

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

On the Thermal Expansion Coefficient and the Temperature Coefficient of Young's Modulus of the Alloys of Iron and Platinum

H. MASUMOTO and T. KOBAYASHI, *J. Japan Inst. Met.*, 1963, 27, (9), 459-460

53.5 to 57.0% Pt alloys with Fe have negative coefficients of thermal expansion with a maximum value of -23.68×10^{-6} for 56% Pt alloy at 0 to 40°C. 51 to 69% Pt alloys have positive temperature coefficients of Young's modulus with a maximum value of $+161.5 \times 10^{-6}$ for 55% Pt alloy in the same temperature range. A vertical dilatometer and a vibrator-controlled oscillator with an electrostatic transducer were used for the respective measurements.

Theory of Hydrogen Adsorption on Platinum

T. TOYA, *J. Res. Inst. Catalysis Hokkaido Univ.*, 1962, 10, (3), 236-260

There are two types of H adsorption on Pt. r-type adsorption increases the work function and electrical resistance of clean Pt while s-type adsorption decreases them. The total effect on Pt is complex as the difference between the two heats of adsorption is only 0.4 kcal/mol whereas for Ni, which behaves similarly, it is 10 kcal/mol. The positions and entropies of the two types of adsorption are discussed. The broad, intense infra-red band at 4.86μ in the spectrum of H on Pt is caused by s-type adsorption and the sharp, weak band at 4.74μ by r-type adsorption.

Ultra-pure Hydrogen by Diffusion through Palladium Alloys

J. B. HUNTER, *Abs. Papers, 145th Meeting, Am. Chem. Soc.*, 1963, 128-130

The development of a stable, highly permeable alloy of Pd has led to its industrial application in a variety of diffusion units. H₂ transfer rate data are presented for wide ranges of pressure and temperature.

Magnetic and Dilatometric Measurements on the Transformation Kinetics of the Iron-Palladium Alloys

A. KUSSMAN and K. JESSEN, *Z. Metallkunde*, 1963, 54, (9), 504-510

Studies on γ - α transformations and γ_1 - γ_2 ordering confirmed the existence of a miscibility gap between 10 and 25 at.% Pd-Fe alloys at high temperatures. The critical temperature curve for γ_1 - γ_2 ordering showed a maximum at 800°C, 65 at.% Pd. A eutectoid occurred at 46 at.% Pd,

605 ± 8°C. The effects of variations in the treatment of the alloys were also studied. Fe-Pd alloys behaved similarly to Ni-Fe alloys after quenching, particularly by showing an Invar effect.

The Iron-Palladium Phase Diagram below 950°C

E. RAUB, H. BEESKOW and O. LOEBICH, *Z. Metallkunde*, 1963, 54, (10), 549-552

The results of room- and high-temperature X-ray analysis of the Fe-Pd system are tabulated. No γ/α eutectoid was observed but a miscibility gap extended from 7 to 23 at.% Fe, with a critical temperature of about 900°C. A eutectoid between α -Fe and the γ_1 phase was confirmed at about 620°C, 43 at.% Fe. The two ordering phases γ_1 and γ_2 were separated by a narrow two-phase region below a eutectoid area. γ_2 has a higher critical temperature than γ_1 . (820 ± 20°C and 790 ± 20°C).

On the Structural Form of Copper-Palladium Solid Solutions near the Composition Cu₃Pd

A. A. PRESNYAKOV, L. I. DAUTOVA and E. A. DZHANBUSINOV, *Fiz. Met. Metalloved.*, 1963, 16, (1), 61-64

28.8 at.% Pd-Cu alloy samples were tempered at 750°C, annealed and studied by X-ray methods. The crystal lattice structure is discussed. At high temperatures a structure was detected which indicated the existence of a new phase but its lattice parameters were not determined.

Properties of Palladium-Rhenium Alloys

M. A. TYLKINA and I. A. TSYGANOVA, *Zh. Neorg. Khim.*, 1963, 8, (10), 2346-2350.

Additions of up to 11.9 wt.% Re increased the hardness and strength and the specific electrical resistance of Pd but decreased the temperature coefficient of resistance. Re also raised the initial temperature of recrystallisation of Pd; by up to 600°C in the case of 8.74 wt.% Re-Pd. Annealing studies on Re-Pd showed that higher temperatures reduced the hardness and strength but improved the elastic properties of the alloys. Electrical properties were unaffected by the annealing treatments.

The Temperature Dependence of the Magnetic Susceptibility of Some Palladium Alloys

W. KÖSTER, D. HAGMANN and R. LUECK, *Ann. Physik*, 1963, 11, (1-6), 52-58

Temperature-reciprocal paramagnetic susceptibility curves for Pd alloys with up to 4 at.% Ru or 10 at.% Cd, In or Rh between 120 and 1100°K

agreed with the transport aspects of Stoner's theory of paramagnetism. Various explanations of the electron specific heat-susceptibility discrepancy in Pd showed that no one definition of Stoner's parameters θ_F , q , θ^1 was possible. An approximation using the reciprocal temperature coefficient of the reciprocal susceptibility explained vacancy variations in the alloys but this quantity was not the same as the Curie constant unless $T \gg \theta_F$. The rigid band model gave a partial interpretation of the results.

Hysteresis in the Palladium-Hydrogen System

N. A. SCHOLTUS and W. K. HALL, *J. Chem. Phys.*, 1963, **39**, (4), 868-870

When H_2 dissolves in Pd, the α phase forms first. The β phase nucleates and grows in this causing plastic deformation of the α phase beyond its elastic limit because of the large $\alpha \rightarrow \beta$ volume change. Absorption is accompanied by β phase growth under α phase compression but desorption takes place from the β phase of the plastically deformed solid. This is not reversible and hysteresis occurs. Earlier theories are discussed. The absorption loop of the isotherm is calculated from the desorption loop and the yield strength of Pd.

