ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

A Thermodynamic Study of the Heat of Ordering CuPt

G. W. GEIKEN, USAEC Rept UCRL-17615, 1967, (June), 20 pp

Heat of formation of Cu-Pt plotted against temperature at $360-1155^{\circ}$ K indicates that the alloy is disordered as it is heated. Heat of formation decreases from -4010 cal/g-atom at 360° K to -4140 cal/g-atom at 800° K; increases to -3070 cal/g-atom at $\approx 1100^{\circ}$ K, the critical temperature, and gives a total ordering energy of 1510 ± 100 cal/g-atom.

Atomic Structure and Ferromagnetism of the Regular Platinum-Manganese Alloys

S. K. SIDOROV and S. F. DUBININ, Fiz. Metall. Metalloved., 1967, 24, (5), 859-867

Studies of regular 20-50 at.% Mn-Pt alloys revealed the structures of the cubic and tetragonal phases and defined their limits of concentration more precisely. The relation of mean magnetic moment on an atom to alloy composition was determined and was explained by the emergence of a complex noncollinear magnetic structure caused by an antiferromagnetic reaction between neighbouring Mn atoms.

Magnetic Properties of Intermetallic Compounds between the Lanthanides and Platinum

W. E. WALLACE and Y. G. VLASOV, Inorg. Chem., 1967, 6, (12), 2216-2219

Magnetic properties, particularly in the paramagnetic region, were measured for $LnPt_2$ compounds with Ct5(MgCu₂) structure, where Ln=Pr, Nd, Gd, Tb, Dy, Ho, or Er. Effective movement μ_{eff} for paramagnetic $LnPt_2$ is close to $g\sqrt{J(J+1)}$, the value for Ln^{3+} , but, in GdPt₂, μ_{eff} is 2% greater owing to conduction electron polarisation effects. Pt in LnPt₂ is nonmagnetic. Low moments in the ferromagnetic state indicate incomplete saturation. All the LnPt₂ compounds become ferromagnetic at 4.2°K, except PrPt₂ which may be a Van Vleck paramagnet at 4.2°K.

Lorenz Number of Pure Palladium at Low Temperatures

J. T. SCHRIEMPF, Phys. Rev. Lett., 1967, 19, (19), 1131-1133

Measurements of the ideal electrical and thermal resistivities of Pd at 2.5–19°K yield an ideal Lorenz number $L_i=0.7\times 10^{-8} \text{ V}^2/\text{deg}^2$, which is independent of temperature below $\approx 5^{\circ}$ K. Comparison with data for Re and Ni indicates that

low-temperature values of L_i are parameters characteristic of each metal.

Magnetic Moment of Pd to 150 kG: Limits of Exchange Enhancement in Pd

S. FONER and E. J. MCNIFF, Ibid., (25), 1438-1441

Magnetic moment of Pd at 4.2°K is a linear function of magnetic field up to 150 kG. Experiments based on Wohlfarth's analysis of the highfield enhanced paramagnetism of Pd showed the limits of exchange enhancement for Pd and an increase in the minimum field for field-induced ferromagnetism in Pd.

On the Diffusion of Hydrogen and Deuterium in Palladium and Pd Alloys. I. Gas-volumetric Measurements

G. BOHMHOLDT and E. WICKE, Z. phys. Chem. (Frankfurt), 1967, 56, (3/4), 133-154

Volumetric studies of the solubility of H_2 and D_2 and of their diffusion rates in Pd and in up to 40% Ag-Pd foils at 20–100°C showed that solubility increases with Ag content at low pressure but decreases with increasing pressure and that diffusion is hindered at higher pressure. The kinetics of this hindrance were evaluated. D_3 had lower activation energy than H_3 .

II. Electrochemical Methods

G. HOLLECK and E. WICKE, Ibid., 155-172

Electrochemical studies at $o-80^{\circ}C$ gave similar results to the above. Sn-Pd alloys as well as Ag-Pd were considered.

Viscosity of Alloys on the Basis of Palladium and Silver

E. L. DUBININ, O. A. ESIN, N. A. VATOLIN and A. A. KURANOV, *Zh. neorg. Khim.*, 1967, **12**, (11), 3156–3158

Composition diagrams were compared with composition-viscosity relationships at various temperatures for the systems Pd-Ag, Pd-Cr, Pd-Si and Ag-Si. Viscosity increases with increasing % Pd in Pd-Ag alloys at 1600 and 1650°C. Pd-Cr alloys at 1600–1700°C possess minimum viscosity at 63% Pd, corresponding to the eutectic point. Pd-Si alloys possess viscosity maxima at compositions corresponding to PdSi and Pd₂Si but, as the temperature rises from 1400 to 1600°C, these maxima are smoothed, which indicates partial dissociation.

Investigation of the Application of Spinodal Theory to the Palladium-Iridium System

G. WALTER, USAEC Rept UCRL - 17470, 1967, (May), 34 pp

No classic spinodal decomposition occurred in

44 at.% Ir-Pd despite long ageing times. Hardness, microstructure and X-ray tests studied existing spinodal theory for the alloy, and ageing took place well below the predicted critical temperature. Modified theory is based upon effects of differing elastic moduli of Ir and Pd, for Ir has five times the modulus of Pd.

Striction Susceptibility of an Alloy near the Fe₃Pd Composition in Weak Magnetic Fields

Z. I. ALIZADE, Izv. Akad. Nauk Turkm. SSR, Ser. Fiz.-tekh. Khim. Geol. Nauk, 1967, (2), 113–114

Following annealing for I h at 600-800°C and slow cooling to room temperature, the magnetostriction susceptibility of 60 wt.% Fe-Pd and of Ni was determined and showed maxima of 200 and 80 units respectively. 60 wt.% Fe-Pd has advantages over Permendur-type alloys.

