ABSTRACTS of current literature on the platinum metals and their alloys

PROPERTIES

Effect of Grain Size on the Creep of Platinum-Rhodium Alloys
Models are described for estimation of the rate of creep of 7-10% Rh-Pt alloys at 1300°C, applied pressure 1.0-1.3 kg/mm² and grain sizes from 0.4 to 2.8 mm.

Deviations from Matthiessen’s Rule in Dilute Gold and Platinum Alloys
Positive deviations 4(T) from Matthiessen’s rule have been observed in several dilute Au and Pt alloys (solute concentration 0.1-5 at. %). A(T) = α log T for Au-Co and Pt-Rh at 30-200 K. A(T) has a sharp peak at 30-50 K for the low solute concentrations. Results are interpreted in terms of the two-band model, the anisotropy of the electron scattering, and the shift in the Fermi surface due to alloying.

Vacancy Formation and the Thermal Expansion of Gold
J. van den Sype, Scripta Metall., 1970, 4, (4), 251-254
The measurement of the coefficient of thermal expansion of Au at 1000-1900 K is discussed. Measurement by optical comparison and by a direct method agree well at 1000-1400 K. Above 1400 K increasing deviation is in evidence, amounting to 26% at 1900 K. The deviation is explained on the basis of a vacancy relaxation effect inherent in the temperature technique for measuring thermal expansion.

Internal Friction in the Equiatomic Alloy CoPt
Internal friction observed in CoPt during annealing is very sensitive to changes caused by magnetoelastic effects, which are affected by the induced magnetism and by the degree of ordering of CoPt.

Specific Heat and Electrical Resistivity of Exchange-enhanced Dilute Pt-Ni Alloys
The specific heat and electrical resistivity of dilute Pt-Ni alloys were measured at 1.2-4.2 K. Specific heat results fitted C=γT+βT³ and resistivity fitted ρ=ρ₀+AT³. Experimental results are used to evaluate current theories of localised spin fluctuation effects.

On the Structure of the Platinum-Copper-Zinc Composition
Structural analysis of the Pt-Zn-Cu system showed its brass-like properties. Both the valence-electron and the core-electron spatial correlations affect the alloy structure.

Field-electron Microscope Study of Pt-Ba Alloy
An emission image of the surface of single crystals of 1.3 wt.% Ba-Pt was obtained. The formation of an adsorbed Ba film on the alloy surface was studied visually during thermal treatment.

The X-ray Structural Investigation of Pt-Ba and Pd-Ba Alloys in the Region of the Compositions PtₓBa and PdₓBa
PdₓBa and PtₓBa are isomorphous with CaCu₅-type structure. X-ray studies of PtₓBa variously heat-treated show that it is stable over a wide range of temperature, whereas Heumann claimed that it was stable only at high temperatures.

Hydrogen Solubility in Electrolytically Deposited Thin Films of Palladium
The quantity of H₂ absorbed in electrodeposited thin films of Pd in equilibrium at atm. pressure was determined in 0.1 M H₂PO₄ solution at 25°C. For a compact Pd or Pd black film the H₂ solubility r is 0.564 ± 0.003; r is less for bright films and is very sensitive to heating. Use of a Pt anode in the electrodeposition of bright films results in an increase in H₂ solubility above the reference value.

Non-linear Magnetisation of Pd
The non-linear magnetisation of Pd at 4.2 K
was determined in semi-continuous fields up to 325 kOe. For the expression \( M = \gamma H(t + \beta H^2) \), \( \beta = \gamma (9.5 \pm 1.7) \times 10^{-21} \text{ m}^3/\text{A}^2 \). Measurements were repeated with a Pt sample where \( \gamma = (0 \pm 3) \times 10^{-21} \text{ m}^3/\text{A}^2 \) compared with \( (10 \pm 1.8) \times 10^{-21} \text{ m}^3/\text{A}^2 \) for Pd.

Elastic Constants of Monocrystalline Alloys of Pd-Rh and Pd-Ag between 4.2 K and 300 K
The elastic properties of six monocrystalline Pd-Rh and Pd-Ag alloys were measured. Results are presented graphically and agree with the theoretical model predicting a correlation between susceptibility and elastic modulus.

Volume and Shape Magnetostriction of Alloys of Pd-Rh and Pd-Ag at 4.2 K
Longitudinal and transverse magnetostriction of Pd-Rh and Pd-Ag alloys was measured in fields up to 50 kOe. Values of the magnetostrictive coefficients \( S \) and \( S_q \) are presented graphically and are interpreted in terms of a band model.