Role of Hydrogen Atoms in Palladium

T. TSUCHIDA, *J. Phys. Soc. Japan*, 1963, **18**, (7), 1016-1019

Ag-Pd alloys are similar in electronic structure to Pd but do not have the narrow regions of H_2 content stability of pure Pd. Measurements of the Hall coefficient and magnetic susceptibility of hydrides of 10 to 30 at.% Ag-Pd alloys were made as functions of H_2 content. As H_2 was occluded the paramagnetic susceptibility decreased and the Hall coefficient decreased considerably in the high H_2 content β -phase alloys. The H atom was considered to act like a proton in the Pt lattice by transferring a valence electron to the Pd $4d$ band.

The Phase Diagram Rh-Sb

R. N. KUZ'MIN and N. N. ZHURAVLEV, *Vestnik Mosk. Univ., Ser. III, Fiz. Astron.*, 1963, **18**, (2), 9-14

X-ray and micrographic studies of the Rh-Sb system indicated the existence of a γ -phase at about the Rh_3Sb_2 composition and a eutectic point between the compositions RhSb and Rh_3Sb . The solubility of Sb in Rh reached about 8 wt.% at 1150°C.

Thermal Analysis of the Rh-Bi System

R. I. KUZ'MIN, N. N. ZHURAVLEV and G. S. ZHDANOV, *Zh. Neorg. Khim.*, 1963, **8**, (8), 1906-1914

Results of thermal analysis of Bi-rich alloys slightly modified previous constitution diagrams of the Bi-Rh system. The eutectic point was detected at 1.4 at.% Rh and 268°C. The transi-

tion temperature between α - and β - Bi_2Rh occurred at 430°C. Peritectic temperatures were 456°C and 775°C.

On the Superconductivity of Ti- and Zr-Rh Alloys

C. J. RAUB and C. A. ANDERSEN, *Z. Physik*, 1963, **175**, (1), 105-114

The connection between superconductivity and valence electron concentration was studied in Ti- and Zr-alloys containing up to 12 at.% Rh. In both the h.c.p. α -phases and b.c.c. β -phases the transformation temperature increased with valence electron concentration. By extrapolation to 0% Rh it was shown that the transformation temperatures for Ti and Zr β -phases lie below those of the α -phases.

The Structure of the Stable Tantalum-Ruthenium Alloys

E. RAUB, H. BEESKOW and W. FRITZSCHE, *Z. Metallkunde*, 1963, **54**, (8), 451-454

The Ru-Ta system is similar to the Ru-V and Ru-Nb systems. X-ray and microscopic analysis of alloys with increasing Ru content showed the occurrence of transitions from the b.c.c. solid solution to an ordered B2 structure, followed by tetragonal distortion, an ordered orthorhombic form and an ordered f.c. tetragonal form at high Ru content.

Melting Points of $LaRu_2$, $CeRu_2$ and $PrRu_2$

R. D. REISWIG and K. A. GSCHNEIDNER, *J. Less-Common Metals*, 1963, **5**, (5), 432-433

The observed melting points of the Laves phases were: $LaRu_2$ at $1431 \pm 30^\circ C$, $CeRu_2$ at $1539 \pm 30^\circ C$, $PrRu_2$ at $1681 \pm 15^\circ C$. Melting was probably incongruent.

Vapour Pressures of Platinum Metals. III. Iridium and Ruthenium

R. C. PAULE and J. L. MARGRAVE, *J. Phys. Chem.*, 1963, **67**, (9), 1896-1897

Vapour pressures, heats of sublimation and boiling points were obtained for solid Ir and Ru. Ir has $\log P_{mm}^{Ir}(\text{solid}) = 10.120 - 33,680/T$ for $2140^\circ K < T < 2477^\circ K$, $\Delta H_{298}^\circ = 160.9 \pm 2.8$ kcal/mole and estimated normal b.p. $\approx 4850 \pm 100^\circ K$. Ru has $\log P_{mm}^{Ru}(\text{solid}) = 11.200 - 33,600/T$ for $2011^\circ K < T < 2330^\circ K$, $\Delta H_{298}^\circ = 151.5 \pm 4$ kcal/mole and estimated normal b.p. $\approx 4350 \pm 100^\circ K$.

The Alloys of Ruthenium with Titanium and Zirconium

E. RAUB and E. RÖSCHEL, *Z. Metallkunde*, 1963, **54**, (8), 455-462

Microscopic and X-ray methods confirmed the existence of intermediate B2 phases TiRu and ZrRu, which melt congruently at 2100-2150°C and show no phase transformations nor decompositions at lower temperatures, and of the $C14$

Laves phase $ZrRu_2$, which decomposes eutectoidally at $1300 \pm 20^\circ C$. Ru has low solubility in α -Ti and α -Zr but more in β -Ti and β -Zr. Ru stabilises β -Ti and can depress the $\beta \rightarrow \alpha$ transformation below room temperature for 16–20 at. % Ru. Considerable precipitation hardening occurs in Ti-rich alloys. Study of the $\beta \rightarrow \alpha$ transformation in Zr-Ru alloys is made difficult by the oxidation of Zr, causing the alloys to appear ternary.

A Study of the Adsorption and Decomposition of Hydrocarbons on Clean Iridium Surfaces

R. W. ROBERTS, *J. Phys. Chem.*, 1963, **67**, (10), 2035–2038

CH_4 , C_2H_6 and C_2H_4 were admitted to Pyrex flasks on the inner surfaces of which Ir films had been prepared under ultra-high vacuum conditions. They were adsorbed on the clean films at 27 and $100^\circ C$. CH_4 did not decompose on Ir but C_2H_6 decomposed to CH_4 and H_2 at $27^\circ C$ and to CH_4 at $100^\circ C$. O_2 preadsorbed on Ir inhibited C_2H_4 decomposition. C_2H_4 was self-hydrogenated to C_2H_6 and CH_4 . The roughness factor of the Ir films was about 7.

