. *British Patent* 904,732

In the hydrogenation of aromatic hydrocarbons with hydrogen at elevated temperature of not