

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

The Adsorption of Krypton on Platinum Films Thermally Treated

YA. ADAMEK, V. D. YAGODOVSKII and V. M. GRYAZNOV, *Kinetika i Kataliz*, 1965, 6, (3), 486-492

Kr adsorption showed that thermal treatment of Pt films at 100-740°C increased their surface areas or maintained them at their original value. Surface heterogeneity was reduced. Treatment of Pt film on glass at 630°C caused ageing and decreased the surface area at lower temperatures due to defect formation.

The Problem of the Nature of the High Coercive Force in Cobalt-Platinum Alloys

D. D. MISHIN, YA. S. SHUR and V. I. TIMOSHCHUK, *Fiz. Met. Metalloved.*, 1965, 19, (5), 793-796

The magnetisation of equiatomic Co-Pt alloys was studied at -196 to 350°C to relate their coercivity H_c to magnetic saturation I_s and magnetic anisotropy constant K . Coercivity is greatly reduced as the temperature rises but I_s changes less. These variations are related to the two-phase b.c. composition of the alloys—cubic and irregular; tetragonal and regular.

Use of Platinum Alloy for Electrical Leads at Liquid Helium Temperatures. Heat Conductivity

A. J. BUHL and W. F. GIAUQUE, *Rev. Sci. Instrum.*, 1965, 36, (5), 703

9% W-Pt has small thermal conductivity and is therefore useful in superconducting leads for work in high magnetic fields. Observed and calculated values were in good agreement between 1 and 4°K.

Equiatomic Transition Metal Alloys of Manganese. IV. A Neutron Diffraction Study of Magnetic Ordering in the PtMn Phase

A. F. ANDERSEN, A. KJEKSHUS, R. M. ØLLERUD and W. B. PEARSON, *Phil. Mag.*, 1965, 11, (114), 1245-1256

PtMn with CuAu I structure has antiferromagnetic arrangement of magnetic moments with spin quantum numbers of 4/2 for Mn atoms, 0 for Pt atoms. Moments of nearest-neighbour Mn atoms in (001) planes are antiparallel. Direction of moments is parallel to c in ≤ 50 at.% Pt alloys, perpendicular to c in > 50 at.% Pt alloys. Néel temperatures are observed at 840-970°K. Weak ferro-magnetism at lower temperatures is caused by canting of the moments.

Semiconducting Properties of PtSb₂

D. H. DAMON, R. C. MILLER and A. SAGAR, *Phys. Rev.*, 1965, 138, (2A), A636-A645

Hall coefficient, electrical conductivity, Seebeck coefficient, magnetoresistance, piezo resistance, magnetic susceptibility, and elastic constants of PtSb₂ were measured in the range 78-1200°K. Samples from a PtSb₂ melt were p -type and additions of Te produced n -type samples.

Mass Spectrometric Knudsen Cell Measurements of the Vapour Pressure of Palladium and the Partial Pressure of Palladium Oxide

J. H. NORMAN, H. G. STALEY and W. E. BELL, *J. Phys. Chem.*, 1965, 69, (4), 1373-1376

Measurements of the vapour pressure of Pd and of the partial pressure of PdO(g) in equilibrium with Pd(s) in an O₂ atmosphere are $\Delta H^\circ_{298} = 91.0$ kcal/mole for Pd(s)=Pd(g), and $\Delta H^\circ_{298} = 83.4$ kcal/mole and $\Delta S^\circ_{298} = 18.8$ e.u. for Pd(s)+1/2O₂=PdO(g). $\log P_{Pd}(\text{atm}) = (-19,370/T) + 6.120$ at 1485-1710°K.

X-ray Investigation of the Solubility of Hydrogen in Dispersed and Compacted Palladium

ZH. L. VERT, I. A. MOSEVICH and I. P. TVERDOVSKII, *Zh. Fiz. Khim.*, 1965, 39, (5), 1061-1064

X-ray measurements of lattice spacings of Pd black and Pd foil during dissolution and desorption of H₂ in near-equilibrium conditions showed that the parameters of the α and β phases at the α - β transition remain constant and are unrelated to H₂ content and process direction. The (Pd-H) β phase grows linearly in agreement with solubility isotherms starting with $C_H : C_{Pd} = 0.53/0.54$. Linear growth also occurs in 10% Cu-Pd in spite of the absence of a horizontal stage on the solubility isotherm.

Dilute Ferromagnetic Alloys

J. CRANGLE and W. R. SCOTT, *J. Appl. Phys.*, 1965, 36, (3/2), 921-928

Magnetic moments and Curie temperatures were measured for dilute Fe-Pd, Fe-Pt, Co-Pt, and Ni-Pd alloys. Ferromagnetism also occurs in Gd-Pd and Fe-Au alloys.

Diffusion of Hydrogen through Palladium and Palladium-Silver Alloys

D. M. JEWETT and A. C. MAKRIDES, *Trans. Faraday Soc.*, 1965, 61, (5), 932-939

Tests on 0.0051 cm thick Pd and 0.0025 cm Ag-Pd membranes showed that the permeation

rate of H_2 at 27°C depends on the pressure by a relation derived for a two-phase system with different diffusion constants and that the permeation rate decreases with increasing Ag content at room temperature. The diffusion constants are 1.6×10^{-7} cm²/s in the low H_2 -content α -phase; 1.5×10^{-6} cm²/s in the high H_2 -content β -phase.