On the Mechanism of the Antiferroferromagnetic Transition in the System of Ordered $Fe(Pd_xPt_{1,x})_3$ Alloys

V. V. KLYUSHIN, V. V. KELAREV, S. K. SIDOROV, R. Z. ABDULOV and R. V. POSPELOVA, *Dokl. Akad. Nauk* SSSR, 1967, 176, (5) 1056–1058

Tests confirmed that the antiferromagneticferromagnetic transition in $Fe(Pd_xPt_{1-x})_3$ alloys occurs by a complex magnetic structural change involving noncollinear orientation of atomic magnetic moments. The cases of $FePt_3$ and $FePd_3$ are discussed. Pd and Pt have opposite tendencies in the ternary alloys. o-37 at.% Pd alloys show antiferromagnetic FePt_3 structure, 55-75 at.% Pd alloys show ferromagnetic FePd_3 structure, and 37-55 at.% Pd alloys have the complex structure with noncollinear orientation of the moments of the alloy components.

Neutron-diffraction Study of Antiferro-ferromagnetic Transition in a System of Ordered Fe(Pd_xPt_{1-x})₃ Alloys

V. V. KELAREV, S. K. SIDOROV, V. V. KLYUSHIN and R. Z. ABDULOV, Phys. Status Solidi, 1967, 24, (1), 385-390

Studies of the antiferro-ferromagnetic transition in ordered $Fe(Pd_xPt_{1-x})_a$ alloys by analysis of the dependence of the intensity of the (100) ferromagnetic reflexion on the average magnetic moment per atom of the alloys showed that it occurs by a set of complex magnetic structures with a noncollinear orientation of the atomic magnetic moment of the components.

Equiatomic Transition Metal Alloys of Manganese. VI. Structural and Magnetic Properties of Pd-Mn Phases

A. KJEKSHUS, R. MØLLERUD, A. F. ANDRESEN and W. B. PEARSON, *Phil. Mag.*, 1967, 16, (143), 1063–1083

Studies of 40-66 at.% Pd-Mn alloys show that

CsCl-type cubic PdMn is stable only at high temperatures, is homogeneous at $\sim 40 - \sim 50$ at.% Pd at 685°C, and is paramagnetic, whereas CuAuI-type tetragonal PdMn is homogeneous at 45 ± 1 to 65.5 at.% Pd according to temperature, is paramagnetic above $825\pm10^{\circ}$ K for ~ 50 at.% Pd to $290\pm10^{\circ}$ K for 66 at.% Pd, and is antiferromagnetic below these temperatures. The magnetic cell structure is discussed.

Metallurgical Problems with the Hot Working of Rhodium and Iridium

G. REINACHER, Z. Metallkunde, 1967, 58, (12), 831-836, 839-840

The low ductility of Rh and Ir compared to other f.c.c. noble metals makes working of them difficult but a review of theory and experiments to elucidate their brittle behaviour suggests that purification to 99.999% and transformation of the normal polygonal structure to fibrous or single crystal structure leads to enhanced ductility. However, this enhancement is limited by the high shear modulus of Rh and Ir.

Superconductivity and Specific Heat of Titanium-Rhodium Alloys

G. DUMMER and E. OFTEDAL, Z. Physik, 1967, 208, (3), 238-248

Specific heats of o-10 at.% Rh-Ti alloys were measured at 0.9-8°K and transition temperatures of hexagonal o-2 at.% Rh-Ti and cubic 3-10 at.% Rh-Ti were determined by calorimetry. Both transition temperature and electronic specific heat increase with % Rh. Influence of cooling rate on transition temperature was studied. Unlike Hf₂Rh and Zr₂Rh, Ti₂Rh is not superconducting down to 1.2°K.

Thermodynamic Properties of Hexagonal Close-packed (hcp) Iron and Iron-Ruthenium Alloys

G. L. STEPAKOFF and L. KAUFMAN, U.S. Rept AD 650,151, 1967, (April), 37 pp; Acta Metall., 1968, 16, (1), 13-22

Results of measurements on h.c.p. Fe-Ru alloys of specific heat at $60-300^{\circ}$ K, and of vapour pressure of Fe over f.c.c. and h.c.p. Fe-Ru alloys at 1600° K, were used to describe the lattice stability of h.c.p. Fe and the thermodynamic properties of the Fe-Ru system. Earlier theory is supported by the vibrational entropy of h.c.p. Fe exceeding that of the b.c.c. form.

A New Structure Type with Octahedral Pairs for Rh₂S₃, Rh₂Se₃ and Ir₂S₃

E. PARTHÉ, D. HOHNKE and F. HULLIGER, Acta Cryst., 1967, 23, (5), 832-840

 Rh_2S_3 has a space group $Pbcn(D_{2h}^{14})$ and lattice constants a=8.462, b=5.985, c=6.138Å. The Rh atoms possess octahedral coordination. Four Rh atoms surround each S atom at the vertices of a distorted tetrahedron. Rh_2S_3 is isotypical with Rh_2Se_3 and Ir_2S_3 . A complete range of solid solubility exists between Rh_2S_3 and Rh_2Se_3 .

Decomposition Pressures and Enthalpies of Formation of Some Transition Metal Diarsenides and Diselenides

J. J. MURRAY and R. D. HEYDING, Can. J. Chem., 1967, 45, (22), 2675-2687

Studies of the decomposition pressures of $PtAs_2$, $OsAs_2$, $RuSe_2$, and $OsSe_2$ as a function of temperature by the torsion effusion technique, and of the heats and entropies of decomposition gave as heats of formation, at $298^{\circ}K$, -42.0 ± 3.5 , -18.5 ± 2.0 , -32.5 ± 5.0 , -4.29 ± 3.5 kcal/mole respectively. Phase relationships of Pt-As, Os-As, Ru-Se, and Os-Se at $850-1250^{\circ}C$ were studied.

Constitution Diagrams of Plutonium with Metals of Groups IIIA, IVA, VIII and IB V. I. KUTAITSEV, N. T. CHEBOTAREV, M. A. ANDRIANOV, V. N. KONEV, I. G. LEBEDEV, V. I. BAGROVA, A. V. BEZNOSIKOVA, A. A. KRUGLOV, P. N. PETROV and E. S. SMOTRITSKAYA, Atomnaya Energiya, 1967, 23, (6), 511-520

Sixteen constitution diagrams of Pu alloys are collected in this article and include those of Pu-Ir, Pu-Pd, Pu-Pt, Pu-Rh, and Pu-Ru.