High Temperature Properties of Refractory Alloys

E. J. RAPPERPORT and A. L. GEARY, *U.S.A.E.C. Report N.M.I.-1253*, 67 pp.

Ten alloy systems of the refractory metals Mo, W, Nb and Ta with additions of Hf, Re, Os, Ru, Rh, Ir and Zr were studied by hot hardness tests up to $1200^\circ C$ and oxidation resistance tests at $1000^\circ C$ to determine their suitability for use in nuclear reactors. Ru, Os and Re additions increased the hardness by up to 7 times at room temperature and up to 17 times compared to the unalloyed refractory metals. These alloys were then tested for tensile strength up to $1800^\circ C$. 2–10 at. % Ru-W, 2–10 at. % Ru-Ta and 2–10 at. % Re-Nb showed greater strength worth further study.

Oxidation of the Platinum-Group Metals

C. A. KRIEBER and R. I. JAFFEE, *J. Less-Common Metals*, 1963, **5**, (5), 411–431

Samples of the six Pt-group metals were heated in a slowly moving stream of dry air at 1000 – $1400^\circ C$ and all showed linear weight loss rates in the range 1200 – $1400^\circ C$ by the formation of volatile oxides. Rh gained weight at $1000^\circ C$ by the formation of an oxide film and Pd initially absorbed O_2 . At $1400^\circ C$ in a slow air stream at 1 atm. the rates of weight loss were 6.8×10^{-3} mg/cm²/hr for Rh, 9.6×10^{-3} for Pt, 3.1 for Ir, 1.2×10^{-2} for Ru and 1.2×10^{-3} for Os. The rates depended on the gas flow rate, the partial pressure of O_2 and the total gas pressure. The kinetics of the reactions also depended on the temperature. The mechanism of reaction of the O_2 at the surface is discussed and specimens are illustrated.

Superconductivity of Some New Pt-Metal Compounds

C. J. RAUB, W. H. ZACHARIASEN, T. H. GEBALLE and B. T. MATTHIAS, *J. Phys. Chem. Solids.*, 1963, **24**, (9), 1093–1100

Tests on compounds of the Pt metals with P, As, Sb, Bi and S revealed several previously unknown superconductors in the systems Rh-As, Pd-P and Pd-As. Transition temperatures and crystallographic data are listed for all known superconductors of the Pt metals with elements of groups IVA, VA, and VIA.

The Problem of Producing Superconducting Materials

E. M. SAVITSKII and V. V. BARON, *Metallurgiya i Gornoe Delo*, 1963, (5), 3–12

Among a large number of superconducting substances reviewed there are more than thirty compounds of the Pt metals, for which the transition temperatures and Curie points are tabulated. Their formation, properties and uses are discussed. (24 references.)

CHEMICAL COMPOUNDS

Structure and Reactivity of the Oxyanions of Transition Metals

A. CARRINGTON and M. C. R. SYMONS, *Chem. Rev.*, 1963, **63**, (5), 443–460

Known oxyanions of the Pt metals are RuO_4 , RuO_2^- , RuO_4^{2-} and OsO_4 and RhO_4^{2-} is also believed to exist. The electronic structure and reactions of these tetrahedral oxyanions, together with those of V, Nb, Ta, Cr, Mo, W, Mn, Ti, Re and Fe are critically discussed. (115 references.)

Unusual Oxidation States of the Noble Elements

N. BARTLETT, *Chem. in Canada*, 1963, **15**, (8), 33–40

The structure and properties of the fluorides, oxides and oxyfluorides of the Pt metals are discussed. Particular note is made of $OsOF_5$ and PtO_2F_6 . Work on the $[PtF_6]^-$ ion led to the discovery of the noble gas fluoride compounds, the bonding of which is also reviewed. (38 references.)

Aromaticity of Five-Membered Rings Containing Platinum (II)

P. HAAKE and P. A. CRONIN, *Inorg. Chem.*, 1963, **2**, (4), 879–880

Conductometric studies on the kinetics of displacement of chloride by dithioamide in methanol indicated that a strong *trans* effect resulting from aromaticity in the Pt- α -diimine chelate ring caused the $Pt(bipy)Cl_2$ complex to react nearly one hundred times faster than the *cis*- $Pt(py)_2Cl_2$ or $Pt(en)Cl_2$ complexes.

Aromatic Complexes of Metals. LXXV. Cyclopentadienyl-palladium-nitrosyl

E. O. FISCHER and A. VOGLER, *Z. Naturf.*, 1963, **186**, (9), 771-772

C_5H_5PdNO was prepared by the reaction of $PdNOCl$ with NaC_5H_5 in pentane with air excluded and its absorption spectrum was studied.

Complexes between Palladium (II) and Pyridine-2-aldoxime

C. F. LIU and C. H. LIU, *Inorg. Chem.*, 1963, **2**, (4), 706-707

The tetrachloropalladate (II), chloride and nitrate of monohydrogen bis-(pyridine-2-aldoxime)-palladium (II) ion were prepared and compared to similar Pt(II) and Cu(II) compounds. The inner complex between pyridine-2-aldoxime and Pd(II) was also prepared. In contrast to the Pt(II) inner complex only the *trans* isomer of Pd(II) was obtained.

Preparation and Properties of Anhydrous Rhodium (II) Acetate and Some Adducts Thereof

S. A. JOHNSON, H. R. HUNT and H. M. NEUMANN, *Inorg. Chem.*, 1963, **2**, (5), 960-962

Rh(II) acetate was prepared by the reaction of $Rh(OH)_3 \cdot H_2O$ with glacial acetic acid. Stable adducts with 2 ligands to each dimer were formed with H_2O , tetrahydrofuran, acetonitrile, dimethyl sulphoxide, dimethyl sulphide, trimethylamine, NH_3 , NO_2 and ethylenediamine. The properties and spectra of Rh(II) acetate and these adducts are discussed.