Optical and Photoemissive Properties of Palladium in the Vacuum Ultraviolet Spectral Region
Optical properties of evaporated films of Pd at \( 10^{-4} \) torr were studied at 2–24 eV. Results are correlated with the photoemissive properties of similar samples for photon energies of 10.2–22.4 eV. Interbond transitions are identified from the optical data at 1.3, 3.6, 15.2, and 20.5 eV; at 7.3 and 7.6 eV peaks appear in energy loss functions \( -1m((e^2 + 1)) \) and \( -1m(1/\epsilon) \), respectively.

Giant Moments of Dilute Fe in Binary and Ternary Pd Alloys
The saturated local moment \( p_{sat} \) and the ordering temperature \( T_c \) of very dilute (\( \approx 1000 \) p.p.m.) Fe in Pd alloys were measured at low temperatures. Alloy systems included Pd-\( _{1-x} \)Ag, Pd-\( _{1-x} \)Pt, or Ni, and Pd-\( _{1-x} \)Rh-\( _x \)Ag, \( p_{sat} \) and the high-field matrix susceptibility \( \chi_{HF} \) were also measured at 1.2–4.2 K up to 60 kG; \( p_{sat} \) was not simply related to \( \chi_{HF} \).

Magnetic Field Dependence of the Specific Heat of Dilute Pd-Co, Pt-Co and Pd-Mn Alloys
The specific heat of Pd-Co-type alloys was measured at 1.2–30 K in external fields of up to 30 kOe; field strength greatly influenced the excess specific heat. A comparison between Pd and Pt alloys emphasised the smaller exchange enhancement in Pt. Results for dilute alloys of Mn in Pd differed greatly from those for Co or Fe in Pd.

The Mechanism of Ordering of Alloys with Periodic Antiphase Domain Structure
Results of electron microscope studies of the dislocation structures of deformed Cu-Pd alloys with regard to the reported ordering mechanism show that, in alloys with a large number of antiphase domain boundaries, ordering mechanisms connected with the movement of pair dislocations have no place.

Low-temperature Specific Heat Study of Cu-Pd Alloys
Variations with composition of the electronic specific heat \( \gamma \) and Debye temperature \( \theta_D \) were determined for Cu-Pd alloys from specific heat measurements at 1.5–4.2 K. Deviations from a rigid-band model were observed for small Pd concentrations. Thermodynamic properties are discussed in terms of the band structure from \( \gamma \) values. Changes in long and short range order have pronounced effects on \( \gamma \) and \( \theta_D \) values.

Magnetic Properties of Mn and Fe in CuPd and AgPd
The magnetic susceptibility of 0.1–1.0 at.% Mn and of dilute solutions of Fe in CuPd and AgPd was measured. Results were interpreted in terms of s-d exchange scattering of conduction electrons at the resonance bound d electrons of Mn, Fe and Pd. This supports a model for AgPd and CuPd with Pd in resonant bound states for low Pd concentrations and in energy band states for high Pd concentrations.

Effect of Atomic Ordering on the Magnetic Structure of the MnPd, Phase
Neutron diffraction and magnetic susceptibility measurements for ordered and disordered MnPd confirmed an antiferromagnetic configuration for 23–30 at.% Mn. The angle \( \theta_C \) of the magnetic moment to the tetragonal axis was 0° below 25% and 90° at higher concentrations. \( \theta_C \) was order-dependent at 25% and increased from 0 to 90° with decreasing order. A decrease in the Néel temperature with decreasing order was also observed.
High Temperature Creep of Rhodium Metal


Studies of the creep of 99.98% Rh in vacuum at 630-1770°C, 0.4-46.2 kg/mm² showed that the activation energy Qc of creep is 91 kcal/mole, agreeing well with estimates of the activation energy Qd.tif of self-diffusion. It follows from the practical agreement in size of Qc and Qd.tif that self-diffusion in Rh controls the rate of deformation during the steady stage of creep.

Electrical Resistance Measurements on Pd Base Alloys


The effect of the presence of 4f magnetic impurity atoms on the electrical resistivity of Pd was investigated at 1.4-60 K. A well defined resistivity minimum exists at ~15 K for 8.9 at. % Gd-Pd with a maximum at ~5 K. This was correlated with magnetic ordering in the alloy.

Magnetic Properties of the Nickel-Rhodium System


Magnetisation and magnetic resonance studies on Ni-Rh alloys, which are ferromagnetic for >63 at.% Ni and paramagnetic for lower Ni concentrations, were compared with data of other workers. A model similar to the Anderson model of dilute magnetic alloys explains all the data qualitatively.

Properties of the Ni-Ir System


Measurements of the lattice parameters, electronic specific heat, magnetic susceptibility and Debye temperature in 0-100 at.% Ir-Ni showed no ordering or decomposition after annealing for several days at 500-1100°C. A sharp peak occurred in the electronic specific heat/concentration curve at ~5 at.% Ni, together with a weak anomaly in the T² term of the low temperature specific heat. Susceptibility was measured on the paramagnetic side only up to 79 at.% Ni, where a spontaneous moment developed at low temperatures.