CHEMICAL COMPOUNDS

Semiconducting d⁸ Metal Complexes Found Chem. engng News, 1967, 45, (52, Dec. 11), 50–51 Studies of transition metal complexes in which the metal has planar d⁸ configuration showed that single crystals of the groups of compounds $[Ir(CO)_{2}acac]$ and $[Rh(CO)_{2}acac]$, $[Pt(NH_{3})_{4}]^{2+}$ $[PtCl_{4}]^{2-}$ and $[Pt(NH_{3})_{4}]^{2+}[PdCl_{4}]^{2-}$ are particularly suitable for electrical measurements. Workers at Research Triangle Institute, University of North Carolina and Manchester University have studied the structures and physical properties of these compounds, which appear to be intrinsic semiconductors, leading to intermetallic polymers capable of being tailored to specific physical and electrical requirements.

Mass Spectrometric-Knudsen Cell Study of the Gascous Oxides of Platinum

J. H. NORMAN, H. G. STALEY and W. E. BELL, J. phys. Chem., 1967, 71, (11), 3686-3689

These studies confirmed the species $PtO_{e}(g)$ and established the existence of PtO(g). Thermodynamic data for their formation are recorded and enthalpy data for the vaporisation of Pt.

Preliminary Investigations in the Systems Au-O, Rh-O and Pt-O at High Oxygen Pressures

0. MULLER and R. ROY, Extended Abstr., 1967 Fall Mtg, Basic Sci. Div., Am. Geram Soc., 5-B-67F Studies on the systems at up to 900°C, 3000 atm.O₂ showed that, whereas Rh₂O₃ is stable at r atm.O₂, RhO₂ is the stable phase at slightly higher pressures. RhO₂ has rutile structure with a=4.489, c=3.090Å. In the Pt-O system, hexagonal α -PtO₂ appears stable at lower temperatures and higher O₂ pressures while β -PtO₂ is formed at 650-750°C, 2000 atm. O₂. Pt₃O₄ is formed at 680-780°C, 2000 atm. and has cubic NaPt₃O₄ structure with a=5.585Å and Na positions vacant. An intermediate phase of stoichiometry between PtO₂ and Pt₃O₄ has also been detected. The α -PtO₂-> β -PtO₂ transition is unusual in involving the break up of peroxide-type O-O bonds.

Synthesis of Thallium Platinate at High Pressure

H. R. HOEKSTRA and S. SIEGEL, Inorg. Chem., 1968, 7, (1), 141-145

 $Tl_2Pt_2O_7$, prepared by reacting Tl_2O_3 with Pt or PtO₂ at 1000°C, 40 kbar, is a brown solid insoluble in aqua regia and thermally stable to 750°C at 1 atm. The f.c.c. lattice has $a = 10.132 \pm 0.004$ Å. Measured density is 11.12 g/cm³. Pt-O and Tl-O bond lengths and structure are discussed. The infrared spectrum has maxima at 684, 562, 449 and 363 cm⁻¹.

The Dissociation Energies of the Molecules PtC and RhC

A. VANDER AUWERA-MAHIEU and J. DROWART, Chem. phys. Lett., 1967, 1, (8), 311-313

Mass spectrometric studies of the Pt-C and Rh-C systems showed that the dissociation energies of the gaseous molecules of PtC and RhC are respectively 145.3 ± 1.5 and 138.5 ± 1.5 kcal/mole.

Structural Investigations on Rhodium Halides

K. BRODERSEN, G. THIELE and I. RECKE, \tilde{J} . less-common Metals, 1968, 14, (1), 151-152

X-ray, magnetic and thermal studies on RhBr₃ and RhI₃ showed that their monoclinic crystals have lattice structures: RhBr₃, $a=6.27\pm0.01$, $b=10.85\pm0.01$, $c=6.35\pm0.01$ Å, $\beta=109.0^{\circ}$; RhI₃ $a=6.77\pm0.02$, $b=11.72\pm0.02$, $c=6.83\pm0.02$ Å, $\beta=109.3^{\circ}$. Atomic positions and distances were recorded.

The Formation of Complexes of Molecular Nitrogen with Compounds of Ruthenium and Osmium

YU. G. BOROD'KO, A. K. SHILOVA and A. E. SHILOV, Dokl. Akad. Nauk SSSR, 1967, 176, (6), 1297-1299

Infrared spectral studies showed that N_2 is coordinated to Ru and Os atoms during the reductions of RuCl₈ and RuOHCl₃ in tetrahydrofuran by Zn amalgam, C₂H₅MgBr, or C₆H₅MgBr and of OsOHCl₈ in similar conditions. The N₂ complexes are similar to [M(NH₃)₈N₂]X₂, where M=Ru, Os; X=Br⁻, I⁻, BF₄⁻, produced by the action of N_2H_4 hydrates on RuCl₃, etc. The stability and bonding of these nitrogenyl complexes have been studied using ¹⁵N labelling.

Ruthenium Complexes Containing Molecular Nitrogen

A. D. ALLEN, F. BOTTOMLEY, R. O. HARRIS, V. P. REINSALU and C. V. SENOFF, *J. Am. Chem. Soc.*, 1967, **89**, (22), 5595–5599

 $[Ru(NH_3)_5N_2]^{2+}$ complexes were prepared by the action of N_2H_4 hydrate on Ru(III) or Ru(IV) salts, or by the action of azide ion on aquopentaammineruthenium (III). Various Ru(II) and Ru(III) ammine complexes could be derived. The reported properties of $[Ru(NH_3)_5N_2]^{2+}$ salts are discussed.

The Formation of $Ru(NH_3)_5N_2^{2+}$ in Aqueous Solution by Direct Action of Molecular Nitrogen

D. E. HARRISON and H. TAUBE, Ibid., 5706-5707

The preparation of $[Ru(NH_3)_5N_2]^{2+}$ is possible between N_2 and $[Ru(NH_3)_5H_2O]^{2+}$ in aqueous solution at room temperature.