Wettability of Metals under Continuous Condensing Conditions

R. A. ERB, *J. Phys. Chem.*, 1965, **69**, (4), 1036-1039
Wettability tests in pure steam for long periods gave contact angles for Au, 55-85°; Ag, 68-89°; Rh, 65-82°; Pd, 74°; Pt, 50°. H_2O condensed as a film on Ni, Cd, Ti, Cr, type 316 stainless steel, 10% Ni-Cu, and quartz, indicating zero or low contact angles. A clean "high-energy surface" of metal substantially O_2 -free is not wettable by H_2O .

Constitution Diagram and Some Properties of Alloys of the Nickel-Rhodium System

I. I. KORNILOV and K. P. MYASNIKOVA, *Izv. Akad. Nauk S.S.S.R., Metall.*, 1965, (2), 175-179

Thermal, microstructural and X-ray tests on the Ni-Rh system showed that there is a continuous series of solid solutions but that the change in the lattice parameter deviates from linearity as Rh content increases. The anomalous increase in hardness which occurs at 61 at.% Rh is probably connected with the formation of a regular structure in the $NiRh_3$ region.

Neutron and X-ray Diffraction Study of $LiRh$

S. S. SIDHU, K. D. ANDERSON and D. D. ZAUBERIS, *Acta Cryst.*, 1965, **18**, (5), 906-907

Rh and Li atoms occupy preferred positions in the hexagonal unit cell with Rh atoms in one layer and Li atoms in the other, the layers alternating along c at $c_0/2$ distances apart. Space group is $P6_3$; $a_0 = 2.649 \pm 0.003$, $c_0 = 4.357 \pm 0.002$ Å. Interatomic distances are Rh-Rh = Li-Li = 2.649, Rh-Li = 2.663 Å.

Phase Relations between Iridium and the Sesquioxides in Air

S. J. SCHNEIDER, J. L. WARING and R. E. TRESSLER, *J. Res. N.B.S., Sect. A, Phys. Chem.*, 1965, **69A**, (3), 245-254

X-ray studies were made of the reactions in air between Ir and IrO_2 with each of Nd_2O_3 , Sm_2O_3 , Eu_2O_3 , Gd_2O_3 , Dy_2O_3 , Ho_2O_3 , Y_2O_3 , Er_2O_3 , Tm_2O_3 , Yb_2O_3 , Lu_2O_3 , In_2O_3 , Sc_2O_3 and Al_2O_3 . Ir oxidises at low temperatures to IrO_2 , which dissociates at 1020°C. Nd_2O_3 - IrO_2 was studied in detail. Nd_2O_3 -2 IrO_2 is a cubic pyrochlore phase which dissociates at 1190°C. 3 Nd_2O_3 -2 IrO_2 dissociates to Nd_2O_3 and Ir after possibly losing O_2 at 1195°C. No further reactions between Nd_2O_3 and Ir occurred up to 2000°C. The other rare earths behaved similarly but no apparent reaction occurred between IrO_2 and In_2O_3 , Sc_2O_3 or Al_2O_3 .

Hot-stage Microscope Determination of the Solidus Temperatures of Iridium Alloys with about 1 wt.% Boron, Phosphorus or Silicon

G. REINACHER, *Metall.*, 1965, **19**, (7), 707-711

Tests on powder samples of 1.5 wt.% B-Ir, 1 wt.% P-Ir and 1.5 wt.% Si-Ir gave their solidus temperatures as 1046, 1262 and 1470°C compared with 750, 588 and 830°C for the corresponding Pt alloys. This confirmed laboratory experience that Ir apparatus is much more corrosion-resistant than Pt apparatus to B, P and Si.

On the Structure of the Ruthenium-Silicon System

W. OBROWSKI, *Metall.*, 1965, **19**, (7), 741-742

The system includes the silicides Ru_2Si , $RuSi$ and Ru_3Si_3 as well as Ru and Si mixed crystals. There are three eutectic and one peritectic reactions. $RuSi$ and Ru_2Si_3 melt without decomposing. Ru dissolves <2 at.% (0.5 wt.%) Si in the solid state and Si dissolves at least 3 at.% (10 wt.%) Ru.

Equiatomic Compounds of the Transition and Lanthanide Elements with Rh, Ir, Ni and Pt

A. E. DWIGHT, R. A. CONNER and J. W. DOWNEY, *Acta Cryst.*, 1965, **18**, (5), 835-839

Crystal structures and lattice parameters are tabulated for 60 equiatomic intermetallic compounds with the orthorhombic $B19_B$ and $B27$ and the cubic $B2$ structures.

CHEMICAL COMPOUNDS

Enhanced Oxidation of Platinum in Activated Oxygen. II. Identity of Active Species and Oxide Formed

G. C. FRYBURG, *J. Chem. Phys.*, 1965, **42**, (11), 4051-4052

The O atom causes the enhanced oxidation of Pt in activated O_2 above 800°C. The oxide formed is PtO_2 which may partly decompose to give the impression that PtO has been formed.

Structural Studies on Platinum(II) Chloride

K. BRODERSEN, G. THIELE and H. G. SCHNERING, *Z. anorg. allgem. Chem.*, 1965, **337**, (3-4), 120-127

X-ray studies of black-red single crystals of $PtCl_2$ prepared by chemical transport methods showed that $PtCl_2$ consists of Pt_6Cl_{12} groups with Cl on the edges of an octahedron built up by 6 Pt atoms. $PtCl_2$ is diamagnetic and has a different reflection spectrum to that of other Pt(II)-Cl compounds.

