

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Specific Heat of Platinum from 1.4 to 100°K

G. E. SHOEMAKER and J. A. RAYNE, *Phys. Lett.*, 1968, **26A**, (6), 222-223

Measurements indicated no anomalous temperature dependence of the lattice heat capacity. The corresponding variation of the Debye temperature was compared to that calculated from elastic data using a central force model.

Measurements of the Thermal Conductivity and Electrical Resistivity of Platinum from 100 to 900°C

D. R. FLYNN and M. E. O'HAGAN, *J. Res. NBS, Sect. C, Engng Instrumentation*, 1967, **71C**, (4), 255-284

Results of two methods show good agreement and indicate that thermal conductivity of Pt increases with temperature. Electrical measurements gave results equivalent to those from conventional nonelectrical methods and the thermal conductivity of Pt does not depend significantly on electric current densities. Further work by the same electrical method on samples of different purity are necessary before Pt can be established as a thermal conductivity reference standard.

Quenches of Deformed Platinum

J. J. JACKSON, *Bull. Am. Phys. Soc.*, 1968, **13**, (1), 74, abstr. EJ2

More than 10^{-4} atomic fraction lattice vacancies can be generated thermally in Pt with indefinite retention of an appreciable number by rapid room-temperature quenching. The number of vacancies lost depends on the number initially present, on the vacancy migration distance, and on the density of effective sinks. Pt deformed at raised temperatures and subsequently quenched has a sink concentration dependent on holding time before quenching.

Vacancies, Divacancies, and Self-diffusion in Platinum

D. SCHUMACHER, A. SEEGER and O. HÄRLIN, *Phys. Status Solidi*, 1968, **25**, (1), 359-371

The electrical resistivity of thin high-purity Pt wires quenched from $\approx 1000^\circ\text{C}$ by the helium-II technique recovers between 380 and 520°C with activation energy of 1.33 ± 0.05 eV; quenched from near the melting point recovery occurs between 200 and 460°C by two second-order processes with activation energies 1.0 and 1.34 eV. Self-diffusion data are reanalysed to allow for both mono- and divacancies and are compared with previous work. A consistent set of vacancy parameters for Pt is proposed.

The Interaction between Liquid Platinum and Some Transition Metal Carbides

R. WARREN, *J. nucl. Mater.*, 1968, **25**, (1), 117-119

Studies of the interaction of liquid Pt with plaques of VC, TiC, WC, and mixed refractory carbides by the sessile-drop method confirmed that they react to form graphite plus metallic solutions or intermetallic compounds. Measurements were qualitative but mixed carbide solid solutions do not appear more stable towards Pt than single carbides. Wettability of WC-TiC by Pt decreased with increasing TiC content.

Effect of Diffusion Barriers on Interdiffusion between Noble Metals and Refractory Metals at 2000°F

H. M. HOFFMAN, R. C. HAM and J. R. OGREN, *J. Metals*, 1968, **20**, (1), 100A

Specimens of commercial Mo and Ta alloys were held in contact with Pt, Rh, 20% Rh-Pt and 40% Rh-Pt at 2000°F for 30 and 120 days, and the extent of interdiffusion was measured by metallographic, microhardness and electron microprobe methods. It proved to be similar in all cases. Chemical vapour deposition of 0.001 inch films and/or plasma arc spraying of 0.005 inch films of Al_2O_3 , ZrO_2 , ZrC and TaC were tested as diffusion barriers. Al_2O_3 was most effective, ZrO_2 less effective, and ZrC and TaC were ineffective in reducing interdiffusion.

Thermodynamic Properties of Solid Palladium-Copper and Platinum-Copper Alloys

K. M. MYLES and J. B. DARBY, *Acta Metall.*, 1968, **16**, (4), 485-492

Activities and free energies of formation at 1350°K of solid Pd-Cu and Pt-Cu alloys were calculated from vapour pressure data. Enthalpies of formation at 298°K were determined by liquid Sn solution calorimetry for Pt-Cu. Entropies of formation of both systems were computed from free energy and enthalpy values. The systems are compared to Pd-Ag, which has similar electronic structure.