ELECTROCHEMISTRY

The Oxygen Electrode on Noble Metals

J. P. HOARE, Advan. Electrochem. electrochem. Engng, 1967, 6, 201–288

A review of the reactions between O_2 and electrodes of Pt, Au, Pd, Rh, Ir and various alloys. (327 references.)

Investigation of the Adsorption of Hydrogen on Platinum Metals at Various Temperatures R. V. MARVET and O. A. PETRII, *Elektrokhimiya*, 1967, **3**, (12), 1445–1449

Adsorption of H_2 on Raney Os and lr electrodes surfaced with Rh and Ru was measured and analysed by charging curves at 20–95°C using $1N H_2SO_4$ and 1N NaOH electrolytes.

The Electrochemical Activation of Platinum Electrodes

S. D. JAMES, J. Electrochem. Soc., 1967, 114, (11), 1113-1119

A review of mechanisms for the electrochemical activation of Pt electrodes led to experiments which showed that impurity desorption is the most important result of conventional brief activation. A second type of activation may exist, produced by prolonged preoxidation and possessing very stable activity. (57 references.)

On the Mechanism of Methanol Oxidation on a Platinum-Ruthenium Electrode

V. S. ENTINA and O. A. PETRII, *Elektrokhimiya*, 1967, **3**, (10), 1237–1240

CH₃OH was oxidised in both H₂SO₄ and KOH

solutions over Pt-Ru and platinised Pt electrodes and results were plotted and compared. Graphs demonstrate the effects of the rate of electrooxidation to the potential of the rate of oxidation to the concentration of CH_3OH , of the surface coverage of the electrodes to the potential, and also the effect of stationary polarisation.

Comparison of the Properties of Compact and Dispersed Platinum-Ruthenium Electrodes

Ibid., 1968, 4, (1), 111–114

Further work is recorded on 10, 20, 30 and 40% Ru-Pt electrodes, which were tested by plotting potentiostatic anodic and cathodic curves for each in the compact and dispersed forms in H_2SO_4 solutions.

ELECTRODEPOSITION AND SURFACE COATINGS

Protecting Refractory Metal at High Temperature

R. E. ENGDAHL, J. R. BEDELL and C. E. KROHA, Mater. Protection, 1967, 6, (10), 49-51

A system is described which offers 2-5 h oxidation protection for W at 2000°C in air. The refractory metal is electroplated with Ir and sprayed with ZrO₂ as a surface coating.

Electrodeposition of Iridium from Fused Sodium Cyanide and Aqueous Electrolytes. A Preliminary Study

R. L. ANDREWS, C. B. KENAHAN and D. SCHLAIN, U.S. Bur. Mines RI-7023, 1967, (Sept.), 12 pp Metals such as W and Mo, which oxidise rapidly at high temperatures, can be protected by plating adherent and coherent deposits of Ir up to 15 mils thick from a fused NaCN bath at 600°C, 10-100 mA/cm². Pure Ir protects Mo up to 1000°C in flowing air but above this temperature the volatility of its oxide prevents its use. Coatings up to 4 mils thick of Ir-Pt, Ir-Pd and Ir-Rh alloys may offer protection above 1000°C. Aqueous electrolytes are unsuitable as they lead to low deposition rates and cracking of heavy deposits.

LABORATORY APPARATUS AND TECHNIQUE

How to Grow King Size Single Crystal YIGs

J. R. CHABRIA, Ceram. Ind., 1967, 89, (5), 52–54 Single crystals of $Y_3Fe_5O_{12}$, $Y_3Ga_5O_{12}$ and $Y_2Al_xFe_{5-x}O_{12}$ are grown in a 3.5% Rh-Pt crucible by prolonged and carefully controlled heating at 2500°C. High purity oxides are the starting materials. The crucible is also of the highest purity to avoid chemical interaction and contamination of the crystals.

Apparatus for Making Sharp Photographic Images with X-Rays

H. F. SHERWOOD, Rev. sci. Instrum., 1967, 38, (11), 1619–1622

The jaws of the knife-edge slit for making sharp photographic images with X-rays are fabricated from 10% Ir-Pt. Their manufacture and mounting, and the operation of the apparatus, are described.

Comparison of Tips, Thin Wires and Sharp Metal Edges as Emitters for Field Ionisation Mass Spectrometry

H. D. BECKEY, H. KRONE and F. W. ROELLGEN, *f. sci. Instrum., f. Phys. E.*, 1968, **i**, (2), 118–120 Although tips give twice the field strength of wires, the latter are preferable for analytical purposes because of their larger emitter area and give more than ten times the field strength of a sharp metal edge. To reduce the breakages of wire by the mechanical forces exerted by the high electrical field, 2.5 μ m Pt wires were strengthened by whisker growing. Uniform quality Wollaston wire of high tensile strength is necessary. A compensating electrode reduces the mechanical forces on the wire. The length of etched Wollaston wire has been reduced to 1.5–2.0 mm.

HETEROGENEOUS CATALYSIS

Noble Metal Catalysts in the Fine Chemicals Industry

G. C. BOND, Chem. and Ind., 1967, (48, Dec. 2), 2018–2025

A review of the uses of Pt metals in heterogeneous and homogeneous catalysis. Topics discussed include the choices of metal, support, and conditions of reaction. Other topics include evaluation of catalysts, the trickle column reactor, and the economics of using these catalysts. (17 references.)

Catalytic Conversions of Hydrocarbons

B. A. KAZANSKII, Kinet. Kataliz, 1967, 8, (5), 977–993

A review of the hydrogenolysis of C_3 - C_8 , C_{13} and C_{15} cyclic hydrocarbons on Pt metal and Ni catalysts, and of the dehydrocyclisation of paraffins to form aromatic and bicyclic compounds using Pt, Pd and Ni catalysts. 50 years of work by KAZANSKII and his colleagues is reported. (69 references.)