On the Hydrolysis of Potassium Chlorplatinit

N. M. NIKOLAEVA, B. V. PITTSYN and I. I. GORBACHEVA, *Zh. Neorg. Khim.*, 1965, **10**, (5), 1051-1057

Equilibrium constants of the first stage of

$K_2[PtCl_4]$ hydrolysis were determined at 25, 35, 45 and 55°C from which the enthalpy is $\Delta H^\circ = 5.35$ kcal and the reaction constants are $E = 22.1$ kcal, $\log PZ = 10$, $\Delta H^\ddagger = 21.51$ kcal, $\Delta S^\ddagger = -12.7$ eV. Measurements on the second stage at 35, 45 and 55°C give $\Delta H^\circ = 31.2$ kcal.

The Hydrolysis of Potassium Chloroplatinate

N. M. NIKOLAEVA, B. V. PTITSYN and E. D. PASTUKHOVA, *Ibid.*, 1058-1061

The rate of the first stage of hydrolysis of $K_2[PtCl_4]$ is less than the second. The rates increase with temperature. Equilibrium in the hydrolysis of $K_2[PtCl_4]$ occurs after 1-5 h. At 22-55°C the orientation constants of the first and second stages are 6.10^{-8} and 2.10^{-4} . Dissociation constants of $[PtCl_5(H_2O)]^-$ are $k = 1.10^{-5}$ and of $[PtCl_4(H_2O)_2]$ are $k_1 \approx 6.3.10^{-5}$ and $k_2 \approx 6.3.10^{-7}$.

Four New Complexes of Platinum and Palladium with Cyclooctene and 4-Vinylcyclohexene

E. KULJIAN and H. FRYE, *Z. Naturf.*, 1965, 20b, (3), 204-205

The syntheses are reported of 4-vinylcyclohexene-Pt(II)-chloride and -bromide, and of cyclooctene-Pd(II)-chloride and -Pt(II)-chloride. Spectral data of these complexes are tabulated.

Cyclooctatetraene Palladium(II) Bromide; Synthesis and Characterisation

H. FRYE, E. KULJIAN and J. VIEBROCK, *Ibid.*, 269

Syntheses are reported for cyclooctatetraene Pd(II) bromide and for bis(benzonitrile) Pd(II) bromide.

Quinquevalent Rhodium Compounds: RhF_5 and $CsRhF_6$

J. H. HOLLOWAY, P. R. RAO and N. BARTLETT, *Chem. Commun.*, 1965, (14), 306-307

RhF_5 was prepared by the action of gaseous F_2 on RhF_3 at 400°C, 90 lb/in.². It is a dark red solid, m.p. $95.5 \pm 0.5^\circ C$. Magnetic properties are tabulated. Crystal data are $a = 12.28$, $b = 9.85$, $c = 5.48$ Å, $\beta = 99.2^\circ$. It is a powerful oxidising and fluorinating agent. CsF and RhF_5 react in IF_5 solution to form $CsRhF_6$ which is similar to $CsPtF_6$. Hexafluororhodates(V) were unknown previously.

On the Structure of Iridium(III) and of Ruthenium(III) Chlorides

K. BRODERSEN, F. MOERS and H. G. SCHNERING, *Naturwissenschaften*, 1965, 52, (9), 205-206

Two modifications of $IrCl_3$ exist: α - $IrCl_3$ as hexagonal, honey-brown, shiny flakes with $a = c = 5.99 \pm 0.01$ Å, $b = 10.37 \pm 0.02$ Å, $\beta = 109.4 \pm 0.2^\circ$; β - $IrCl_3$ as dark-red, bipyramidal crystals. Atomic distribution within α - $IrCl_3$ crystals was studied. α - $RuCl_3$ exists as black, shiny flakes but its parameters have not been determined exactly yet.

Iridium Pentafluoride

N. BARTLETT and P. R. RAO, *Chem. Commun.*, 1965, (12), 252-253

IrF_5 was prepared by heating Ir metal in F_2 gas, the elements being in stoichiometric ratio. The crystals are yellow and monoclinic with $a = 12.5$, $b = 10.0$, $c = 5.4$ Å, $\beta = 99.8^\circ$, m.p. $105^\circ C$. Magnetic susceptibilities were measured between 77 and 296°C and are typical of d^4 octahedral or near octahedral third-transition-series metal fluorides.

α - and β -Ruthenium Trichloride

K. R. HYDE, E. W. HOOPER, J. WATERS and J. M. FLETCHER, *J. Less-Common Metals*, 1965, 8, (6), 428-434

Systematic study of the chlorination of Ru metal led to methods for the preparation of pure α - and β - $RuCl_3$. The properties of these forms are described and previous confusion was dispelled.

Fluorine Bomb Calorimetry. XII. The Enthalpy of Formation of Ruthenium Pentafluoride

H. A. PORTE, E. GREENBERG and W. N. HUBBARD, *J. Phys. Chem.*, 1965, 69, (7), 2308-2310

The standard enthalpy of formation of RuF_5 from calculations based on direct combination measurements in a combustion bomb calorimeter is $\Delta H_f^\circ 298.15 = -231.41 \pm 0.3$ kcal/mol.

Carboxylates of Palladium, Platinum, and Rhodium, and their Adducts

T. A. STEPHENSON, S. M. MOREHOUSE, A. R. POWELL, J. P. HEFFER and G. WILKINSON, *J. Chem. Soc.*, 1965, (June), 3632-3640

Pd(II) nitrate reacted with CH_3COOH and C_2H_5COOH to form brown carboxylates $Pd(OCOR)_2$. Benzoates formed by exchange reaction were trimeric at 37°C but fluorocarboxylates were monomeric. The carboxylates reacted with amines, triphenylphosphine and triphenylarsine to give *trans*- $[Pd(OCOR)_2L_2]$ complexes. Trimeric diacetatoplatinum(II) was formed by reducing CH_3COOH solution of hexahydroxyplatinate(IV) with $HCOOH$. It is not isomorphous with $[Pd(OCOMe)_2]_3$.