On the Preparation and Electrical Properties of PtSb₂

C. T. ELLIOTT and S. E. R. HISCOCKS, *J. mater. Sci.*, 1968, **3**, (2), 174-177

Single crystals of PtSb₂, prepared by a liquid encapsulation technique and pulled by the Czochralski method, consist of n-type material with a carrier concentration $\approx 6 \times 10^{16}/\text{cm}^3$, a ratio of electron to hole mobility $\mu_e:\mu_h=0.57$ at 110°K , and max. electron mobility $2100 \text{ cm}^2/\text{V}$ sec at 50°K . Thermal energy gap is 0.112 eV.

The Low Temperature Thermoelectric Power of Some Palladium and Platinum Alloys

R. FLETCHER and D. GREIG, *Phil. Mag.*, 1968, 17, (145), 21-35

Thermoelectric power S was measured at 2-120°K for Pd-Ag, Pd-Rh, Pd-Pt, Pt-Au and Pt-Ir alloys and it proved possible for alloys of Pd and Pt with their neighbouring elements to correlate the sign of S_d , the diffusion component of thermopower in the residual resistance temperature range, with the slope of density of states versus concentration curves. Observed values of S_d/T agreed with calculation from the rigid band model for all Pt-Au and Pd-Ag alloys studied apart from that with <1% Ag. S_d was not predicted correctly for Pd-Pt. Each specimen had large positive phonon drag component of S , which persisted to high temperatures despite alloying. These phenomena are caused by phonon-induced scattering of either s-d or d-d processes.

The Enthalpies of Formation of the Palladium-Nickel, Platinum-Nickel and Palladium-Platinum Systems

J. B. DARBY, *J. Metals*, 1968, 20, (1), 74A.

Enthalpies of formation of Pd-rich Pd-Ni alloys are negative, i.e. exothermic, and are slightly positive for 70-100% Ni content. Values for Pt-Ni are exothermic with a maximum of -2250 cal/g atom at equiatomic composition. Ordered Pt₃Ni₂ has twice the enthalpy of formation of the disordered alloy. Pd-Pt alloys also have negative enthalpies with a maximum of -850 cal/g atom at equiatomic composition.

Specific Heat Enhancement in Strongly Paramagnetic Pd-Ni Alloys

A. I. SCHINDLER and C. A. MACKLIET, *Bull. Am. Phys. Soc.*, 1968, 13, (1), 124, abstr. HJ9

Low-temperature specific heat measurements on 0-1.95 at.% Ni-Pd alloys show that γ , the electronic specific heat coefficient, has strongly linear dependence on Ni content and increases by 18% per at.% Ni addition. No $T^3 \log T$ dependence occurs in the low temperature heat capacity and data were analysed according to $\alpha T + \beta T^3$.

Application of the Electron-donation Model for Hydrogen Absorption to Palladium-rich Alloys Hydrogen-Gold-Palladium

K. ALLARD, A. MAELAND, J. W. SIMONS and T. B. FLANAGAN, *J. phys. Chem.*, 1968, 72, (1), 136-143

Absorption data for low contents of H₂ in α -phase Au-Pd alloys give heats of absorption at infinite dilution by extrapolation of the isosteric heats as 5980, 7000, 7540, 9040, and 9340 cal/mole H₂ for 5.7, 15.3, 18.8, 26.5, and 44.7% Au-Pd respectively. Measured entropies of absorption are compared with those calculated from a model of localised protons treated as three-dimensional oscillators. Both Au and H are assumed to donate electrons to the vacant s and d bands of Pd.

Investigation of the Thermodynamic Properties of Solid Solutions of the Ag-Pd System by the Method of Measurement of the Vapour Phase

V. N. EREMENKO, G. M. LUKASHENKO, and V. L. PRITULA, *Zh. fiz. Khim.*, 1968, 42, (3), 657-659

Studies at 1000°C by measuring the rate of vaporisation of Ag in the alloys produced isotherms of the thermodynamic activity of both parts and enables the isobaric-isothermal mixing potentials to be calculated. Ag has negative deviation from Raoult's Law at all compositions while for Pd the activity is more ideal in Pd-rich alloys and less ideal in Ag-rich alloys. The extreme value is -3.7 kJ/H atom at ≈ 60 at.% Ag.