Ruthenium Tetrafluoride

J. H. HOLLOWAY and R. D. PEACOCK, *J. Chem. Soc.*, 1963, (July), 3892-3893

RuF_4 was formed by the reaction of I_2 with RuF_5 dissolved in IF_5 . RuF_4 was highly reactive and reacts violently with H_2O to form RuO_2 . The magnetic moments of RuF_4 were measured in the range 90 to 300°K. X-ray diffraction analysis suggested that it has a simple structure.

Anhydrous Ruthenium Chlorides

J. M. FLETCHER, W. E. GARDNER, E. W. HOOPER, K. R. HYDE, F. H. MOORE and J. L. WOODHEAD, *Nature*, 1963, **199**, (4898), 1089-1090

The preparation and magnetic properties of α - $RuCl_3$, β - $RuCl_3$ and Ru_2OCl_6 are described. α - $RuCl_3$ formed by heating Ru and Cl_2 in siliceous vessels at 600°C contains some Ru_2OCl_6 which is diamagnetic and reduces the susceptibility. α - $RuCl_3$ has now been made by heating β - $RuCl_3$ above the β -transition temperature of 450°C. β - $RuCl_3$ is formed by reacting Ru in CO and Cl_2 at 360-390°C, with some α - $RuCl_3$ formation. Ru_2OCl_6 occurs as a volatile oxide chloride in the mixture of aquochloro complexes known as commercial $RuCl_3$. α - $RuCl_3$ is antiferromagnetic and β - $RuCl_3$ has low magnetic susceptibility.

ELECTROCHEMISTRY

Relation between the Activation Energy of Some Electrochemical and Catalytic Processes and the Properties of Metals

V. V. DEMCHENKO, *Zh. Fiz. Khim.*, 1963, **37**, (8), 1718-1725

Electrochemical and catalytic processes such as hydrogenation, isotope exchange and H_2 formation at the electrode, where metal- H_2 bonding occurs as an intermediate step, are reviewed. Activation energy is proportional to the increase in surface tension of the cathode or catalyst surface. Graphs illustrate this effect for Pt, Pd, Rh, Ir, Os and a number of base metals. (16 references).

On the Thermodynamics of Platinum Oxide Electrodes

B. NOVAK and T. MARKOVIC, *Monat. Chem.*, 1963, **94**, (3), 607-620

The energy of formation of each oxide, hydroxide and oxide hydrate of Pt in aqueous solution was determined. Data are fully tabulated and extensively discussed.

Electrochemical Oxygen- and Hydrogen-Chemisorption on Smooth and Rough Platinum

H. DIETZ and H. GÖHR, *Z. phys. Chem., Leipzig*, 1963, **223**, (1/2), 113-131

The chemisorbed H_2 or O_2 films which can be formed on Pt electrodes are produced continuously only if the electrodes are continually cleaned. Film formation then becomes a steady process whereas if the films are allowed to build up the potential of the circuit alters and the current is reduced.

The Mechanism of Electrochemical Oxidation of Carbon Monoxide and Methanol on Platinum. I. Carbon Monoxide Adsorption and Desorption and Simultaneous Oxidation of the Platinum Surface at Constant Potential

S. GILMAN, *J. Phys. Chem.*, 1963, **67**, (9), 1898-1905

The oxidation of the surface of a Pt electrode covered with adsorbed CO in a saturated solution in 1 N $HClO_4$ of a 100% or 1% CO gas mixture is rate-controlled by the removal of adsorbed CO, as shown by current-time traces after raising the electrode potential from 0.4 to >0.8V.

II. Interpretation of the CO and "Oxygen" Adsorption Data Obtained at Constant Potential

S. GILMAN, *Abs. Papers, 145th Meeting, Am. Chem. Soc.*, 1963, 22B-49

The oxidation of both the adsorbed CO and the

Pt surface are interpreted by a reactant-pair mechanism which assumes that the actual reactants are adjacent CO and H₂O adsorption molecules.

Mechanism of Anodic Oxidation of Organic Compounds on Platinum

V. S. BAGOTZKY, *Abs. Papers, 145th Meeting, Am. Chem. Soc.*, 1963, 21K-58

The adsorption of reacting species on the Pt surface affects the rate of oxidation. Adsorption of O₂ on the surface reduces the reaction rate exponentially.

The Normal Oxygen Potential on Bright Platinum

J. P. HOARE, *J. Electrochem. Soc.*, 1963, **110**, (9), 1019-1021

Experiments showed that when a Pt surface was completely covered by a chemisorbed monolayer of O₂ the surface was passivated with respect to its reaction with oxygen. The layer was produced by passivating Pt beads in HNO₃. A rest potential of 1225 ± 10 mV was observed for up to 24 hours or more.

Electrochemical Corrosion of Iridium in Hydrochloric Acid Solutions

J. LLOPIS and L. JORGE, *J. Electrochem. Soc.*, 1963, **110**, (9), 947-951

Electrolysis of Ir in HCl showed that in all respects Ir is more corrosion resistant than Pt. Ir was attacked more strongly as the HCl concentration and temperature increased. An a.c. superimposed on the d.c. increased the effect, especially at low frequencies, but the corrosion was negligible until a threshold value of $i_{a.c.} \gg i_{d.c.}$ was reached. Dissolution and passivation mechanisms were studied.

LABORATORY APPARATUS AND TECHNIQUE

Purity of Hydrogen Permeating through Pd, Pd-25% Ag, and Ni

J. R. YOUNG, *Rev. Scient. Instrum.*, 1963, **34**, (8), 891-892

A technique for determining the purity of diffused H₂ is described. Impurities in H₂ permeating through Pd or 25% Ag-Pd alloy tubes were a few parts in 10¹⁰. The lowest impurity content from Ni was found to be 1 part in 10⁸. CO was the main impurity in all cases.