ELECTROCHEMISTRY

Formation and Reduction of the Oxygen Layer on Cold-worked Platinum-Gold Alloys in Acid Solutions

M. W. BREITER, *Electrochim. Acta*, 1965, 10, (5), 543-547

Periodic potentiostatic current/potential curves for 5-70 at.% Au-Pt alloys at 30°C, in NH_2SO_4 and $NHClO_4$, at 30 and 300mV/s have a characteristic shape with two reduction waves during the cathodic sweep and, to a first approximation, are composed additively of the curves for the pure metals.

Anodic Properties of Platinum Chromium Alloys in Sulphuric Acid Solution

M. W. BREITER, *Extended Abs., Theoretical Div., Electrochem. Soc.*, 1965, 3, (May), 18-19, abs. 254
Voltammetric studies of 3, 10, 20 and 44.49 wt. % Cr-Pt alloys at 30°C in NH₂SO₄ saturated with He gave current-potential curves which showed similarities with pure Pt at 3wt. % Cr but changes at higher Cr content indicating changes in the surface layer of the alloys. Impedance measurements distinguished those parts of the surfaces with electrochemical behaviour like Pt and those like Cr.

Effect of the Adsorption of Foreign Ions and Molecules on the Rate of Oxidation of Organic Substances on Platinum Electrodes

O. A. KHAZOVA, YU. B. VASIL'EV and V. S. BAGOTSKII, *Elektrokhimiya*, 1965, 1, (4), 439-445
Ions and molecules such as SO₄²⁻, HPO₄³⁻, Cs⁺, Na⁺, (CH₃)₄N⁺, C₆H₁₃OH affect the rate of oxidation of CH₃OH and HCOOH on Pt in 1 N HClO₄ and 1 N LiOH. Studies of the relation of ion and molecule adsorption to electrode potential show that the curve for neutral molecules has a maximum at 0.55 V where the O₂ and H₂ adsorption is a minimum. A mechanism for the anodic regeneration of Pt electrode catalysts is suggested.

LABORATORY APPARATUS AND TECHNIQUE

High Temperature, Small Diameter, Radial Heat Flow Thermal Conductivity Apparatus

C. J. GLASSBRENNER, *Rev. Sci. Instrum.*, 1965, 36, (7), 784-990

A cylindrical apparatus with radial heat flow and accurate to $\pm 5\%$ includes radiation shields made of 40% Rh-Pt, and Pt: 10% Rh-Pt thermocouples to measure the temperature gradients of specimens. Thermal conductivities of Ge and Si from 300°K to their melting points were measured. Mo was chosen for the crystal heater as tests showed that Ge had eutectics with Ir and Ta at 909°C and 932°C respectively.

Evaluating Corrosion Resistance of Fused Cast Refractories

D. E. EMHISER and W. J. ENGLERT, *Glass Ind.*, 1965, 46, (7), 393-397, 423-424

Two dynamic methods used by Pittsburgh Plate Glass Co. are described. A relatively quick, cheap simulation of tank conditions is obtained using a Pt tank into which cullet flows. Four 2 in \times 2 in \times 6 in refractory samples are placed round the overflow in the base of the tank. Losses of weight and volume of these are measured at the end of the test. Advantages of this method are simple control, reproducibility and no need of standard specimens. The tank and samples are

contained in a Pt-wound electric furnace controlled by Pt: 10% Rh-Pt thermocouples. The second method is to use a small-scale glass-melting furnace.

CATALYSIS

Platinum Metal Sulphides as Heterogeneous Hydrogenation Catalysts

F. S. DOVELL and H. GREENFIELD, *J. Am. Chem. Soc.*, 1965, 87, (12), 2767-2768

Pt metal sulphides are more active and stable than base metal sulphides for liquid and vapour phase hydrogenations, whether as bulk or supported catalysts. They are insensitive to S poisoning and reduce halogen-containing nitro compounds to amines without dehalogenation. They are useful for reductive alkylation of aliphatic amines and their nitroalkene precursors with aliphatic ketones and for selective hydrogenation of aryl disulphides to the corresponding thiophenols.

Hydrogenation of Olefins. Part 2. Reaction of Ethylene with Deuterium over Alumina-supported Ruthenium and Osmium

G. C. BOND, G. WEBB and P. B. WELLS, *Trans. Faraday Soc.*, 1965, 61, (5), 999-1006

Tests in a static system at 0-80°C with various C₂H₄ and D₂ pressures showed that, over Ru/Al₂O₃, ethylene-*d*₁ forms about 50% of the initial products, that ethane-*d*₂ is the main ethane and that no ethylene-*d*₃, -*d*₄ nor ethane-*d*₅, -*d*₆ were formed. Over Os/Al₂O₃, less ethylene-*d*₁ was observed, and other deuterated ethanes besides ethane-*d*₂. Hydrogenation rates were proportional to p_{D₂}. Activation energies were ~8.5 kcal/mol for hydrogenation; ~12 kcal/mol for H₂ exchange and/or olefin exchange. The behaviour of ethyl radicals is discussed.