The W-Re-Ir Composition Diagram


The W angle of the W-Re-Ir system was studied and ordering was investigated throughout the system. Ternary alloys which are α-solid solutions are produced at high temperatures. From them can be produced bars, wires and sheet by hot working, wire drawing and rolling respectively.

On the Composition and Thermodynamics of the Uranium-Ruthenium-Carbon System


The U-Ru-C phase diagram was established at 1300°C using arc-melted and sintered samples of different compositions. The system has two ternary solid phases: URu₃Cₓ and URu₃Cₓ⁺ₓ where xmax≈0.7. Values of the Gibbs free energy of formation are given, and confirmation of the reaction UC → URu₃Cₓ+(1-x)C.

Activation of the Sintering of Tungsten by Platinum-group Metals

G. V. SAMSONOV, Poroshkovaya Metal., 1970, (1), 37-44

Studies of the effect of stable electron configuration of Rh, Pd, Os, and Ru as activators for sintering of W powder compacts at 1000-2000°C showed that it was due to localisation of non-localised electrons from the W atoms in the nuclei of the Pt-metal atoms, thereby promoting mutual dissolution. Activation rose in the order Os, Ru, Rh, and Pd.

CHEMICAL COMPOUNDS

Activation of Nitrogen by Transition-metal Complexes


The synthesis and properties of many N-containing complexes of Ir, Os, Rh, and especially Ru are described.

On the Chemistry of Ruthenium

E. SCHLEITZER, Chem. Z., 1970, 94, (6), 189-192

Ru nitrosyl complexes are important in the reprocessing of used nuclear fuels. Aqueous Ru(III) chloride solution contains complexes of the type [RuX₃(H₂O)_n]^2⁻ with n=1-6, and X=Cl, Br, I, BF₄⁻, or PF₆⁻. Ru and Ru-chloro complex hydrogenation catalysts are discussed.

Properties and Reactions of Ruthenium(II) Amine Complexes


The synthesis, properties and reactions of a large number of Ru(II) complexes with N-containing ligands are described. Complexes with and without π-acceptor ligands, with N₄, N-heterocycles, organonitriles, and with nitrosyls are considered, as are substitution and redox reactions peculiar to the complexes.

Electrical Transport Properties of IrO₂ and RuO₂


Electrical resistivities of single crystals of RuO₂ and IrO₂.
and IrO₂ were measured at 10–1000 K. Hall constants were obtained at 77 and 300 K. The temperature dependence of the resistivity is explained in terms of electron-photon and electron-electron interband scattering.

Thermal Conductivity and Lorenz Ratio of RuO₂
Thermal conductivity and Lorenz ratios of very pure RuO₂ crystals were investigated. Conductivity temperature curves show that $\kappa = 8.42 \times 10^{-3} \text{cm deg K}^{-1} \text{W}^{-1}$, $\beta = 18.1 \text{ cm deg K}^{-2} \text{W}^{-1}$, and n = 1.66. At low temperatures the Lorenz ratio reached a constant value of $(2.60 \pm 0.1) \times 10^{-8}$ WΩ⁻¹ deg K², which is close to the theoretical value of $2.45 \times 10^{-8}$ WΩ⁻¹ deg K².

Refinement of the Crystal Structure of Ruthenium Dioxide
RuO₂ has a rutile structure, crystallises in space group $P4_3/mm$ of the tetragonal system. The unit cell contains two formula units, and has dimensions $a = 4.491$, $c = 3.106$, and $V = 64.48 \text{ Å}^3$.

Precision Determination of the Crystal Structure of Osmium Dioxide
Ibid., 123–128
OsO₄ has a rutile structure crystallising in space group $P4_3/mnm$ of the tetragonal system with two formula units per unit cell. Unit cell dimensions are $a = 4.500$, $c = 3.183$, and $V = 64.48 \text{ Å}^3$.

Some New Organometallic Compounds of Osmium Tetraarenebonyl
The reactions of Os carbonyl compounds with H₂ and allyl halides were studied. Dialkyl complexes, e.g., cis-Os(C₂H₅)₂(CO)₄ and cis-Os(C₂H₅)(CO)₄, were isolated and their structures and spectral were determined. Their reactions with CO at elevated temperature and pressure were studied; the former was converted to Os(CO)₅ and the latter to cis-Os(COC₂H₅)₂(CO)₄.

ELECTROCHEMISTRY

The Oxidation of Hydrazine in Alkaline Solution at Platinum and Mercury
The mechanism of N₂H₄ oxidation in alkaline solution was investigated at Pt and Hg. On Pt the oxidation is a surface process involving a fast three-electron transfer preceding a one-electron rate-determining step. The reaction is fourth order in $\text{H}_2^+$.