Structural Transformations and Magnetic Properties of Iron-Palladium Alloys

L. M. MAGAT, G. M. MAKAROVA and YA. A. SHUR, *Fiz. Metal. Metalloved.*, 1968, 25, (3), 431-438

Studies of changes of magnetic properties and phase structure of high-coercivity alloys of ≈ 30 at.% Pd-Fe during annealing were related to the effect of prior plastic deformation.

The Relative Thermodynamic Properties of Cobalt-Palladium Solid Solutions

L. R. BIDWELL, F. E. RIZZO and J. V. SMITH, *J. Metals*, 1968, 20, (1), 76A

EMF studies at 800-1100°C show that the thermodynamic activity of Co in Pd departs positively from ideal solution behaviour in Co-rich alloys and negatively in Pd-rich alloys. Heats of mixing were endothermic for Co-rich and exothermic for Pd-rich alloys. A miscibility gap below 600°C may exist for Co-rich alloys. Compositions up to 40% Pd-Co were studied in the ferromagnetic state. Relative integral molar excess entropies were all positive.

The Titanium-Palladium Alloys

E. RAUB and E. RÖSCHEL, *Z. Metallkunde*, 1968, 59, (2), 112-114

The existence was confirmed of Ti₄Pd₃, TiPd₂ and TiPd₄, the latter with LI₂ type crystals. Ti₄Pd₃ occurs only between 1280° and 795°C. TiPd shows a transformation at 510-520°C with orthorhombic crystals below this temperature. Maximum solubilities of Pd are <1.1% in α -Ti, ≈ 31 at.% in β -Ti. The disordered solid solution and the LI₂ phase have similar properties which makes it difficult to find the boundary of the f.c.c. Pd-Ti solid solution.

X-ray Studies of Palladium-Cadmium and Palladium-Antimony Alloys

J. N. PRATT, K. M. MYLES, J. B. DARBY and M. H. MUELLER, *J. less-common Metals*, 1968, 14, (4), 427-433

Lattice parameters of Pd-rich f.c.c. and f.c. tetragonal Cd-Pd alloys are tabulated. The solid solubility limit of the cubic phase was determined.

An attempt to characterise the crystal structure of the f.c. tetragonal phases was made. Lattice parameters of Pd-rich f.c.c. Pd-Sb are tabulated. Solid solubility limit of Sb in Pd at 500–1000°C was determined. Lattice parameters of PdSb and PdSb₂ were measured.

Electronographic Investigation of the Pd-Sb System in Thin Layers

T. P. KARPOVA, R. M. IMAMOVA and S. A. SEMILETOV, *Kristallografiya*, 1968, **13**, (2), 316–321

Studies of thin films of Pd-Sb revealed PdSb and PdSb₂ and the new hexagonal compounds Pd₃Sb₃ with $a=7.59$, $c=13.86\text{Å}$, $Z=4$, and PdSb₃ with $a=7.59$, $c=43.2\text{Å}$, $Z=24$.

Pressure Dependence of the Magnetic Transitions in Fe-Rh, Fe-Rh-Pd, and Fe-Rh-Ir Alloys

R. C. WAYNE, *Bull. Am. Phys. Soc.*, 1968, **13**, (3), 442, abstr. DK15

50–60 at.% Rh-Ir alloys exhibit first order antiferromagnetic transitions at temperatures somewhat dependent on the binary alloy composition but the addition of a few % of Pd lowers and of Ir raises these temperatures considerably. Pressure coefficient of Curie temperature and transition temperature T_0 are constant with pressure up to 25 kbar for the alloys studied. T_0 and dT_0/dP depend on the heat treatment. A triple point occurs in the P-T plane at ≈ 15 kbar for the 6% Ir alloy. At pressures above this only antiferromagnetic and paramagnetic phases exist.

New A₃B₅ Phases of the Ti-Group Metals with Rh

B. C. GIESSEN, R. WANG and N. J. GRANT, *J. Metals*, 1968, **20**, (1), 108A

The A₃B₅ phase in the Ti-Rh system is isomorphous with orthorhombic Ge₃Rh₅.