Hydrogenation of But-2-yne. Part 1. Ruthenium- and Osmium-catalysed Reactions

G. WEBB and P. B. WELLS, *Ibid.*, (6), 1232-1245

Reactions with H₂, D₂ at 80-150°C in a static system were studied. Total butene yields exceeded *n*-butane yields by nine times over Ru, four times over Os. Butene proportions were *cis*-but-2-ene > but-1-ene > *trans*-but-2-ene. D₂ distributions were determined. Stereochemistry and selectivity in the stages of H₂ addition are discussed.

Role of Catalytic Metals in Hydrocracking

H. BEUTHER and O. A. LARSON, *Ind. Engng. Chem., Proc. Design & Dev.*, 1965, 4, (2), 177-181

Tests on Pt/SiO₂-Al₂O₃ and Ni/ η -Al₂O₃ catalysts showed that the principal role of the metals was to keep the acidic sites free of coke precursors. They also formed the olefin intermediates needed in subsequent carbonium ion reactions. Rate of hydrocracking for on-stream or aged catalysts depends on the size of the metal crystallites, which controls the area of support which remains cake-

free and available for cracking and isomerisation. Pt catalysts tested contained between 0.13 and 2.86% Pt.

Feeling the Jolt

Chem. Week, 1965, **96**, (20), 69-74

A review of newly-patented hydrocracking processes in the petroleum industry. Catalyst and H₂ needs are likely to increase but olefin output will diminish. As well as Ni and W, there are new catalysts such as nitrided Ag and Rh on SiO₂-MgO and Pd on activated zeolite.

Catalytic Isomerisation of the Leading Fractions of Straight-run Petroleum Distillate

N. R. BURSIAK, G. N. MASLYANSKII and N. K. VOLNUKHINA, *Khim. i Tekhnol., Topliv i Masel*, 1965, (6), 1-4

A study of the isomerisation of pentane and hexane fractions over Pt catalysts established the process method, the product yield, composition and properties of these products. The octane number of fractions distilled up to 62°C can be raised from 73 to 85. If these fractions are jointly treated with hexane raffinate separated from the products of catalytic reforming then an octane number of 80 can be obtained.

The Influence of Gaseous Oxygen Atoms on the Catalytic Oxidation of Ammonia on Pt-Rh

E. MOLINARI, F. CRAMAROSSA, A. PULLO and L. TRIOLO, *J. Catalysis*, 1965, **4**, (3), 341-353

O atoms in the gas phase significantly reduce the activation energy of the catalytic oxidation of NH₃ on Rh-Pt gauze. Tests were carried out at 350-750°K, 1 Torr. The kinetics of the reaction are controlled by diffusion processes. NO and H₂O were practically the only oxidation products. Small activation energies are compensated by small pre-exponential factors.

Catalytic Synthesis of Hydrogen Cyanide from Acetonitrile and Ammonia

A. OZAKI, Y. SHIRATSUTI and K. MORI, *J. Chem. Soc. Japan., Ind. Chem. Sect.*, 1965, **68**, (2), A14, En. abs.

Studies at 700-1000°C gave optimum yields of 1.5 mole HCN/mole CH₃CN using Pt/Al₂O₃ and of 1.4 mole HCN/mole CH₃CN using Pt gauze.

Investigation of the Effect of Thiophene on the Properties of Pd-, Rh-, Ru- and Pt-Al₂O₃ Catalysts during the Dehydrogenation of Cyclohexane

KH. M. MINACHEV, D. A. KONDRAT'EV and P. I. SLYUNTAEV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1965, (6), 999-1003

Cyclohexane both pure and with 0.5, 1.0 and 2.0% thiophene was reacted over 1% Pd, Rh, Ru and Pt/Al₂O₃ at 450°C, 20 atm H₂, v=2 h⁻¹, molar ratio H₂:HC=5:1. Pd/Al₂O₃ and Rh/Al₂O₃

showed less hydration of pure cyclohexane but more isomerisation activity than Pt/Al₂O₃. Ru/Al₂O₃ was relatively inactive. Thiophene reduced the activity for dehydration with increasing concentration. S distribution within the catalyst bed varied with the catalyst used.

The Hydrogenation of Acetylene. I. The Reaction of Acetylene with Hydrogen Catalysed by Alumina-supported Platinum

G. C. BOND and P. B. WELLS, *J. Catalysis*, 1965, **4**, (2), 211-219

Kinetics and product analyses for C₂H₂ hydrogenation in a static system over 5 mol.% Pt/α-Al₂O₃ at 40-140°C indicate more selectivity for C₂H₄ formation as the temperature rises and the H₂ pressure decreases. C₂H₂ is selectively removed when C₂H₂/C₂H₄ mixtures are hydrogenated. The composition of C₄ hydrocarbons produced by C₂H₂ polymerisation has been determined. The reaction mechanism is discussed. Thermodynamic and mechanistic factors enable this catalyst to produce olefin rather than paraffin, while at the same time it possesses very high olefin hydrogenation activity.

The Catalysed Low-temperature Hydrogen-Oxygen Reaction

M. LADACKI, T. J. HOUSER and R. W. ROBERTS, *Ibid.*, 239-247

Best catalyst at low temperatures for the H₂-O₂ reaction was Pt-Rh-Pb/Al₂O₃. Pd, Pt and Rh were effective metals but Ni was poor. Various catalyst pretreatments and changes in the gas flow were studied on 19 catalysts between 25°C and -196°C. High surface area and thorough drying of the catalysts before use were essential, the nature of the support was important, and yields of H₂O were sensitive to changes in gas flow rates. The reaction may require a higher activation energy than the similar H-D isotopic exchange reaction at low temperatures.