Hydrogen Sorption by Palladium in Hydrazine Electro-oxidation
The amount of H₂ absorbed by Pd in N₂H₄ electro-oxidation increases with anodic polarisation. H₂ is present in Pt after N₂H₄ electro-oxidation at high positive potentials, (up to 1.0 V). H₂ is an intermediate product of N₂H₄ electro-oxidation and is probably produced by the decomposition of intermediate radicals.

On the Interaction of Carbon Monoxide with an Iridium Electrode Catalyst
Charging curves were obtained at 20, 30, 50, and 70°C for Ir electrodes in 1 N H₂SO₄ in the presence of H₂. CO reduces the Slade potential more than with Pt or Rh.

Electrosorption of Molecular Oxygen from Aprotic Solvents on Noble Metal-Mercury Alloys
Chronocoulometry shows that O₂ is adsorbed on alloys of Hg with Pt, Au, Ir, and Rh from solutions in acetonitrile, dmf and dms reaching 200–800 μC/cm². Adsorption depends on alloy composition, electrode potential and O₂ concentration. Double layer capacity increases with alloy formation.

ELECTRODEPOSITION
AND SURFACE COATINGS

Internal Stresses of Platinum Coatings on Titanium
The internal stresses arising during electrodeposition of Pt on Ti are discussed and optimum conditions for formation of coatings with minimum internal stress are described.

LABORATORY APPARATUS
AND TECHNIQUE

An Automatic Spherical High Temperature Adiabatic Calorimeter
The calorimeter, which was developed for determination of specific heats and enthalpies of transformation of Fe alloys at 650–1750 K, has ±1.2% reproducibility and ±1.5% absolute accuracy for an enthalpy of transformation of 923 J/g atom at 1184 K. Energy is supplied to the specimen by a small 10% Rh-Pt immersion heater which also supports the specimen in the inner spherical.
chamber. Temperature distribution in the calorimeter is measured with Pt:10% Rh-Pt thermocouples at the poles and equators.

Production of Micro-steam Quantities for Thermocouples at the Poles and Equators

Production of micro-steam quantities for thermocouples at the poles and equators utilizes a calorimeter measured with Pt:10% Rh-Pt thermocouples. A cell capable of giving as little as 3 ml of steam per minute was constructed using Pt wire electrodes wound on glass formers to electrolytically convert water to H₂ and O₂, and Pt/Asbestos to catalytically recombine them as steam near as possible to the reactor to be dosed with gas of consistent composition.

HETEROGENEOUS CATALYSIS

Here's How New Platforming Catalysts Are Performing

Production of Petrol with Octane Number 95 at Industrial Catalytic Reforming Plant

Conversion of C₆ Hydrocarbons on Platinum Alumina Catalysts Modified by Manganese

Deactivation of Platinum/Alumina Reforming Catalysts by Carbon Deposits

Studies of the Regularity of Crystallisation of Platinum on Supports. IV. Effect of Conditions of Preparation on the Dispersion of Platinum

Dehydrocyclodimerisation. I. Dehydrocyclodimerisation of Butanes over Supported Platinum Catalysts

Dehydrocyclodimerisation of Propane and Pentane over Supported Platinum Catalysts

Production of Petrol with Octane Number 95

Conversions of C₆ Hydrocarbons on Platinum Alumina Catalysts Modified by Manganese
IV. The Reactions of Butenes

To clarify the role of olefins as possible key intermediates in this process, C,H4 was reacted over Pt/Al2O3 and the product contained a large fraction of C5-C8 olefins and naphthenes. These and some aromatics also form over acidic catalysts with no dehydrogenation component. Results indicate that dehydrocyclodimerisation proceeds via conversion of light paraffins to olefins, dimerisation of these olefins and aromatisation of the dimers.

Effect of Heat Treatment on the Catalytic and Physical Properties of Pt/Al2O3 Adsorption Catalysts


Studies of the sintering of Pt/Al2O3 at various stages of charging with Pt showed that in vacuum a steady amount of activity and surface is reached at each stage. Isochronous sintering has a minimum at 300-400°C. A decrease in activity during roasting is accompanied by a decrease in surface area and a decrease in size is accompanied by a drop in the number of Pt crystals. The number of active centres on the catalysts was determined.

Dehydrogenation of Dicyclohexyl over a Platinum-Alumina Catalyst without Added Hydrogen


The effects of pressure, temperature and space velocity on the rates of reaction over Pt/Al2O3 were determined in the range 10-30 atm, 700-1300°C. High selectivity for the production of diphenyl was favoured by high temperature, high conversion and low pressure.

The Form of Active Centres of Adsorption Platinum Catalysts in Vapour-phase Processes


Active centres of Pt/SiO2 catalysts for vapour-phase hydrogenation of cyclohexene and dehydrogenation of cyclohexane are pairs of Pt atoms [Pt]2 as established during the reduction of CH3CO.CH3, which showed that reduction of the C=O bond requires the proximity of two Pt atoms each with two free valencies.