Specimen Heating with Temperature Measurement from -150°C to 2200°C inside the EM6 Electron Microscope

J. A. HEADLEY and J. MCGEAGH, *J. Scient. Instrum.*, 1963, **40**, (10), 484-486

Equipment is described to enable the temperature range -150 to 2200°C to be studied. The high

and medium temperature heating stages incorporate solid Pt in the grid holders and caps because of its high melting point, low electrical resistance and resistance to oxidation. The Pt carries the current to heat the grid in the high temperature stage. Pt wire forms a resistance furnace in the other case.

The Durability of Pt-Rh Alloys in Analytical Apparatus

G. REINACHER, *Werkstoffe u. Korrosion*, 1963, **14**, (7), 574-579

Five typical analytical laboratory operations tested Rh-Pt alloys to show that they can well be used in corrosive conditions up to 1000°C. A tarnish developed during annealing in air and during soda-potash fusions but weight constancy was of the same order as ordinary apparatus Pt. Resistance to acids was as good as with Pt. Weight losses during potassium bisulphate fusions increased with temperature but, by lining with Pt, the crucibles combined resistance to attack with resistance to deformation. 20% Rh-Pt has been used for ferrophosphorus and ferrosilicon extractions and 10% Rh-Pt for HF and H₂SO₄ evaporations and various fusions. The dark Rh oxide tarnish could be avoided by Pt linings. Lined and unlined 10, 20 and 30 wt. % Rh-Pt alloy apparatus is therefore profitable for many high temperature analyses.

BRAZING

New Era Brazing Turns to Filler Metals with Palladium

A. S. CROSS and J. B. ADAMEC, *Welding J.*, 1963, **42**, (8), 645-649

Pd-containing brazing alloys are ductile with good wetting and flowing properties and do not erode the base metals with which they are used. Sixteen alloys are described of which five Ag-Pd and Ag-Cu-Pd alloys cover the melting range 1490°C to 2250°C which is so important for electronic equipment. The alloys possess considerable strength at high temperature. They also fill gaps satisfactorily and reduce stress cracking. Their low vapour pressure makes them suitable for vacuum applications. (13 references).

Ceramic-to-Metal Seals for High Temperature Operation

E. L. BRUNDIGE and G. S. HANKS, *U.S.A.E.C. Report LAMS 2917*, 1963, 36 pp.

A nuclear fuel element design required Nb components to be separated by Al₂O₃-Y₂O₃, a ceramic capable of withstanding Cs vapour at 1500°C. Bonding the ceramic to Nb was by metallising with W and then brazing with Pd applied by plating the W surface or as Pd foil before joining and sealing. Seals for use to 1000°C can be made from Co-Pd braze alloy added to the joint as foil or by plating with alternate layers of Co and Pd.

CATALYSIS

Active Centres of Platinum Adsorption Catalyst in the Oxidation of Ammonia

V. I. SHEKHOBALOVA and N. I. KOBOZEV, *Zh. Fiz. Khim.*, 1963, 37, (9), 2131-2132

Analysis of the reaction products of oxidation of NH_3 over Pt/SiO_2 showed that the Pt exists in monoatomic form on the catalyst support. Theoretical relations were established such that for SiO_2 with $300 \text{ m}^2/\text{g}$ and temperatures of 300 and 350°C , the apparent activation energy could be calculated as $10,700 \text{ cal/mol}$.

The Relation of the Catalytic Properties of Platinised Silica Gel to the Conditions of its Preparation

M. D. ADAMENKOVA and O. M. POLTORAK, *Vest. Mosk. Univ., Ser. II, Khim.*, 1963, (5), 12-16

The catalytic activity of Pt/SiO_2 prepared by the adsorption of amines of Pt on SiO_2 depends on the SiO_2 grain size, the drying temperature and the conditions of ammine reduction by H_2 . SiO_2 should be homogeneous but too much grinding reduces the activity. Pt ammine adsorption is uniform after 3 days but not after 5 minutes. Drying at 100°C gives higher activity than drying at 60°C . 300°C is the optimum reduction temperature for the Pt amines. Tests on three series of differently prepared samples showed that the level of activity for 0.5 to 3.15% Pt contents is higher than for 3.5 to 7% Pt.

The Hydrogenation of Diene Hydrocarbons over a Platinum Catalyst in Liquid Phase

L. KH. FREIDLIN and E. F. LITVIN, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1963, (7), 1307-1312

Saturated hydrocarbons were formed by the hydrogenation of dienes over Pt black catalyst at conversions of up to 70 to 80%, mainly by two H_2 molecules becoming attached to each diene molecule without desorption of intermediate products from the catalyst surface. Tests with isoprene, *trans*-piperylene and 2, 3-dimethylbutadiene-1, 3 and binary mixtures of α -olefins with isoprene showed that, at high degrees of diene conversion, some saturated hydrocarbon was derived from the α -olefins, simultaneous hydrogenation having taken place. There was high diene selectivity with alkaline solution but poor selectivity with acid solutions.

Kinetics of Dehydration of Cyclohexadiene-1, 3 on Platinum Films over a Wide Range of Temperature

V. D. YAGODOVSKII, V. M. GRYAZNOV and E. A. SAVEL'eva, *Kinetika i Kataliz*, 1963, 4, (5), 746-752

The activation energy of the dehydrogenation of cyclohexadiene-1, 3 on thin Pt films was shown to increase sharply at higher temperatures in the 200 - 500°C range. Treatment of the Pt films at

700°C further increased the activation energy for tests in the 500 - 600°C range. An interpretation of the results relates the condition of the active part of the Pt surface to the thermodynamic equilibrium of the system.