The Compound U₂Ru₃

A. F. BERNDT and A. E. DWIGHT, *Trans. metall. Soc. AIME*, 1968, **242**, (2), 340–341

U₂Ru₃ formed at $1025 \pm 5^\circ\text{C}$ by peritectoid transformation of U₃Ru₄ + U₃Ru₅ has f.c.c. structure with $a=12.895 \pm 0.001\text{Å}$ and density 14.45 g cm^{-3} but it has not been identified with any other known A₂B₃-type structure.

Magnetic Susceptibilities of the Hexagonal Close-packed Alloys of the Later 4d and 5d Transition Metal Series

J. G. BOOTH, *Phil. Mag.*, 1968, **17**, (145), 205–209

Magnetic susceptibilities were measured for 41 alloys of the h.c.p. systems Mo-Ru, Mo-Rh, Ru-Rh, Ru-Pd, Ru-Nb, Re-W, Re-Os, Re-Ir, Re-Pt, Os-Pt and Os-Ir from the 4d and 5d series at 77–330°K. Results largely suggest a rigid (or plastic) band model for these h.c.p. alloys. An apparent minimum in the density of states curve occurs at an average group number of

≈ 8.1 . Re-Pt is the exception, perhaps because of enhanced exchange contribution to the susceptibility.

Superconductivity, Susceptibility, and Specific Heat in the Noble Transition Elements and Alloys. I. Experimental Results

K. ANDRES and M. A. JENSEN, *Phys. Rev.*, 1968, **165**, (2) 533–544

Studies of superconductivity and magnetic susceptibility in mostly Ir-rich f.c.c. Ru-Ir, Rh-Ir, Pd-Ir, Re-Ir, Os-Ir, and Pt-Ir alloys show that filling of the first *d* band first depresses the superconducting transition temperature T_c and then causes a rapid increase of χ . Metals with exchange enhanced susceptibilities are not superconducting above 0.015°K . It is predicted that Pd will not superconduct even at 0°K and that superconductivity will occur well below 10^{-3}K for Pt and Rh, if at all.

II. Comparison with Theory

M. A. JENSEN and K. ANDRES, *Ibid.*, 545–555

Spin fluctuations seem to be suppressing T_c , since there appears to be correlation between decreasing T_c and increasing χ/γ , where γT is the electronic specific heat.

CHEMICAL COMPOUNDS

On Iridium Bromide

N. I. KOLBIN and V. M. SAMOILOV, *Zh. neorg. Khim.*, 1968, **13**, (3), 906–908

IrBr₃ prepared by bromination of Ir at 8–9 atm, 840°K is an insoluble powder with density 6.45 g/cm^3 and specific magnetic susceptibility -0.2×10^{-6} . Dissociation to the elements commences at $\approx 440^\circ\text{C}$, dissociation pressure is 1 atm at 846°K , and the heat of formation is 50.0 kcal/mole . Treatment of IrO₃·2H₂O by HBr produces IrBr and IrBr₂ as well as IrBr₃ with properties somewhat different, which are tabulated.

Thermal Dissociation of Iridium Triiodide

Ibid., (4), 915–918

Measurements of the thermal dissociation pressure of IrI₃ at $585\text{--}723^\circ\text{C}$, which dissociates according to IrI₃ (solid) = Ir + 3/2 I₂ (gas) without formation of the lower iodides, give dissociation constants according to $\log K_{p_{\text{atm}}} = -8975.0/T + 12.42$. The change of enthalpy for IrI₃ formation from Ir metal and I₂ gas is $\Delta H_{298.15}^\circ = -183.2 \times 10^{-3} \pm 5.0 \times 10^{-3}\text{ J/mole}$, the change of entropy is $\Delta S_{298.15}^\circ = -282.0 \pm 9.0\text{ J/deg C mole}$ and the standard entropy of solid IrI₃ is $S_{298.15}^\circ = 145.0\text{ J/deg C mole}$.