On the Orientation of Cyclic Hydrocarbons with Medium-sized Rings in the Adsorption of Complexes on Platinum Catalysts


Differential heats of adsorption on C5-C12 cycloparaffins and n-paraffins over 5% Pt/asbestos were determined by chromatography. Cyclane molecules were oriented to the surface by CH4 groups containing transannular H atoms when in H2 atmosphere but in N2 atmosphere they were oriented by the maximum number of CH4 groups. The difference in entropy of adsorption of cycloparaffins in the two atmospheres was calculated. The high reactivity of medium-sized cycloparaffins in transannular dehydrocyclisation is due to the specific orientation of their molecules on the catalyst surface by reacting C atoms.

Kinetics and Mechanism of Oxidation of Carbon Monoxide on Platinum, Purified in High Vacuum

I. I. TRET’YAKOV, A. V. SKLYAROV and B. R. SHUB, Ibid., (1), 166-175

A scheme is proposed for the oxidation of CO on Pt, purified in high vacuum at 10^-1-10^-2 torr, 175-1000°C. The reaction proceeds by a shock mechanism between adsorbed O2 and CO from the gaseous phase.

Determination of Surface Area by Chemisorption: Unsupported Platinum


Adsorption of H2 and O2, as well as reaction of H2, was studied gravimetrically and volumetrically on Pt black. H2O formed leaves the surface but is not replaced by additional H2. Amount of H2 adsorbed is the same on a reduced and evacuated surface as on a preoxidised surface. Ratio of adsorbed H and O atoms to surface Pt atoms is close to unity at room temperature and 50 torr.

The Problem of Standardising Pt-Catalysts


Exact control of alkali metal cation content is required to produce at PtO2 catalyst most suitable for a given reaction. The electrochemical potential of Pt black varies inversely with cation content and indicates the degree of purity of PrO2. Hydrogenation rate of compounds with various types of chemical bonds depends on the potential of the Pt black.

On the Effect of the Structure of Medium Size Cyclanes on their Catalytic Reactions in the Presence of Platinum


Studies of the reactions of C8 and C12 cycloparaffins on Pt/C showed the kinetics of decomposition of cyclooctane, cyclononane and cyclodecane, whose reactivities depended on their structures.
Hydrogen Chemisorption and Surface Composition of Silica-supported Platinum-Copper Alloys


9, 14, 19, and 25% Cu-Pt alloys were formed into 5 and 0.55 wt. % metal/SiO₂ catalysts. Surface composition of alloy crystallites depended upon crystallite size; the larger the crystallite, the more the surface was enriched with Cu. Surface composition of 30Å crystallites approached that of their interior.

The Hydrogenation of Ethylacetylene. III. Reaction of Ethylacetylene with Hydrogen Catalysed by Platinum and Iridium

R. S. Mann and K. C. Khulse, Ibid., (1), 46-53

When ethylacetylene and H₂ reacted over pumice-supported and unsupported Pt and Ir at 20-80°C in various reactant ratios, the orders of reaction with respect to ethylacetylene and H₂ were zero and one, respectively. Overall apparent activation energies were determined. Changes in selectivity and activity in relation to physical properties are discussed.

Vinyl Acetate. Vapour-phase Process


The Hoechst-Bayer vapour-phase process for the catalytic conversion of C₂H₄, CH₃COOH and O₂ to vinyl acetate uses noble metal fixed bed catalysts, e.g., 0.1-2.0 wt. % Pd on Al₂O₃ and/or SiO₂. An alkali acetate moderator improves the yield but requires constant replenishment. 91-94% selectivity is achieved and activity remains high for several months. Fluidised bed technique is also possible.

The Mechanism of the Palladium-catalysed Synthesis of Vinyl Acetate from Ethylene in a Heterogeneous Gas Reaction


Studies of Pd in the synthesis of vinyl acetate from C₂H₄ suggest that C₂H₄ and CH₃COOH are activated by abstraction of H by Pd, (even when O is absent for C₂H₄ whereas it only occurs for CH₃COOH when O is present). Vinyl acetate is produced by combining dissociatively adsorbed CH₃COOH and C₂H₄, which is the rate-determining step in industrial reactions. Co-catalysts, e.g., K or other alkali metals, promote abstraction of H from CH₃COOH and weaken Pd-O bonds in dissociatively adsorbed CH₃COOH.

Study of Catalytic Hydrogenation in Liquid Phase


The selectivity of hydrogenation on a Pd/C catalyst does not depend on temperature, and is not influenced by catalyst poison, but increases with H₂ partial pressure. Hydrogenation and isomerisation probably proceed on identical catalytic centres, their extent being governed by the strength of the olefin-active centre bond.