Vapour-phase Dehydrocyclisation of Some Aromatic Hydrocarbons

D. A. SCOLA, *Ind. Engng. Chem., Product Res. Dev.*, 1965, **4**, (2), 136-139

Fused ring systems were formed when diphenylmethane, bibenzyl, *trans*-stilbene, 1,4-diphenylbutadiene and 1,1'-binaphthyl were treated over 0.6% Pt/SiO₂ at 550°C in H₂ atmosphere. Major reaction was abstraction of nuclear H₂ followed by intramolecular bond formation.

Reaction of *p*-Xylene with Deuterium on Supported Platinum Catalysts

J. W. HIGHTOWER and C. KEMBALL, *J. Catalysis*, 1965, **4**, (3), 363-373

H-D exchange and deuteration of *p*-xylene on various Pt catalysts showed that, after allowing for different dispersions of Pt by expressing rates in terms of Pt available to chemisorb H₂, results

were similar for catalysts on the same support but obtained from different sources. At 100°C, exchange of ring atoms \geq exchange of methyl H atoms $>$ deuteration, but rates varied as the support changed from γ -Al₂O₃ to α -Al₂O₃ or to SiO₂. H₂O strongly held on the supports may effect catalytic activity.

Chemisorption and Catalysis on Platinised Silica Gel. I. Dispersion of Platinum According to Chemisorption Data

O. M. POLTORAK and V. S. BORONIN, *Zh. Fiz. Khim.*, 1965, **39**, (6), 1476-1482

Tests at -196 to 200°C, 10⁻⁵ to 1.7 mm Hg showed that optimum conditions (-196°C, 10⁻⁵ to 10⁻² mm Hg) for H₂ chemisorption on Pt/SiO₂ occur when the number of Pt atoms on the crystal surface equals the number of adsorbed H atoms. Best conditions for catalyst preparation are those that cause all the Pt to be deposited on the surface of the SiO₂ so that it can adsorb H₂. This was confirmed using three series of differently prepared catalysts containing up to 7.2 wt.% Pt. The Pt dispersion did not depend on the amount of Pt used.

Conversions of Methycyclooctane in the Presence of Platinum Catalysts

E. S. BALENKOVA, N. A. KHAFIZOVA, S. I. KHROMOV and B. A. KAZANSKII, *Dokl. Akad. Nauk S.S.S.R.*, 1965, **161**, (6), 1329-1332

The products of the conversion of methylcyclooctane over 5% Pt/C are exo- and endo-2-methyl-*cis*-pentalane (40%), exo- and endo-3-methyl-*cis*-pentalane (28%), 1-methyl-*cis*-pentalane (8%), hydrogenation products of these isomers (23%), and methyl-octane (1%). Conversion over an Fe-Pt catalyst gave slightly more of the methyl-*cis*-pentalanes.

Determination of the Area of Active Surface of Platinum Black during Catalytic Reactions

T. I. GOROKHOVA, A. N. MAL'TSEV and N. I. KOBOZEV, *Zh. Fiz. Khim.*, 1965, **39**, (5), 1206-1210

A linear relationship exists between poisoning of Pt black catalysts by Pb acetate and the rate of H₂O₂ decomposition or of C₂H₅OH oxidation, showing that Pb ions block active centres. Poisoning data show that 1/3 of the Pt surface is active; adsorption data show that 1/5 is active.

Catalytic Activity of Platinum Black. III. Adsorption and Decomposition of Butanes

D. W. MCKEE, *J. Am. Chem. Soc.*, 1965, **87**, (8), 1681-1686

Studies on adsorption and catalytic decomposition of *n*- and *iso*-C₄H₁₀ on sintered Pt black at 0-180°C showed that below 50°C physical adsorption occurred with coverages more than a monolayer, that at 50-80°C there was an increasing amount of irreversible chemisorption, and that above 80°C desorption of CH₄, C₂H₆ and C₃H₈

occurred with a carbonaceous residue left on the surface. *n*-C₄H₁₀ decomposed more than *iso*-C₄H₁₀ above 100°C. Both cracked more readily than C₃H₈. Product distribution was different from hydrocracking with excess H₂. There was no isomerisation. The reaction kinetics depend on the rate of hydrogenation of adsorbed hydrocarbon residues.

The Recombination of Atoms on Pd-Au Alloys

P. G. DICKENS, J. W. LINNETT and W. PALCZEWSKA, *J. Catalysis*, 1965, **4**, (2), 140-152

The time of exposure of annealed Pd-Au foils to radiation affected the atom recombination co-efficient γ for H₂. For short exposures, the maximum activity occurred with 0-55% Au ($\gamma \sim 10^{-2}$) and activity decreased as Au content rose to 100% ($\gamma \sim 10^{-3}$). For long exposures, γ varied less but was still 10⁻³ at 100% Au. $\gamma \sim 10^{-3}$ to 10⁻⁴ for O₂ and was not related to alloy composition. In all cases the disappearance of atoms from the gas phase was first order.

Catalytic Studies on Alloys. XXV. The Parahydrogen Conversion on Silver-Palladium Alloys

G. RIENÄCKER and S. ENGELS, *Z. anorg. allgem. Chem.* 1965, **336**, (5-6), 259-269

Tests on Ag-Pd foils at 200°C showed that maximum activity for conversion occurs at 80-70% Pd, with decreasing activity down to 0% Pd, i.e. pure Ag. Activation energies increase to ~9 kcal for 100-70% Pd, decrease to 6 kcal at 53.5% Pd, and increase to 11 kcal for Ag-rich alloys with between 50 and 20% Pd. The effects of Ag and H₂ on the catalytic activity of Pd for the hydrogenation of gaseous C₆H₆ were also studied.