The Crystal Structure of Ruthenium (III) Bromide

K. BRODERSEN, H.-K. BREITBACH and G. THIELE, *Z. anorg. allgem. Chem.*, 1968, **357**, (4–6), 162–171

RuBr₃ forms orthorhombic crystals with $a=6.47$,

b=11.205, c=5.855 Å, Z=4, consisting of (RuBr₃)Br_{6/2} groups with Ru in approximately octahedral coordination.

Magnetic and Other Studies of Ruthenium Dioxide and its Hydrate

J. M. FLETCHER, W. E. GARDNER, B. F. GREENFIELD, M. J. HOLDWAY and M. H. RAND, *J. Chem. Soc., A, inorg. phys. theor.*, 1968, (3), 653-657

Magnetic behaviour of RuO₂ up to 1000°K suggests that K is $\approx 3000 \text{ cm}^{-1}$ in dioxo-bridged chains of Ru atoms. High electrical conductivity and structure suggest that the average oxidation state of Ru atoms is $\geq +4$. The oxide hydrate is RuO_{2+x}yH₂O, where x is up to 0.12 due to excess chemisorbed O₂ after removal of some H₂O and where y is often 1-1.3. Susceptibility, similar to that of RuO₂, varies in relation to adsorbed groups and to some Ru atoms behaving like Ru (V), i.e. in the d² state.

The Formation of [Ru(NH₃)₅N₂]²⁺ from Ruthenium Trichloride and Ammonia

J. CHATT and J. E. FERGUSSON, *Chem. Commun.*, 1968, (3), 126

[Ru(NH₃)₅N₂]Cl₂ was produced while preparing [Ru(NH₃)₆]Cl₂ by reductions of RuCl₃ in NH₃ by Zn dust. The N₂ ligand in [Ru(NH₃)₅N₂]²⁺ appears to be produced by dehydrogenation of NH₃ on the Ru ion and indicates great stability of RuN₂.

Fixation of Atmospheric Nitrogen by Ruthenium Compounds

A. D. ALLEN and F. BOTTLEY, *Can. J. Chem.*, 1968, 46, (3), 469

[Ru(NH₃)₅N₂]²⁺ was prepared using atmospheric N₂ from [Ru(NH₃)₆Cl]Cl₂⁺, and this was the first time that such a compound had been prepared from atmospheric N₂. [Ru(NH₃)₅Cl]Cl₂⁺ was alternately reduced with amalgamated Zn and H₂SO₄ under Ar, and exposed to air for 5-7h.

Triphenylphosphine Complexes of Ruthenium and Rhodium. Reversible Combinations of Molecular Nitrogen and Hydrogen with the Ruthenium Complex

A. YAMAMOTO, S. KITAZUME and S. IKEDA, *J. Am. Chem. Soc.*, 1968, 90, (4), 1089-1090

A triphenylphosphine complex of Ru combines with N₂ in a C₆H₆ solution and the coordinated N₂ ligand can be expelled from the Ru complex simply by passing an Ar stream through the C₆H₆ solution at room temperature. The N₂ complex has not yet been isolated. A similar combination with H₂ has been observed. N₂ is not coordinated to a similar complex of Rh.

Oxide Chlorides of Osmium

R. COLTON and R. H. FARTHING, *Aust. J. Chem.*, 1968, 21, (3), 589-593

Os₂OCl₆ was prepared from OsO₄ and HCl. I.R.,

mass spectroscopic and oxidation state determinations showed its structure to be polymeric with oxo bridges. SCl₂ reduction of OsO₄ gave OsCl₄ and OsOCl₄. Attempts to prepare Os₂OCl₆ failed.

Thio- and Seleno-compounds of the Platinum Metals

W. RÜDORFF, A. STÖSSEL and V. SCHMIDT, *Z. anorg. allgem. Chem.*, 1968, 357, (4-6), 264-272

Twelve A₂Me^{IV}X₆ crystalline compounds were prepared. K₂Pt₄S₆, Rb₃Pt₄S₆, Cs₂Pt₄S₆, K₂Pt₄Se₆, Rb₂Pt₄Se₆, K₂Pt₂IrS₆, and K₂Pd₃PtS₆ had hexagonal rhombohedral structures with Z=3. K₃Pt₃SnS₆, Rb₂Pt₃SnS₆ and K₂Pd₃SnS₆ were hexagonal with Z=2. K₂Pt₃TiS₆ and K₂Pd₃TiS₆ were prepared also.