Catalytic Properties of the Pt+Ag System

M. A. INDZHIKYAN, Arm. khim. Zh., 1967, 20, (5), 349-352

The activity of Pt-Ag metallic catalysts for C_6H_6 hydrogenation decreases with increasing Ag content until it is zero at 25 at.% Ag because d levels in Pt are filled by electrons from Ag.

Catalytic Properties of the Pt-+Cu System *Ibid.*, 353-357

The activity of Pt-Cu metallic catalysts for C_6H_6 hydrogenation decreases with increasing Cu content until it is zero at 75 at. % Cu because *d* levels in Pt are filled by electrons from Cu.

Study of the Adsorption and Energetic Properties of Metallic Catalysts. I. Specific Surface of Catalysts

A. A. BALANDIN, V. I. SPITSYN, L. I. BARSOVA, A. E. AGRONOMOV and N. P. DOBROSEL'SKAYA, Zh. fiz. Khim., 1967, 41, (10), 2623–2628

Specific surfaces of Pt, Pd, Rh and Ru blacks are compared by the BET method with C_8H_6 and Kr adsorption, and by the electrochemical methods from the capacity of the double layer region and the amount of H_2 adsorbed. The double layer region method gives higher results than the H_2 adsorption method. There is a reciprocal relation between the mean size of the crystallites in the blacks and the specific surface.

The Retention of Hydrogen by Supported Metal Catalysts

G. F. TAYLOR, S. J. THOMSON and G. WEBB, J. Catalysis, 1967, 8, (4), 388-390

He treatment of Al_2O_3 -supported catalysts does not remove all the reactive H_2 from the surface. Less remains on Pt/Al_2O_3 than on Pd/Al_2O_3 or Rh/Al_2O_3 although the total amount of H_2 retained on Pt/Al_2O_3 is similar to that on Rh/Al_2O_3 and greater than that on Pd/Al_2O_3 . There is less self-hydrogenation of C_2H_4 on Pd/Al_2O_3 than on Rh/Al_2O_3 .

The Study of Catalysts and Adsorbents by the Thermal Desorption Method. II. Platinised Alumina

T. S. USTINOVA, A. P. FILONENKO and I. V. KRYLOVA, *Zh. fiz. Khim.*, 1967, **41**, (11), 2941–2943.

There exists for Pt/Al_2O_3 a direct connection between the amount of adsorbed gas and the intensity of exoelectronic emission. Maxima on curves of temperature against emission, for Pt/Al_2O_3 , depend on the existence of centres on the Al_2O_3 surface which are activated by adsorption of H_2O and O_2 . Tests were carried out in the range 20-300C°C.

Investigation of the State of Platinum in Platinum Catalysts for Dehydrocyclisation by the Extraction Method

N. R. BURSIAN, S. B. KOGAN and Z. A. DAVYDOVA, Kinet. Kataliz, 1967, 8, (6), 1283-1289

Pt dehydrocyclisation catalysts treated by air at 20-800°C and by H₂ at 250-550°C were studied by extraction methods, which showed that, in reduced Pt/Al₂O₃, the Pt bonded chemically to Cl and Al₂O₃ has specific activity for the formation and closing of ring compounds but does not catalyse the dehydrogenation of cyclo-hexane.

Investigation of the Selectivity of Platinum Catalysts on Various Supports in the Hydrogenolysis of Methylcyclopentane

V. V. VORONIN, KH. M. MINACHEV and I. I. LEVITSKII, Izv. Akad. Nauk SSSR, Ser. Khim., 1967, (12), 2616-2619

 H_2 treatment up to 550°C of Pt/zeolite, Pt/SiO₂ and Pt/C catalysts does not alter their selectivity for hydrogenation of methylcyclopentane. The C₅ ring is split away from the side chain. Activity is either decreased or remains constant. Similar treatment of Pt/Al₂O₃ causes a sharp increase in activity and a change in selectivity so that the C₅ ring is split at the bond adjacent to the CH₃ group. The change is caused by changes in the Al₂O₃, e.g. as a result of dehydration.

Chemisorption and Catalysis on Platinised Silica. III. Chemisorption of Oxygen

V. S. BORONIN, V. S. NIKULINA and O. M. POLTORAK, Zh. fiz. Khim., 1967, **41**, (10), 2668-2674

Studies at 20-470°C, 10^{-3} -1.5 mm Hg on the sorption of O₂ on Pt/SiO₂ with various amounts of Pt form the basis for a method of measuring the Pt surface by the chemisorption of O₂.

Vapour-phase Hydrogenation of Benzene on Pt/Asbestos Catalyst with Control of Catalyst Potential

N. I. UTEGULOV, V. S. DRUZ' and D. V. SOKOL'SKII, *Ibid.*, (12), 3128-3131

The possibility of measuring the catalyst potential during vapour-phase hydrogenation of C_6H_6 on Pt/asbestos was studied. Equilibrium and stationary catalyst potentials, and catalyst activity, depend on catalyst pretreatment and perhaps on processes of exchange adsorption on the support. The limiting factor is activation and reactivation of H_2 weakly bonded to the support. The apparent order of the reaction depends on the gaseous phase ratio $C_6H_6: H_2$.

Effect of Noble Metal Concentration upon the Isomerisation Activity of Molecular Sieve Zeolite Catalysts

M. A. LANEWALA, P. E. PICKERT and A. P. BOTTON, J. Catalysis, 1967, 9, (1), 95-97

Tests on isomerisation of N-C₆H₁₄ showed that the optimum catalyst concentrations for methylpentane formation were 0.05 wt.% Pd or 0.10 wt.% Pt, and for dimethylbutane formation were 0.25 wt.% Pd and ~0.40 wt.% Pt. The metals are equally effective when compared on an atomic wt.% basis. Results suggest that ion exchange incorporation of noble metals on to zeolites gives high, almost atomic, dispersion. The Pt(NH₃)₄Cl₂.H₂O and Pd(NH₃)₄Cl₂ salts introduced Pt(NH₃)₄³⁺ and Pd(NH₃)₄²⁺ ions into the zeolite and calcining deposited the metal atoms.