Fundamental Studies on Supported Palladium Catalysts


The amount of H₂ adsorbed on a Pd/C catalyst is much larger than on Pd wire or Pd black under the same conditions. The specific surface area has a great effect on the absorption isotherm. The relation between the specific surface area of Pd and the amount of H₂ absorbed was studied using Pd/SiO₂-Al₂O₃.

Asymmetric Hydrogenation Using Modified Cellulose-Palladium Catalysts

K. Harada and T. Yoshida, Naturwissenschaften, 1970, 57, (3), 131

Benzoylformic acid and α-acetamidoacrylic acid were hydrogenated using a series of Pd/cellulose catalysts to mandelic acid and alanine respectively. The products were of high optical purity, which was not obtained when unmodified catalysts were used. The celluloses used were carboxymethyl cellulose, aminoethyl cellulose and diethylaminoethyl cellulose.

Asymmetric Hydrogenation Using Modified Ion Exchange Resin-Palladium Catalysts

Ibid., (6), 306-307

The same hydrogenations as above were carried out using a Pd-resin complex. The carboxylic acid resin was modified with optically active L-alanine or L-phenylalanine to give optically active products.

The Change of Adsorption and Catalytic Properties of Rh Black in the Presence of Cations


Tests in H₂SO₄ electrolytes with additions of Cd, Ti, and Zn sulphates and of Pb acetate showed that the amount of H₂ absorbed on Rh black decreases as the cation concentration rises. Thus hydrogenation of dimethylacetylenediol and of butyn-1-ol-3 on modified Rh black is slower than on Rh black without cations.

Catalytic Properties of Iridium Deposited on Alumina. III. Application of Thermo-desorption to the Study of Adsorbed Ammonia


NH₃ adsorbed on γ-Al₂O₃, Ir/Al₂O₃ and Ir/SiO₂...
was studied by thermodesorption. The desorption activation energy was studied as a function of surface coverage from which the desorption sites energy distribution was calculated. For Ir/Al₂O₃, catalysis the desorption activation energy is 10.7 kcal/mole and is independent of the surface coverage.

**Catalytic Reactions in an Ultrasonic Field**


An ultrasonic field acting on an aqueous N₂-H₂ solution in the presence of Pt-, Rh- and Pd-blacks increased the NH₃ yield from 2 up to 6.5 times with the greatest yield using Rh. An ultrasonic field during H₂O₂ decomposition on Pt, Rh and Pd showed increased activity up to 10 times on Pt black, up to 2.5 times on Rh black but lower activity on Pd black. Change of activity was related to quantity of catalyst, e.g., reduction from 5 to 1 mg increased the activity of Pd by up to 4.5 times.

**On the Relation of the Stereochemistry of Hydrogenation of Cyclo-olefins to the Nature of the Catalysts - Refractory Group VIII Metals**


The activity of Group VIII metal catalysts for liquid-phase hydrogenation of methylcyclopentane decreases in the order: Pt > Rh > Pd > Ir > Os > Ru > Co. Studies of the stereochemistry of hydrogenation of dialkylcyclopentanes over Pt/C, Pd/C, Rh/C, and Ir/C showed that the mixture of stereoisomeric 1,2-dialkylcyclopentanes produced was richer in the trans isomer over Pt/C and Pd/C, and richer in the cis isomer over Rh/C and especially over Ir/C. A new mechanism for the hydrogenation of substituted cyclo-olefins is discussed.

**Liquid-phase Hydrogenation of cis- and trans-Cyclo-olefines over Group VIII Metals**

V. I. ALKERESEVA, E. S. BALENKOVA, L. E. MARININA and S. I. KHROMOV, Neft' khimiya, 1970, 10, (3), 315–320

The constants were determined of the ratios of hydrogenation of cis-cyclodecene over Pt, Ir and Rh blacks, of trans-cyclodecene over Pt and Ir blacks, and of the rates of isomerisation of trans- to cis-cyclodecene over Pt, Ir and Pd blacks. The hydrogenation rate constants of cyclo-olefines are related to ring size, which is connected with the pressure of the cycloparaffins formed; the higher this pressure, the less is the rate constant of hydrogenation of the initial cyclo-olefin. Both cis- and trans-forms of cyclodecene are reduced at the same rate during this reaction.

**HOMOGENEOUS CATALYSIS**

**Intramolecular Aromatic Substitution in Transition Metal Complexes**


An aryl C-H bond in a donor ligand of a transition metal complex reacts with the central metal atom to form a metal-C bond. The H originally attached to C adds to the metal to form a metal-H bond or is eliminated as H⁺. This reaction is generally intramolecular and involves an ortho H bond of an aromatic N- or P-donor ligand. Reactions involving these ligands and complexes of Pt, Pd, Ir, Rh, and Ru are reviewed and the catalytic activity of triarylphosphine complexes is related to the studied mechanism.