Stereoisomeric 3 β , 17 β -Dihydroxyandrostane-16-ylacetic Acids

P. KURATH, W. COLE, J. TADANIER, M. FREIFELDER, G. R. STONE and E. V. SCHUBER, *J. Org. Chem.*, 1963, 28, (9), 2189-2194

The conditions of hydrogenation of 3 β , 17 β -diacetoxy-5-androsten-16-ylidenacetic acid over PtO_2 were adjusted to improve the yield of 3 β , 17 β -diacetoxy-5-androsten-16 β -ylacetic acid and the stereochemistry of the four possible tetrahydro products was derived.

The Hydrogenation of the Stereoisomers of Piperylene on Metallic Catalysts

L. KH. FREIDLIN and E. F. LITVIN, *Neftekhimiya*, 1963, 3, (3), 326-329

The hydrogenation of the *cis* and *trans* isomers of piperylene (1, 3-pentadiene) in methanol using Pt and Pd blacks and Raney Ni as catalysts yields all the three possible pentenes in amounts which differ substantially from one system to another. Very little pentane is formed in the early stages of the reaction over Pd and Ni, but pentane constitutes about 35% of the initial products formed over Pt. No isomerisation between the piperylene isomers was detected.

Selectivity and Stereospecificity in the Hydrogenation of Acetylene Hydrocarbons on Metal Catalysts

L. KH. FRIEDLIN and YU. YU. KAUP, *Doklady Akad. Nauk S.S.S.R.*, 1963, 152, (6), 1383-1386

Tests on pentyne-2 and pentyne-1, using Raney Ni, Raney Co, Pd black, Pt black, and Rh black catalysts established that the order of selectivity in the first stage of hydrogenation is $\text{Pd} > \text{Pt} > \text{Rh} > \text{Ni} > \text{Co}$ and that the order of stereospecificity is $\text{Pd} > \text{Ni} = \text{Co} > \text{Pt} > \text{Rh}$. Isomerisation of the products was also studied.

Hydrogenation of 2-Methyl-5-acetylfurans in Liquid Phase

N. I. SHUIKIN, I. F. BEL'SKII, G. K. VASILEVSKAYA and V. M. SHOSTAKOVSKII, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1963, (8), 1475-1478

When 2-methyl-5-acetylfuran was hydrogenated over Pt/C and Pd/C in liquid phase at 100°C with 100 atm. initial pressure of H_2 , the furan ring was not reduced but hydrogenolysis occurred at the C-O bond adjacent to the CO group. Heptanedione-2, 6 was produced which was further converted by cyclisation to cyclohexanone and cyclohexanol (20-30%) and by reduction to heptanediol-2, 6, which was partly cyclised to 2, 6-dimethyltetrahydropyran (about 50-60%). Over $\text{Pd}/\text{Al}_2\text{O}_3$ at 180°C the CO group was

reduced to CH₂ followed by hydrogenation of the furan ring to produce 2-methyl-5-ethyltetrahydrofuran (about 60%).

The Oxidation of Olefines by Palladium Chloride Catalyst

J. SMIDT, *Bull. Assoc. Franc. Tech. Pétrole*, 1963, (160), 467-487

The oxidation of olefines to carbonyl compounds with the same number of C atoms by O₂ in aqueous solutions of PdCl₂ and CuCl₂ is described and reaction mechanisms are discussed. Higher olefines and other unsaturated compounds are attacked by O₂ at points within the molecule depending on the groups attached to the double-bond C atoms and on the Pd ligands. Ketones and aldehydes are formed from α-olefines in fixed proportions. The transesterification of vinyl esters is the most important non-oxidation reaction of unsaturated compound in which Pd salts act as catalysts.

Kinetic Study on the Oxidation of Propylene in the Presence of Palladium Chloride

T. DOZONO and T. SHIBA, *Bull. Japan Petroleum Inst.*, 1963, 5, (March), 8-12

The rate of the catalytic oxidation of propylene to form carbonyl compounds by Smidt's process, using acidic PdCl₂/CuCl₂ solution, was shown to be $r = k \frac{[\text{PdCl}_2]}{[\text{Cl}^-]^{2.21} [\text{H}^+]}$ p_{prop}, where [PdCl₂] and [Cl⁻] are the total concentrations of PdCl₂ and Cl⁻ ion respectively, where [H⁺] is the initial H⁺ ion concentration and where p_{prop} is the partial pressure of propylene; k is a constant.

Oxidation of Alcohols by Palladium Salts in Aqueous Solution

A. V. NIKIFOROVA, I. I. MOISEEV and YA. K. SYRKIN, *Zh. Obshch. Khim.*, 1963, 33, (10), 3239-3242

Aliphatic alcohols were oxidised to aldehydes and aliphatic-aromatic alcohols to ketones by PdCl₂ in aqueous solution. The reactions were slower than for the corresponding olefines. Alcohols tested were ethyl-, isopropyl-, N-butyl-, N-amyl- and benzoyl-alcohol.

Isomerisation of Hexenes in Liquid Phase Hydrogenation Conditions in the Presence of Palladium Black

I. V. GOSTUNSKAYA, A. I. LEONOVA, N. B. DOBROSERDOVA and B. A. KAZANSKII, *Neftekhimiya*, 1963, 3, (4), 498-502

Double bond transfer from position 1 to position 2, but no further along the C chain, was observed during partial hydrogenations of hexene-1, 2-methylpentene-1, 3-methylpentene-1, 4-methylpentene-1 and 2, 3-dimethylbutene-1 in the presence of Pd black at atm. pressure and 20°C in C₂H₅OH medium. Compounds with two H atoms in the allyl positions were isomerised more readily than those with only one. Where

the numbers of H atoms were equal, isomerisation occurred more readily with the compound more difficult to hydrogenate.

Isomerisation of Hexenes in the Presence of Palladium on Charcoal

B. A. KAZANSKII, N. B. DOBROSERDOVA, G. S. BAKHMET'EVA and I. V. GOSTUNSKAYA, *Neftekhimiya*, 1963, 3, (4), 503-506

The transfer of double bonds in hexenes was studied at 80°C in the presence of Pd/C and a stream of H₂. The relation between the initial hexenes and the rates of transfer was obtained and this agreed with the associative mechanism for the reaction.