Metal Sulphide Catalysts for Hydrogenation of Halonitrobenzenes to Haloanilines

H. GREENFIELD and F. S. DOVELL, J. org. Chem., 1967, 32, (11), 3670-3671

Hydrogenations of chloro- and bromo-substituted nitrobenzenes over metal sulphide catalysts showed that Pt sulphide is probably best because of its good selectivity and commercial availability. Sulphides of Ni and Pd are satisfactory for reduction of chloronitro- but not bromonitroaromatic compounds. Pt sulphide was also suitable for quantitative hydrogenation of 2,5dichloronitrobenzene to 2,5-dichloroaniline. *p*-Nitrochlorobenzene reacted with H₂ and CH₃COCH₃ over Rh sulphide to form *N*-isopropyl-*p*-chloroaniline.

Liquid-phase Hydrogenation of Organic Compounds on Mixed Ruthenium Catalysts. Ruthenium-Platinum Catalysts

D. V. SOKOL'SKII, K. K. DZHARDAMALIEVA, A. G. SARMURZINA and T. TONMANOV, Dokl. Akad. Nauk SSSR, 1967, 176, (5), 1093-1095

Tests showed that two maxima occur on each graph of catalyst activity against alloy composition for liquid-phase hydrogenations of a number of organic compounds on Ru-Pt catalysts. These maxima are related to the nature of the reduced compound, and to the solvent used in the case of the maximum at the higher Ru concentration. The surface area decreases with increasing Ru content.

Catalytic Reduction of Waste Nitrogen Oxides

s. JAROŠ and J. KŘÍŽEK, Chem. Prumsyl, 1967, 17, (11), 581–586

 Pt/Al_2O_3 and Pd/Al_2O_3 pellet or bead catalysts have the greatest activity for reduction of nitrogen oxides, according to laboratory tests. Gases with low ignition and operating temperatures are most suitable for reduction of the oxides. High temperature affects the catalyst adversely; its life is reduced and more catalyst is needed because of the lower space velocity. Results of this work form the basis for a new reactor design.

On the Catalytic Properties of Platinum Group Metals and their Alloys Containing Palladium

R. G. DAVLESUPOVA and D. V. SOKOL'SKII, Kinet. Kataliz, 1967, 8, (6), 1378–1381

A study of the activity of the Pt group metals, Re, and Pd₃Me-type alloys as catalysts for the reduction of dimethylethynylcarbinol in H₂O, 96% C₂H₅OH and 0.1 N KOH in H₂O or C₂H₅OH at 10-40°C showed that the alloys possess more activity than Raney catalysts of the individual elements. Raney Ru, Os, Re and Ir were completely inactive. The rate of the process was lower in alkaline solution. In the alcoholic alkaline solution the process was checked at the semireduction stage.

The Effect of Sulphur-organic Compounds on the Purification of Gases from Nitric Oxide and Acetylene by the Method of Catalytic Hydrogenation

T. A. SEMENOVA, M. I. MARKINA, T. N. LILEIKINA, N. B. GORBACHEVA and A. V. GERASIMOVA, *Khim. Promyshlennost'*, 1967, **43**, (10), 10-13

Thiophene, ethylmercaptan and CS_2 all reduce the degree of hydrogenation of NO over Pd-Ru catalysts. CS_2 has the greatest deactivation effect. CS_2 also reduces the activity of Pd catalysts more than Ru-Pd catalysts for hydrogenation of C_2H_4 and C_2H_2 . However, the degree of hydrogenation of C_2H_4 is reduced far more than that of C_2H_2 , hence Pd catalyst is more selective. Mercaptans do not form between H_2S and C_2H_2 or C_2H_4 in N_2 but ethylmercaptan is formed in a H_2 atmosphere as the product of reaction between C_2H_2 and C_2H_4 with CS_2 formed by hydrogenation of S-organic compounds.

Catalytic Conversions of Alkyl Derivatives of the Benzene and Naphthalene Series under Pressure of Hydrogen in a Flowing System N. G. BEKAURI, N. I. SHUIKIN and T. S. SHAKARASHVILI, *Kinet. Kataliz*, 1967, **8**, (6), 1275–1282

Studies of dehydrocyclisations of N-octyl and dodecylbenzene, and of 2-N-butyl and 2-N-octyl-naphthalene, in the presence of 0.5% Pd/clay or of activated clay at 450° C, 30 atm. H₂ in a flowing system showed that polycyclic aromatic hydrocarbons with high capacity for luminescence are formed. The yield rose as the molecular weight of the aromatic ring increased.

The Catalytic Activity of Rhodium in Relation to its State of Dispersion

D. J. C. YATES and J. H. SINFELT, J. Catalysis, 1967, 8, (4), 348-358

Studies of the catalytic activity of Rh for hydrogenolysis of C_2H_6 , using Rh/SiO₂ and Rh as catalysts, showed that the specific catalytic activities of unsupported Rh and of severely calcined Rh/SiO₂ are much lower than those of well-dispersed Rh crystallites 40 Å or smaller. Catalytic activity ultimately falls again when the dispersion is extremely fine.

Ruthenium Catalysts for the Liquid-phase Hydrogenation of Sulpholene

N. M. SINITSYN, A. V. MASHKINA and YU. A. SAVOSTIN, Neftekhimiya, 1967, 7, (5), 785–789 Ru catalysts, with high activity for liquid-phase hydrogenation of sulpholene and sulpholane, are more effective when prepared by applying potassium ruthenate to C than RuCl₃ to the support. 5% Ru catalysts were tested on a number of supports and are shown to enhance the activity of Pt/Al₂O₃.

Polymethylene Synthesis from Carbon Monoxide and Hydrogen on Ruthenium Catalysts. Part 11. On the Influence of Physical Factors on the Formation of High Molecular Weight Products

H. PICHLER and W. BURGERT, Brennstoff-chem., 1968, 49, (1), 5-9

Discontinuous synthesis for paraffin formation at various temperatures and pressures of the reacting gases showed that stirrers of special shape increased the exchange of gas at the double bond. At 1000–2500°C, this exchange was pressure-independent, unlike the molecular weight of polymethylene. At <100°C, 2000 atm. the molecular weight of the polymethylene produced was >200,000.