**Reactions of Acetylenes with Noble-metal Halides. VIII. The Palladium Chloride Catalysed Trimerisation of 2-Butyne and 1-Phenyl-1-propyne**


A series of these reactions was carried out. The mechanism was examined.

**IX. The Decomposition of the Complex [Cl(Me₂C₆H₅)₂PdCl]₂, Particularly to Vinylpentamethylcyclopentadiene**

H. REINHEIMER, J. MOFFAT and P. M. MAITLIS, Ibid., 2285–2294

The mechanism of this reaction is discussed.

**Organic Syntheses by Means of Noble Metal Compounds. XLI. Reaction of Isocyandie with π-Allyl-palladium Chloride**


The treatment of cyclohexyl isocyanide with π-allyl Pd chloride in C₆H₆ at room temperature gave di-μ-chloro-bis[1-(cyclohexylimino)-3-butenyl]-bis(cyclohexyl isocyanide)dipalladium by the insertion reaction, whose progress was followed by NMR spectroscopy.

**Kinetics and Mechanism of the Oxidation of Olefins by Palladium Salts**


Experimental data are reviewed for the equilibrium formation of olefin π-complexes of Pd and for the kinetics of reduction of Pd salts by olefins in hydroxyl-containing solvents. The reduction includes the intermediate formation of π-complexes, their conversion into σ-bonded organopalladium compounds, and their heterocyclic decomposition. The mechanism of π-σ isomerisation and of the decomposition of organopalladium compounds is discussed.

Ligand Factors in the Isomerisation of Olefins by Palladium Complexes
Studies of the equilibrium isomerisation of 1-hexene in methyl chloride catalysed by a series of 1,3-dichloro-2-hex-1-ene-4-(pZpyridine-N-oxide)Pd(II) complexes showed that it is sensitive to the electronic nature of the trans N-oxide ligand, isomerisation only occurring when this ligand dissociates from the Pd-olefin complex. When the complex contains a strongly electron-withdrawing ligand the equilibrium favours free ligand and the catalyst system is then very effective.

Polymerisation of Butadiene by Rhodium Trichloride in Aqueous Medium
K formate and saturated aldehydes increase the rate of butadiene polymerisation by RhCl₃, probably due to the reducing action of these compounds, which support the Rh having a lower degree of oxidation. Even low concentrations of K acetate lower the polymerisation rate.

Hydride Transfer Reactions Catalysed by Rhodium-Tin Complexes
Rh-Sn chloride complexes catalyse dehydrogenation of isopropyl alcohol to acetone, and H-D exchange between the C=CH and OH group of the alcohol. Reaction mechanisms are suggested.

Rhodium Catalysts for the Homogeneous Hydrogenation of Ketones
[RhH₃X₃L₃]⁺ complexes, where L=solvent and X=CH₂Me, CH₂Me₂ or PMe₃, catalyse the reduction of ketones under mild conditions, when promoted by small amounts of H₂O.

Desulphonation of Aromatic Sulphonyl Halides Catalysed by Some Platinum-metal Complexes
Desulphonylation of arenesulphonyl chlorides and bromides using RhCl(PPh₃)₃, RhCl(CO)(PPh₃)₂, IrCl(CO)(PPh₃)₂, RuCl₂(PPh₃)₂, and PdCl₂ catalysts is assumed to proceed mainly by a metal ion-promoted mechanism and partly by homolytic decomposition. A theory of the former accounting observations includes the steps ArSO₂IrCl₃(CO)(PPh₃)₂ → ArSO₂IrCl₄(CO)(PPh₃)₂ → ArIrCl₃(CO)(SO₂)₂(PPh₃) and loss of SO₂ from the last compound. Some new Rh and Ir complexes are described.

Homogeneous Olefin Hydrogenation over Oxidised Rhodium Complexes
R. L. AUGUSTINE and J. F. VAN PEPPEN, Ibid., 571–572
Hydrogenation of oxides obtained by oxidation of [Rh(Ph₃P)Cl] in C₆H₅H and C₆H₆ gives materials capable of olefin hydrogenation but double-bond isomerisation occurs in the reaction. Hydrogenation of these species in the presence of Ph₃P gives catalysts much more active for olefin hydrogenation and which also inhibit isomerisation.

Homogeneous Catalytic Hydrogenation of α,β-Unsaturated Nitro Compounds Using Triarylphosphine-rhodium Complexes
RhCl(Ph₃P)₃ and trichlorotris [4-biphenyl] (1-naphthyl)phenylphosphine)rhodium(III) were used as homogeneous catalysts for the hydrogenation of α,β-unsaturated nitro compounds.

Synthesis of Trichlorotris(4-biphenyl-1-naphthylphosphine)rhodium(III). New Octahedral Complex
The complete synthesis of this complex is described. This complex is another potential homogeneous catalyst.