Inhibitors in the Palladium-Catalysed Hydrogenation of Aryl Nitro Groups

H. GREENFIELD, *J. Org. Chem.*, 1963, 28, (9), 2434-2435

Potential inhibitors of the hydrogenation of *p*-nitrotoluene to *p*-toluidine over 5% Pd/C were added to the reaction mixture at the rate of 5 mole% with respect to *p*-nitrotoluene, i.e. more than trace amounts. Sodium nitrate, acetate, sulphate, carbonate, phosphate, hydroxide, fluoride, bromide and chloride and ferrous chloride, *n*-octyl chloride, chlorobenzene, bromobenzene, aniline, piperidine, sodium methoxide, phenol and *p*-nitrophenol caused no inhibition. Various amounts of poisoning were caused by potassium nitrite and sodium nitrate, sulphite, iodide, cyanide, sulphide and bisulphite and also by nickel (II), ferric, cobalt (II), chromium (III), copper (II), silver, aluminium, zinc and lead nitrates, ferric chloride, copper chloride and by certain nitroso compounds. Phenyl disulphide caused inhibition at very low concentrations.

Comparison of the Rates of Catalytic Reduction and Electroreduction of Some Organic Substances on Rhodium. III

T. M. GRISHINA, L. P. KHOMCHENKO and G. D. VOVCHEENKO, *Vest. Mosk. Univ., Ser. II, Khim.*, 1963, (4), 55-58

The catalytic reduction rate on Rh was several times as great as its electroreduction rate for crotonaldehyde, acetone and amylaldehyde. Both rates decreased in the same order of substances. The rates decreased with changes in the electrolyte in the order H₂SO₄, HCl, KOH and HBr. Br⁻ ions particularly poisoned the reductions. Rh has lower reduction rates than Pt but higher than Ru.

Study of Ruthenium Catalyst. I. Hydrogenation of Organic Compounds by Ruthenium Catalyst

Y. TAGAKI, *Sci. Papers Inst. Phys. Chem. Res. (Japan)*, 1963, 57, (2), 105-109

Ru and Ru/C catalysts were prepared and used in liquid phase hydrogenations at ordinary and

high pressures. Carbonyl groups were more easily hydrogenated at ordinary pressure over Ru than over Pd. H₂O and alkaline solvents were more effective than alcohol for these reactions. The hydrogenation of double bonds was difficult. Nitro groups could be hydrogenated but nitriles could not. At high pressure the rate of hydrogenation of allyl alcohol was rapid. Citronellal was used for studies on the hydrogenation of unsaturated aldehydes and the selectivity of such processes.

The Production of Polyhydroxy Alcohols from Wood-Polysaccharides

V. I. SCHARKOW, *Chem. -Ing. -Tech.*, 1963, 35, (7), 494-497

Optimum conditions for the simultaneous hydrolysis and hydrogenation of polysaccharides in the presence of Ru/BaSO₄ or of Ru/C are 0.7% H₃PO₄ solution, 160-165°C, 60-80 atm. pressure of H₂ and a reaction time of 50-60 min. Other processes developed in the U.S.S.R. are based on the hydrolysis of the polysaccharides to monosaccharides which are subsequently hydrogenated, on hydrogenolysis of monosaccharides and on the pyrolysis of cellulose.

An Investigation of Catalysts Produced by Reactions between Sodium Borohydride and Salts of Heavy Metals

A. M. TABER, B. D. POLKOVNIKOV, N. N. MAL'TSEVA, V. I. MIKHEEVA and A. A. BALANDIN, *Doklady Akad. Nauk S.S.S.R.*, 1963, 152, (1), 119-121

0.25 g samples of PdCl₂, RhCl₃ and H₂PtCl₆ were reacted with 1 g samples of NaBH₄ and the products were analysed chemically, thermally and by spectrography. The infra-red spectra of Pd-B alloys and of borided Pd catalyst were very similar. H₂ in the catalysts acted similarly to adsorbed H₂.

Charging Curves of the Boride Catalysts of Pt-Group Metals

A. M. TABER, A. A. BALANDIN, D. V. SOKOL'SKII and B. D. POLKOVNIKOV, *Doklady Akad. Nauk S.S.S.R.*, 1963, 152, (2), 379-381

Results were plotted for Pt, Pd and Rh boride catalysts in 0.1 N solutions of NaOH, H₂SO₄ and HCl and for the anodic polarisation of phenylacetylene and diphenylacetylene. Charging was most rapid for the NaOH electrolyte and the acetylenes were most readily polarised over Pt. Isotherms for the solution of H₂ in the catalysts were also determined.

Hydrogenolysis and Reciprocal Transitions of *cis*- and *trans*-1, 2-Dimethylcyclopentanes in the Presence of Rhodium, Osmium, Iridium and Palladium Catalysts

O. V. BRAGIN, A. L. LIBERMAN, G. K. GURIANOVA and B. A. KAZANSKII, *Doklady Akad. Nauk S.S.S.R.*, 1963, 152, (4), 865-868

Studies at 150 to 280°C over Rh/C, Os/C, Ir/C

and Pd/C showed the relative amounts of isomerisation and hydrogenolysis of *cis*- and *trans*-1, 2-dimethylcyclopentane. The amount of hydrogenolysis and the proportion of *cis*- to *trans*-isomer increase with temperature. Pd/C and Rh/C appeared to be most active in these respects. The reaction mechanism is discussed and the effects are compared with Pt/C catalyst action.