ELECTROCHEMISTRY

Enhanced Catalytic Activity of Platinum Electrodes Resulting from Cathode Pre-treatment

J. N. HIDDLESTON, *Nature*, 1968, 217, (5133, Mar. 16), 1047

Potential-current density curves plotted for anodic oxidation of HCOOH in 2N solutions of H₂SO₄, HClO₄ and HNO₃ show enhanced oxidation rates, i.e. increased currents at lower potentials, with stability provided that electrode potential was not increased beyond 600 mV for long periods, i.e. <4 min.

The Anodic Behaviour of Palladium in Aqueous Solutions

R. KAMMEL, T. TAKEI, H. WINTERHAGER and H. YAMAMOTO, *Metalloberfläche*, 1968, 22, (4), 107-111

Rest potential measurements and potentiostatic studies of Pd electrodes in buffer solutions and in aqueous HCl and H₂SO₄ solutions enabled possible reactions and equilibria to be derived from potential-pH and potential-pCl graphs. Pd dissolves in the divalent state and the dissolution is reversible. Flade potential measurements indicated the stability of the oxide-like surface layers of the electrodes.

ELECTRODEPOSITION AND SURFACE COATINGS

Electrocrystallisation of Mercury, Silver and Palladium

D. J. ASTLEY, J. A. HARRISON and H. R. THIRSK, *Trans. Faraday Soc.*, 1968, 64, (1), 192-201

Kinetics of electrodeposition of Ag, Hg and Pd on inert C electrodes were studied potentiostatically. Pd formed a three-dimensional crystalline growth with rate constant $\approx 3.3 \times 10^{-9}$ moles/cm² sec and $\alpha = 0.6$ for 5.12×10^{-2} M PdCl₂ solution.

Electrolytic Deposition of Palladium-Nickel Alloy

S. N. VINOGRADOV and N. T. KUDRYAVTSEV, *Zashchita Metal.*, 1968, 4, (2), 145-151

Studied in the electrodeposition of Ni-Pd were composition, yield according to current, resistance, internal stress, microhardness, and wear resistance of cathodic deposits in relation to electrolyte composition and the conditions of electrolysis. As Ni content increases, internal stress of the deposit decreases but microhardness and wear resistance increase. 25% Ni-Pd has 1.5 times the microhardness and 14 times the wear resistance of pure Pd. Wear resistance is related to temperature, acidity and current density but microhardness is not. Discharge of the Pd ions is made more difficult but of the Ni ions more easy during joint deposition. Optimum conditions are given for bright 20-25% Ni-Pd deposits.

Platinum-metal Alloy Deposition from Bromide Electrolytes

C. J. N. TYRRELL, *Synopsis Papers, 7th Internat. Metal Finish. Conf., Hanover, 1968, (May), paper 21*

Aqueous electrolytes based on acid solutions of complex bromides were developed for Ir, Pt, Pd, Rh, and Ru and satisfactory deposits up to 5 μ m were obtained. Each pair of these metals could be co-deposited to produce true alloys and the ternary Pd-Ru-Rh combination was deposited also. An electrolyte suitable for 5-50% Ir-Pt deposits on etched Ti or Au-flashed Cu contained 3.5 g/l Pt, 1.5 g/l Ir as complex bromides at pH 1-2. 20-80% alloys of Pd-Pt and Rh-Pd were obtained as adherent, reasonably bright deposits, and up to 50% Ru-Pt and Ru-Pd were of the same standard but, for more Ru, "black" non-adherent deposits tended to be formed.

Wear Behaviour of Rhodium Coatings on Variesly Hard Underlays

A. KEIL and E. MAHLE, *Metalloberfläche*, 1968, 22, (2), 44-48

Effects occurring during dry friction of metals are discussed in terms of the hardness of the loaded faces. The hardness of Rh therefore makes it important as a coating for rubbing contacts and a thicker layer of another metal is usually deposited below it. Tests showed that Rh deposited on Ni directly is more stable than when an intermediate layer of Ag is used. This is true for electrical contacts in almost continuous operation.