HOMOGENEOUS CATALYSIS

The Reactivity of Pt(II) Complexes in the Oxidation of Carbon Monoxide in Aqueous Solutions

N. K. EREMENKO, K. I. MATVEEV and L. N. RACHKOVSKAYA, *Kinet. Kataliz*, 1967, **8**, (6), 1246–1251

 $K_{2}PtX_{4}$ complexes in the oxidation of CO show decreasing reactivity in the order: $PtI_{4}^{2-} > PtBr_{4}^{2-} > Pt(CNS)_{4}^{2-} \approx PtCl_{4}^{2-} > Pt(NO_{8})_{4}^{2-} > Pt(NH_{3})_{4}^{2+} > Pt(CN)_{4}^{2-}$.

Application of the Mobile Equilibrium of Isomerisation to the Polymerisation of Olefin Mixtures. I. Prototropic Displacement by Salts and Complexes of Noble Metals

N. H. PHUNG, Y. CHAUVIN and G. LEFEBVRE, Bull. Soc. chim. Fr., 1967, (10), 3618-3626

The addition of $TiCl_3$ to $PdCl_2$ produced a new catalytic system more active than $PdCl_2$ alone. It encouraged different stoichiometry in the polymer.

Olefin Oxidation with Palladium(II) Catalyst in Solution

A. AGUILÓ, Advan. organometall. Chem., 1967, 5, 321–352

A review of process for the oxidation of C_2H_4 and other olefins using Pd(II) catalysts in aqueous and non-aqueous solvents. The Pd-olefin complexes are considered as reaction intermediates and their structures and mechanisms are examined. (85 references.)

The Catalytic Activity of π -Complexes of Straight-chain Olefins with Palladium Chloride

G. PREGAGLIA, M. DONATI and F. CONTI, Chim. e Ind., 1967, 49, (12), 1277-1283

The π -complexes were synthesised by direct interaction of PdCl₂ with straight-chain olefins or by exchange between $(C_nH_{2n}PdCl_2)_2$ π -com-

plexes and other olefins. Exchange with 1,5cyclooctadiene displaces the coordinated olefin with unchanged configuration. When PdCl₂ dissolves in α -olefins the free olefin isomerises until the *trans: cis* ratio is greater than one, a result due perhaps to different rates of reaction of the α -olefin with the *cis*- and *trans*- π -complexes. An intramolecular mechanism for rearrangement of the π -complex of an α -olefin is inferred from the lack of isomerisation of the olefin while entering or leaving the complex.

Organic Syntheses by Means of Noble Metal Compounds. XXXIII. Carbonylation of Azobenzene-palladium Chloride Complexes

H. TAKAHASHI and J. TSUJI, J. organometall. Chem., 1967, 10, (3), 511-517

The preparation and carbonylation of $PdCl_2$ complexes of several symmetrically and asymmetrically substituted azobenzenes took place smoothly under mild conditions. Study of their structure indicated that $PdCl_2$ formed a σ bond with the benzene ring by electrophilic substitution, substitutes exerting inductive influences. The carbonylation mechanism was not clear.

Polymerisation by Transition Metal Derivatives. IV. Investigations on the Mechanism of Butadiene Polymerisation by Rhodium Salts

R. DAUBY, F. DAWANS and P. TEYSSIÉ, J. polymer Sci., Part C, polymer Symposia, 1967, (16), 1989-2000

Tests on the polymerisation of butadiene using RhCl₃ as catalyst showed the effects of catalyst concentration, different activation energies, requirements in emulsifier structure and concentration, and the effects of other diolefins. Mixtures of butadiene and piperylene were also polymerised.

Rhodium Complexes for Allene Polymerisation in Polar Media

s. OTSUKA and A. NAKAMURA, *J. polymer Sci.*, Part B, polymer Lett., 1967, 5, (10), 973–975

Polyallenes are produced in high yield at relatively low temperatures and pressures in polar solvents using as catalysts the Rh complexes $[RhCl(CO)_2]_2$, $[RhCl(C_2H_4)_2]_2$, $[RhCl(PPh_3)_3]_3$ and $[RhCl(PPh_3)_2]_2$. The rate of polymerisation is faster with $[RhBr(CO)_2]_2$ than with $[RhCl(CO)_2]_2$, and $[Rhacac(C_2H_4)_2]$ is also effective in C_2H_5OH as solvent. Ru complexes, such as $RuCl_3.nH_2O$, $RuCl_3-PPh_3$ and $RuCl_2(PPh_3)_3$, catalyse allene polymerisation similarly but Pd complexes, such as $Pd(PPh_3)_4$ and $PdCl_2-SnCl_2$, are ineffective.

Polymerisation of Allene with Rhodium Complexes

S. OTSUKA, A. NAKAMURA and K. TANI, Kogyo Kagaku Zasshi, 1967, 70, (11), 2007–2011, A121 Most active catalysts for polymerisation of

allenes to a regular structure were combinations of Rh(I) with appropriate donor ligands, e.g. [RhCl(CO)₂]₂-2PPh₃. Almost quantitative polymerisation is possible in 95% C₂H₅OH at 60-70°C in <5h. Studies of the reaction mechanism suggest insertion of π -coordinated allene monomer to the asymmetric π -allyl- or σ - π -allyl-metal bonding.

The Catalytic Hydrogenation and Deuteration of Steroids in Homogeneous Phase

W. VOELTER and C. DJERASSI, Chem. Ber., 1968, 101, (1), 58-68

Olefin reduction by $(PPh_3)_3RhCl$ suggested a new method for specific hydrogenation of double bonds in steroids. The effects of the solvent, the pressure and the rate of reaction on reactions at the C=C double bonds of steroids were studied. D₂ labelling depended on the solvent and on the catalyst concentration.