FUEL CELLS

A High Performance Saturated Hydrocarbon Fuel Cell

W. T. GRUBB and L. W. NIEDRACH, *J. Electrochem. Soc.*, 1963, 110, (10), 1086-1087

Propane has been oxidised rapidly in a new propane-oxygen fuel cell operating at only 150°C with a new porous electrode structure to preserve the catalytic properties of the Pt incorporated in it. The electrolyte was H₃PO₄. A voltage-current density curve when 14.6 M H₃PO₄ was used showed no limiting current in the range examined thanks to the thin structure of the electrodes.

A Direct Hydrocarbon/Air Fuel Cell

H. G. OSWIN, A. J. HARTNER and F. MALASPINA, *Nature*, 1963, 200, (4903), 256-257

The combustion of propane in a fuel cell using Pt black electrodes and H₃PO₄ electrolyte at temperatures up to 220°C produced currents of 100-200 mA/cm² at 20-35% thermal efficiency. The process appeared to consist of catalytic cracking followed by combustion and again demonstrated the feasibility of direct hydrocarbon/air fuel cells.

The Development of a High-efficiency Hydrogen-diffusing Palladium-Alloy Anode for Use in Fuel Cells

H. G. OSWIN, S. M. CHODOSH and N. I. PALMER, *Abs. Papers, 145th Meeting, Am. Chem. Soc.*, 1963, 14K-39

Thin Pd alloy membranes for use as H₂-diffusing anodes were studied electrochemically and the effect of various operating parameters on anode polarisation were determined. Variables discussed include temperature, electrolyte composition, gas pressure and composition, membrane thickness and surface preparation.

Thin Fuel Cell Electrodes

R. G. HALDEMAN, W. P. COLMAN, S. H. LANGER and W. A. BARBER, *Abs. Papers, 145th Meeting, Am. Chem. Soc.*, 1963, 15K-42

Thin electrodes consisting of Pt and Pt-C supported on screens were found to be capable of very high performance. The Pt used was from 1 to 9 mg/cm². Electrodes were tested in acidic and basic media and were studied for initial polarisation, length of service, effect of temperature and operation in air.

ANODIC PROTECTION

Anodic Protection of Carbon Steel in Sulphuric Acid

W. P. BANKS and J. D. SUDBURY, *Corrosion*, 1963, **19**, (9), 300T-307T

Pt cathodes were used in tests on 1020-type mild steel samples. The tests showed that the effectiveness of anodic protection and the current density for maintaining protection depended on acid concentration and temperature. H_2SO_4 varied from 45 to 105% concentration and temperature from 80 to 535°F. Graphs illustrate the large increase in current density required with higher temperatures.

ELECTRICAL ENGINEERING

Effect of Organic Vapours on Contact Materials in Communication Engineering

J. TLAMSA and J. NUSZBERGER, *Nachrichtentechnik*, 1963, **13**, (7), 272-277

Ag and Pd contacts were tested for the effects of organic vapours arising from the atmosphere around them or from wire sheathing materials. The vapours can cause sparking, deposits, erosion and changes of resistance. Results are tabulated and cover most of the more common organic materials likely to be present. The activities of contacts in various surroundings are also listed.

NEW PATENTS

Production of Semi-Conductor Devices

THE INTERNATIONAL NICKEL CO. (MOND) LTD. *British Patent* 930,091

An electrically conducting joint is made between a wire and a metal layer adherent to a semi-conductor material with the use of a paste-like dispersion of a metal powder in a liquid vehicle consisting of a thermally decomposable compound. Pt metal and a decomposable Pt compound is used.

Catalytic Decomposition of Hydrazine

ENGELHARD INDUSTRIES INC. *British Patent* 930,499

Hydrazine is contacted with a catalyst composed of one or more of Rh, Ir, Ru and Pd, with, if desired, Pt.

Preparation of 20-Alkylamine Steroid Derivatives

SMITH KLINE & FRENCH LABORATORIES. *British Patent*, 930,676

A Pt oxide hydrogenation catalyst is used in the preparation of the above substances.

Isomerisation of Olefinic Hydrocarbons

BRITISH PETROLEUM CO. LTD. *British Patent* 931,922

The isomerisation of an olefine is carried out using as catalyst a compound of the olefine with a halide of a Pt group metal.

Preparation of Cyanoalkyl Chlorosilanes

GENERAL ELECTRIC CO. *British Patent* 932,380

Relates to a method of forming alpha-cyanoethyl methyl dichlorosilane which comprises reacting methyl dichlorosilane with acrylonitrile in the presence of a catalyst composition comprising palladous chloride, a trialkylamine and a polyamine.

Isomerisation of Olefines

BRITISH PETROLEUM CO. LTD. *British Patent* 932,748

The isomerisation of a branched chain olefine is carried out using as catalyst a complex of the olefine with a halide of a platinum group metal.

Electrolytic Apparatus

D. J. EVANS (RESEARCH) LTD. *British Patent* 932,945

Provides an improved closed electrolytic cell for the production of chlorine by the electrolysis of brine. Electrodes consist of thin sheets of Ti coated with Pt.

Reforming Catalyst

THE STANDARD OIL CO. *British Patent* 934,080

A hydroforming catalyst comprises Pt/ Al_2O_3 in which at least 40% by wt. of the Pt is maintained in an HF-soluble form.

Selective Hydrogenation

FARBENFABRIKEN BAYER A.G. *British Patent* 934,429

Process for the selective hydrogenation of acetylene/diolefine components of a liquid hydrocarbon mixture comprises trickling the hydrocarbon mixture over a Pt or Pd hydrogenation catalyst carried on a macroporous support.

Ignition Device

ROLLS-ROYCE LTD. *British Patent* 934,499

Ignition device for combustion equipment comprises a mass of refractory material and a foraminated catalytic element of Pt, or Rh, or a Pt alloy of less than 0.030 in. thick.

Fuel Cells

LEESONA CORP. *British Patent* 935,430

Provides a fuel cell constructed for high temperature operation in which at least one electrode is composed of a mixture of zinc oxide and