HETEROGENEOUS CATALYSIS

Study of the Adsorption and Energetic Properties of Metallic Catalysts. II. Catalytic Activity of Blacks

V. I. SPITSYN, A. A. BALANDIN and L. I. BARSOVA, *Zh. fiz. Khim.*, 1968, 42, (2), 345-350

Specific activities for catalyst blacks for liquid-

phase hydrogenations of cyclohexene decrease in the order Pd>Rh>Pt>Ru for those prepared by Zelinski's method but in order Rh>Pt>Pd>Ru for those prepared radiochemically. Measurements of stationary potential against reaction time indicate slight adsorption of cyclohexene on the catalyst surface and show that the surface energy is almost independent of the method of catalyst preparation. The measurements also lead to a theory for the negative activation energy on Rh and to the cause of the induction period on Ru black. A compensation effect bears little relation to the method of catalyst preparation or to the type of catalyst.

The Rates of Hydrogenation of Cycloalkenes from the Liquid on Platinum-Alumina Catalysts

A. S. HUSSEY, G. W. KEULKS, G. P. NOWACK and R. H. BAKER, *J. org. Chem.*, 1968, 33, (2), 610-616

Reaction rates were determined for hydrogenations of 18 cycloalkenes in C₆H₁₂ solution over Pt/Al₂O₃ at 25°C, \approx 1 atm H₂. Reactions were first order in p_{H₂} and amount of catalyst; zero order in cycloalkenes. Activation energies for cyclohexene and cycloheptene were 5.7 and 6.5 kcal/mole. Discussion in terms of the Horiuti-Polanyi mechanism leads to the suggestion that Pt surfaces have two types of site, one involved in H₂ addition and the other in olefin exchange.

On the Conversion of Propylene on Platinum on Alumina Catalyst

V. I. KARZHEV, N. V. SHAVOLINA and V. Z. ZLOTNIKOV, *Neftekhimiya*, 1968, 8, (1), 46-49

Pt/Al₂O₃ possesses appreciable activity for polymerisation of C₃H₆ at 70 atm, 250-300°C. It promotes formation of significant amounts of aromatic hydrocarbons above 350°C. The 75-200°C fraction contains up to 90% aromatics, mainly C₈ and C₉ homologues of benzene.

Isotopic Exchange of Oxygen on Platinum Powder

Y. L. SANDLER and D. D. DURIGON, *J. phys. Chem.*, 1968, 72, (3), 1051-1057

Kinetic studies on the isotope exchange of O₂ on Pt powders at -195 to +300°C showed three different weak modes of chemisorption, all varying with time and temperature. No O₂ beyond the equivalent of a monolayer was in or on the powders, which were well annealed and free of C or H₂. Previous reports of the uptake of several layers seem due to impurities or defects. N₂ does not exchange on Pt nor interfere with O₂ exchange up to 600°C.

The Relative Specific Activity for Benzene Hydrogenation of Some Supported Group VIII Metals

W. F. TAYLOR, *J. Catalysis*, 1967, 9, (2), 99-103

Specific activity studies of C₆H₆ hydrogenation

on Ni/SiO₂, Co/SiO₂ and Pt/SiO₂ at 70–175°C and at a common set of reactant partial pressures revealed apparent activation energies of 14.0, 5.8 and 2.3 kcal/mole for the respective catalysts. Apparent activation energy increases with p_{H₂}. Below 90°C the relative specific activity is Pt > Co > Ni; above 90°C it is Pt > Ni > Co. It is difficult to relate apparent activation energy to the stability of the proposed surface π complexes because of its complexity.

Influence of Hydrogen in the Dehydrogenation of Cyclohexane on Platinum

B. MENCIAER, F. FIGUERAS, L. DE MOURGES and Y. TRAMBOUZE, *C.r., Ser.C.*, 1968, **256**, (9), 595–598
Activity of Pt/SiO₂ is affected by reversible deactivation caused by H₂, and by permanent fouling on the catalyst which H₂ reduces.

Heterogeneous Oxidation of Methane over Palladium Catalysts

J. G. FIRTH and H. B. HOLLAND, *Nature*, 1968, **217**, (5135, Mar. 30), 1252–1253

Reaction parameters were established for oxidation of CH₄ on Pd and on Pd/zeolite formed in different ways.