Use of Transition Metal Complexes as Selective Hydrogenation Catalysts
Several specific examples of selective catalysis by noble metal complexes are given. Catalysts discussed include: IrX(CO)(Ph₃P)₂, where X=H or halogen; IrH₃(Ph₃P)₃; (Ph₃P)₃MCl₃, where M=Pt or Pd; and especially complexes of Rh with Ph₃P, CO, H₂ and halogens.

CORROSION PREVENTION
Anodic Behaviour of Pb-Pt Bielectrodes in Low Salinity Electrolytes
The Pb-Pt bielectrode was studied in various salinities. A thin film of PbO+PbS formed on the surface aids PbO₂ formation and growth. In solutions >0.1 M NaCl the Pt microelectrode influences the sequence of events leading to the initial passivation prior to PbO₂ formation and subsequently is vital to the nucelation and growth of PbO₂.
ELECTRICAL AND ELECTRONIC ENGINEERING

Beam Lead Technology
Beam leads of Au for Si monolithic circuits are produced in four stages: passivation, metal deposition, circuit delineation, and chip separation. During the second stage a thin layer of Pt is sputter-deposited over the whole slice and sintered into the contact window areas to produce Pt silicide. Excess Pt is etched away without masking. Layers of Ti and Pt are then deposited in sequence over the whole slice. Ti keys the metallising to the passivation surface. Pt acts as a diffusion barrier to subsequent Au deposition.

TEMPERATURE MEASUREMENT
Investigations on Very Thin Thermocouple Wires Made from Noble Metal Alloys
Measurements with 20 μm diam. wire 52% Au-46% Pd-2% Pt-5% Rh-95% Pt thermocouples were irreproducible because of deformation of the wire but a heat treatment was developed to standardise the structure.

NEW PATENTS

METALS AND ALLOYS
Silver Alloy for Electrical Contacts
TEXAS INSTRUMENTS INC.
British Patent 1,191,675
An improved alloy for contacts consists of 1-20% CdO, 0.001-0.5% Ru or Hg and the balance Ag. The Ru is superior to Co in increasing the erosion resistance of Ag Cd oxide alloys.

Sheathed Metal
JOHNSON MATTHEY & CO. LTD
British Patent 1,195,349
A core of W or Mo or a W-Mo alloy is sheathed with a Pt group metal, or an alloy based on at least one Pt group metal. A barrier layer is disposed between core and sheath, and Pd, in the interfacial space is reduced to < 1 μ.

Palladium-Iridium Alloy for Glass Fibre Production
OWENS-CORNING FIBREGLASS CORP.
U.S. Patent 3,488,172
A bushing fabricated from an alloy containing 95-99.7% Pd and 5-0.3% Ir by weight made by melting and casting under a vacuum of about 1 mm of Hg can be used for glass fibre production.

Platinum-Rhodium-Gold Alloy
JOHNSON MATTHEY & CO. LTD
German Appl. 1,533,284
Pt-Rh-Au alloys, suitable for use in contact with molten glass, consist of: 60-97 wt.% Pt, 2-25 wt.% Rh and 1-10 wt.% Au.

Alloy
JOHNSON MATTHEY & CO. LTD
German Appl. 1,533,290
An alloy suitable for use in the fabrication of spinetteres consists of: 50-80 wt.% Au, 0.04-0.5 wt.% Ir and the remainder Pt. Preferred quantities are 70, 0.2 and 29.8 wt.% respectively.

Dispersion Hardened Metals and Alloys
JOHNSON MATTHEY & CO. LTD
Dutch Appl. 69.10,671
The metal or alloy to be hardened is flame sprayed with a reactive component which is then converted to a dispersed phase component. The examples show the use of the process in hardening precious metals and alloys.

CHEMICAL COMPOUNDS
Ruthenium Tetracarbonyl Trimer
RHONE-POULENC S.A.
British Patent 1,189,255
[Ru(CO)₃]₄₈ is prepared by heating CO with a tris (β-dionato)Ru at 100° to 250°C and atmospheric pressure in an alcohol boiling between 100° and 250°C.

Osmium Carbonyl
JOHNSON MATTHEY & CO. LTD
U.S. Patent 3,508,870
A method of preparing Os carbonyls wherein a solution of OsO₄ in an inert hydrocarbon solvent is heated at an elevated temperature at super-atmospheric pressure in the presence of CO. The product is primarily Os₉(CO)₁₄ with traces of Os₈O₄(CO)₁₂.

ELECTROCHEMISTRY
Electrochemical Cells
LEESONA CORP.
British Patent 1,199,017
A light-weight electrode consists of an expanded layer of a catalytic metal such as Au, Pd, Pt, Ir, Rh, Ru or Os.