Catalytic Reduction of Inorganic Compounds by Carbon Monoxide in the Liquid Phase

A. B. FASMAN, V. D. MARKOV and D. V. SOKOL'SKII, *Zh. Prikladnoi Khim.*, 1965, **38**, (4), 791-800

Studies on catalysts and their concentration, on temperature, on pH, on P_{CO} and on anion concentration during liquid phase reduction by CO of Cr₂O₇²⁻, IO₃⁻, Fe³⁺, [Fe(CN)₆]³⁻, Cu²⁺, and Sn⁴⁺ showed that the reduction rate depends on the respective sizes of the oxidation-reduction potentials and that the complex salt catalysts have activity Pd²⁺ > Rh³⁺ > Pt⁴⁺. Most active was [Pd Br₄]²⁻. Cl⁻ showed the reaction but Br⁻, down to 0.2 g.ion/l, speeded it up. Reduction rates are given for various ions and a reaction mechanism is proposed.

The Synthesis of $\beta\gamma$ -Unsaturated Esters from Conjugated Dienes

S. BREWIS and P. R. HUGHES, *Chem. Commun.*, 1965, (8), 157-158

The yield of methyl pent-3-enoate from butadiene, CO and CH₃OH, which depends on the Pd

catalyst used, was only 1-2% with sodium chloropalladite or sodium bromopalladite but was 35-40% with sodium iodopalladite. To prevent catalyst decomposition above 70°C a ligand such as tributylphosphine was added which raised the optimum reaction temperatures to 150°C. Bridged Pd complexes were the best catalysts. The reaction appears to be general for synthesis of $\beta\gamma$ -unsaturated esters from conjugated dienes. Yields were up to 73%.

The Isomerisation of Olefins by Palladium Complexes

M. B. SPARKE, L. TURNER and A. J. M. WENHAM, *J. Catalysis*, 1965, 4, (3), 332-340

Various Pd complexes are efficient catalysts and completely specific for low-temperature, liquid-phase olefin isomerization. 0.1 mole % Pd complex concentrations may give almost complete equilibrium of isomers at 50-60°C. The olefin-PdCl₂ complex appears to be the true catalyst and is formed by addition to the olefin of PdCl₂ or a complex with a displaceable ligand such as PdCl₂-bis-(benzotrile). Relative rates of methyl-pentene isomerisation were studied. During the process certain isomers are formed preferentially but simple stepwise migration of the double bond does not adequately explain this.

The Selectivity of the Cu/Pd Catalyst in the Oxidation of Hydrogen/Carbon Monoxide Mixtures and the Mechanism of this Reaction

A. KRAUSE, *Roczniki Chem.*, 1965, 39, (3), 355-356
The influence of Pd content on catalyst selectivity is explained in terms of the reactor mechanism.

Reactions of Methoxy Hydroperoxides Derived from Methyl Oleate. Catalytic Hydrogenation

E. H. PRYDE, R. A. AWL and J. C. COWAN, *J. Am. Oil Chem. Soc.*, 1965, 42, (6), 549-553

Better yields of carbonyl compounds from the hydrogenation of methyl oleate ozonolysis products were obtained using poisoned catalysts and the proper choice of catalyst support. Formation of dimethyl azelate byproduct over Pd/C was 20% with no poison, 10% with CH₃COONa in the support, 8% with triethylamine in solution. Pd/CaCO₃-(CH₃COO)₂Pb gave 7%, Pd/ZnO with C₆H₅N or (CH₃COO)₂Pb gave 9%. Byproduct formation increases with support according to the order BaSO₄, CaCO₃, SiO₂, Al₂O₃, ZnO, C; i.e. BaSO₄ is the best support and C is the poorest.

On the Aromatisation Power of Boride Catalysts of the Platinum Group Metals

M. I. ROZENGART, B. D. POLKOVNIKOV, V. L. POLININ, A. M. TABER and K. M. GITIS, *Izv. Akad. Nauk. S.S.S.R., Ser. Khim.*, 1965, (5), 919-922

Dehydrocyclisation of normal paraffins is catalysed by Pt group metals supported on active C. Pd-B

and Pt-B gave sufficiently high stability in tests on N-octane at 550°C.

Low-pressure Hydrogenation of Alkoxyamines with Noble Metal Catalysts

M. FREIFELDER, YEW HAY NG and P. F. HELGREN, *J. Org. Chem.*, 1965, 30, (7), 2485-2486

5% Rh/Al₂O₃ gave the best yields of alkoxy-cyclohexylamines under low-pressure conditions. Hydrogenolysis and secondary amine formation were both small. Reaction time was shorter when CH₃COOH was present than in neutral solvent. Rh/C is equally reactive but presented a greater fire hazard. 5% Pd/C and PtO₂ were less successful.

FUEL CELLS

Behaviour of Fuel Cell Porous Electrodes Fed with a Methanol Vapour Stream

P. LONGHI, *Chim. e Ind.*, 1965, 47, (6), 606-610

Anodic oxidation of CH₃OH at 25 and 65°C in H₂SO₄ and H₃PO₄ solutions was studied using porous graphite disc electrodes coated with Pt group metals blacks. Pt, Rh and Ir behaved satisfactorily but Pd, Ru and Os were inactive or were quickly poisoned. For Pt black the highest current density was obtained with 0.5M H₃PO₄ at 65°C. Higher current densities generally occurred with low electrolyte concentrations at high temperatures. H₃PO₄ solutions give higher current densities than H₂SO₄ solutions of equivalent concentration.