FUEL CELLS

An Intermediate Temperature Fuel Cell. Operation on Hydrogen and Oxygen. Operation on Dilute Hydrogen, Carbonaceous Fuels, and Dilute Oxygen

W. B. MATHER and A. N. WEBB, Ind. engng Chem., Process Design Dev., 1968, 7, (1), 11-15, 15-21

Fuel cells with BPO4-H3PO4 paste electrolyte and Pt/Ta or Pt/C electrodes were operated continuously on H, and O, at 200°C for up to 3 months and produced up to 110 mw/cm², although 65-70 mw/cm² was more usual. The thermally stable electrolyte rejects CO₂, has high ionic conductivity and good mechanical properties and needs no regeneration with H₂O. Pt/Ta gauze electrodes were 20% superior to Pt/porous C. Similar cells operated on dilute H₂, steamreformed CH₃OH and shifted CO gave 70-90% the performance of those on pure H2. Carbonaceous fuels including hydrocarbons led to lower efficiency due to high activation polarisation, partly caused by oxidation of Pt anode. When operated on steam-reformed CH₃OH and air, the cell produced 45 mw/cm².

The Effect of Preoxidation and Meniscus Shape on the Hydrogen-Platinum Anode of a Molten-carbonate Fuel Cell

J. T. COBB and L. F. ALBRIGHT, *J. Electrochem.* Soc., 1968, 115, (1), 2-6

Studies at 723°K of a H_2 -O₂ fuel cell with Pt electrodes and molten electrolyte, composed of a eutectic mixture of Li, K and Na carbonates, showed that smooth Pt anodes are activated by preoxidation to give bigger currents. Contact angle of unactivated Pt with the eutectic is 90°, of activated Pt is 0° and decreases with deactivation. H_2 diffuses to the reaction site along the Pt/molten carbonate interface and/or diffusion through the Pt but not appreciably through the molten carbonate film above the meniscus.

CHEMICAL TECHNOLOGY

The Process of Activated Sintering of Tungsten with Palladium Additives

G. V. SAMSONOV and V. I. YAKOVLEV, Porosh. Metall., 1967, 7, (7), 45-49

0.05-1.0% amounts of Pd in the form of aqueous PdCl₂ solution were added to 75μ W powder and, after mixing, drying, sieving, reduction, and sieving, were compressed and sintered in H₂, a process which gave the highest density of $> 17g/\text{cm}^3$ at 0.2% Pd and 1600°C . These samples had microhardness $< 300 \text{ kg/mm}^3$ and compressive strength 105 kg/mm^2 . The activating effect of Pd occurred by transfer of nonlocalised electrons from Pd to W with an accompanying decrease in free energy and increase of statistical weight of the stable electron configurations of the Pd and W atoms.

GLASS TECHNOLOGY

Creep of Alloys of Platinum with Rhodium at Temperatures 1350–1500°C

I. I. NOVIKOV, F. S. NOVIK, E. I. RYTVIN, S. S. PRAPOR and E. N. LOVINSKAYA, *Ivz. Vysshikh* Ucheb. Zaved., Tsvetnaya Metall., 1967, (4), 132-135

Strip samples of 7, 10 and 15% Rh-Pt were examined for creep by metallography at 1350, 1400 and 1500°C and at 0.2, 0.15 and 1.3 kg/mm² for up to 5 h. Graphs of test results show that creep increases with temperature. Creep was most intense at 1500°C, 1.3 kg/mm² and 7 and 10% Rh-Pt alloys failed after 90 and 240 min. in these conditions. No other failure occurred at other temperatures and loadings for any alloy. Creep decreases with greater Rh content. 10% Rh-Pt is more expensive but not much stronger.

Experience in Industrial Determination of Glass Viscosity at a Tank Furnace Feeder M. V. OKHOTIN, E. I. RAEVSKAYA and A. I. TUZIKOV, *Steklo Keram.*, 1967, 24, (12), 16–18

Cylindrical Pt electrodes of diameter 10 mm were placed 40 mm apart in the furnace and 20 mm deep in the molten glass. The viscosity of the glass was calculated from the resistance measured between the electrodes. A Pt: Rh-Pt thermocouple measured the temperature, whose fluctuations are matched by fluctuations of viscosity.

ELECTRICAL AND ELECTRONIC ENGINEERING

Fluorescence of Rhodium-activated Aluminium Oxide

G. BLASSE and A. BRIL, J. Electrochem. Soc., 1967, 114, (12), 1306-1307

Fluorescence emission of 0.1–1.0 at.% Rhactivated Al_2O_3 consists of a broad band in the far red at 680 nm, probably due to the spinforbidden ${}^{3}T_{Ig} \rightarrow {}^{1}Ag_{Ig}$ transition but other Rh³⁺-activated aluminates had very weak photoluminescence.

TEMPERATURE MEASUREMENT

Apparatus for Measuring the Hall Effect of Low-mobility Samples at High Temperatures N. Z. LUPU, N. M. TALLAN and D. S. TANNHAUSER, *Rev. sci. Instrum.*, 1967, **38**, (11), 1658–1661 A thermocouple is a more desirable sensor than a resistance thermometer for high stability of the sample temperature and a Pallador I thermocouple with output $60\mu V/deg C$ was found to be suitable. The double a c measuring method uses a c at 510 Hz with a 2 Hz magnetic field.

NEW PATENTS

METALS AND ALLOYS

Tungsten-base Alloys

MALLORY METALLURGICAL PRODUCTS LTD. British Patent 1,090,561

Tungsten alloys with improved tensile strength and ductility are produced by incorporating 0.5-10 wt.% Ru. Small amounts of Mo, Ni and Fe give another range of alloys of high strength and ductility.

Treatment of Palladium and Palladium-base Alloys

JOHNSON, MATTHEY & CO. LTD. British Patent 1,091,051

When placed under conditions of stress these materials tend to give "discontinuous yield" due to the presence of Si in the material. This defect is now prevented by adding an alloying element which more readily combines with Si than Pd, e.g. Ca, Ba, Sr, Ti, Zr, etc.