CATHODIC PROTECTION

Cathodic Protection of Jetties

P. B. CHERRY, *Corrosion Prevention and Control*, 1965, 12, (7), 26-28

Platinised Ti anodes are superior to linseed oil impregnated graphite, silicon iron or scrap steel anodes, and can be used at 50-100A/ft² in water with resistivity 25-2000 ohm cm. Oil wharves at Thameshaven and in the Persian Gulf have been protected by anodes mounted on unplasticised PVC and fixed to steel tubes immersed 6 ft below low water line and projecting 2½ ft from the steel jetty piles.

TEMPERATURE MEASUREMENT

The Design and Application of a Steady-state Heat Flux Transducer for Aerodynamic Heat-transfer Measurements

D. L. JOHNSON, *I.S.A. Trans.*, 1965, 4, (1), 46-53
The temperature gradient across a thin ceramic disc is measured by thin-film Pt resistance thermometers painted on each side and fired at 1400°C. These transducers have been used to measure local convective heat transfer co-

efficients on models in the Boeing hypersonic wind tunnel.

Study of the Instability of Noble Metal Thermocouples in Vacuum

B. E. WALKER, C. T. EWING and R. R. MILLER, *Rev. Sci. Instrum.*, 1965, **36**, (5), 601-606

Studies were carried out at 800-1600°C on noble metal thermocouples and on thermoelements of Pt, Rh, Ir, Rh-Pt and Rh-Ir alloys. In vacuum, as in oxidising and neutral atmospheres, the main cause of instability is contamination by impurities, especially Fe, from the ceramic protection tubes.

Precise Temperature Measurement in Debye-Scherrer Specimens at Elevated Temperatures

R. G. MERRYMAN and C. P. KEMPTER, *J. Am. Ceram. Soc.*, 1965, **48**, (4), 202-205

In this method lattice parameters are measured against the temperature of a primary standard forming one leg of a calibrated thermocouple with both specimen and junction in the X-ray beam, and mixing the internal standard with the specimen so that the lattice parameters of the former denote temperature. Au is the primary standard, Pt is the other thermocouple leg and N.B.S. have calibrated the Pt : Au thermocouple at 0-1000°C

NEW PATENTS

METALS AND ALLOYS

Alloys

GENERAL DYNAMICS CORP. *U.S. Patent* 3,172,759

High temperature resistant alloys useful in the brazing of Nb and its alloys comprise 35-74 wt.% Cr, 25-65 wt.% Pd and 1-20 wt.% Ge.

High Strength Platinum-base Alloys

NEW ENGLAND MATERIALS LABORATORY INC.

U.S. Patent 3,175,904

Dispersion strengthened precious metals and alloys are produced by providing under inert conditions Pt, Pd, Rh, Ir, or Ru or alloys of at least two of these metals with each other of such particle size that under normal conditions they would be pyrophoric, adding it slowly to a solution of refractory oxide-forming salt so that a thick slurry is formed and 6-20 vol.% refractory oxide will be provided, evaporating the solvent and drying the residue, spreading it evenly in a decomposition chamber and heating so that a precious metal powder product having a uniform dispersion of refractory oxide is formed.

ELECTROCHEMISTRY

Platinum-coated Titanium Anodes

IMPERIAL CHEMICAL INDUSTRIES LTD.

U.S. Patent 3,177,131

Anodes are produced by applying to the Ti support a number of coatings of Pt-bearing preparation containing 2-9 wt.% Pt in the form of H_2PtCl_6 or H_2PtBr_6 or Pt resinate, in an organic vehicle, drying each coating and then firing it by heating in an oxidising atmosphere at 350-550°C to form a deposit consisting essentially of Pt.

Electrolytic Condenser Cathode

SIEMENS & HALSKE A.G. *German Patent* 1,190,105

A new form of cathode giving increased capacity consists of silver coated with Pt, Pd or Os.

ELECTRODEPOSITION AND SURFACE COATINGS

Deposition of Palladium

INTERNATIONAL NICKEL LTD.

British Patent 994,560

A bath for the electroless deposition of Pd is operated at 68-100°C and comprises an aqueous solution of 1-20 g/l Pd (II), 0.04-0.5 g/l unsymmetrical dimethyl hydrazine, and one or more of the compounds NH_3 , aminoethyl ethanolamine or amylamine in a total molar concentration equal to 100-350 g/l NH_3 .

Electrodeposition of Platinum Group Metals

JAINOMOTO CO. INC. *British Patent* 998,709

Noble metal plated Ti electrodes are produced by immersing the Ti electrode in a fused bath containing alkali metal halide and dispersed graphite powder and then electrodepositing Pt, Pd, Rh or their mixtures on the roughened surface.

CATALYSIS

Production of Mesitylene

ESSO RESEARCH & ENGINEERING CO.

British Patent 990,781

Mesitylene is produced by distilling a hydrocarbon mixture to provide a first fraction containing ethyl toluene, propyl benzene and mesitylene and isomerising the second fraction containing 1,2,4-trimethyl benzene by treating it with H_2 at 850-975°F, 200-350 p.s.i. and in the presence of an Al_2O_3 -supported Cl_2 -containing Pt catalyst.

Organopolysiloxanes

IMPERIAL CHEMICAL INDUSTRIES LTD.

British Patent 990,800

Pt residues are removed from organopolysiloxanes prepared by a process involving the use of a Pt catalyst by treating the mixture in the presence of