The Decomposition of Formic Acid Vapour on Silver-Palladium Alloys

G. RIENÄCKER and H. MÜLLER, *Z. anorg. allgem. Chem.*, 1968, **357**, (4–6), 255–263

Catalytic activity of Pd for decomposition of HCOOH vapour is unaffected by addition of up to 30 at. % Ag. A sharp decrease of activity occurs at 30–40 at. % Ag. The activity at > 40 at. % Ag is steady at the lower value for Ag-rich alloys and pure Ag. Activation energy of the catalysts depended on the experimental conditions and on their pretreatment.

On Changes of Selectivity of the Action of Pd Catalysts by Modification in the Hydrogenation of 6-Methylhepta-3,5-dien-2-one

L. KH. FREIDLIN, N. V. BORUNOVA, L. I. GVINTER and S. S. DANIELOVA, *Zh. fiz. Khim.*, 1968, **42**, (1), 98–100

Hydrogenation of 6-methylhepta-3,5-dien-2-one over 5% Pd/CaCO₃, 1% Pd/Al₂O₃ or 1% Pd/TiO₂ occurs principally by addition of H₂ at the 5,6 double bond but when the catalysts are modified with Cd the addition of H₂ occurs principally at the 3,4 double bond. Addition of (CH₃COO)₂Pb to Pd/CaCO₃ does not change the point of H₂ addition but initiates deactivation.

Isomerisation of Hexenes in the Presence of Ruthenium, Rhodium, Osmium and Iridium, Supported on Carbon

M. ABUBAKER, I. V. GOSTUNSKAYA and B. A. KAZANSKII, *Vest. Moskov. Univ., Ser. II, Khim.*, 1968, (1), 105–107

Studies of double bond migration in hexene-1,

2-methylpentene-1, 3-methylpentene-1, and 2,3-dimethylbutene-1 in the presence of Ru/C, Rh/C, Os/C, and Ir/C at 80°C showed that activity varies in the order Rh > Ru > Os > Ir.

Catalytic Hydrogenation of Allene

R. S. MANN and D. E. TO, *Can. J. Chem.*, 1968, **46**, (2), 161–166

The order of activity of metal/pumice catalysts is Pt > Pd > Rh > Ir > Ni > Co > Fe > Ru > Os and their apparent activation energies are 17.4, 13, 9.6, 5.3, 7.8, 10.8, 9.4, 3.0, and 4.6 kcal/mole respectively. Pressure-time curves for the reaction showed a dependence on reactant ratios and their order of admission. The reaction was first order, or slightly higher, in H₂ and zero order in allene. A mechanism similar to hydrogenation of acetylene is suggested.

HOMOGENEOUS CATALYSIS

A Comparison of Heterogeneous and Homogeneous Platinum-catalysed Exchange Procedures for the Isotopic Hydrogen Labelling of Synthetic Hormones and Steroids

J. L. GARNETT, J. H. O'KEEFE and P. J. CLARINGBOLD, *Tetrahedron Lett.*, 1968, (22), 2687–2690

K₂PtCl₄ catalyses deuteration and tritiation of synthetic hormones and steroids faster and at lower temperatures than Pt/NaBH₄ or self-activated PtO₂. Homogeneous deuteration of oestrone, cholesterol and testosterone is confined to positions close to the points of unsaturation. In hexestrol, *trans*-stilbene and bibenzyl, both ring and side chain H is exchanged. Homogeneous exchange is simpler than heterogeneous and will probably replace the latter for deuteration and tritiation. The methods are complementary for labelling of other substances.

Initiation of Vinyl Polymerisation by Tetraakis(triphenylphosphine)(0)

C. H. BAMFORD, G. C. EASTMOND, and K. HARGREAVES, *Trans. Faraday Soc.*, 1968, **64**, (1), 175–184

Pt(PPh₃)₄ effectively initiated vinyl polymerisation at 25–80°C in the presence of CCl₄ because of its low activation energy, 11.2 kcal/mole, and the lack of inhibition at high concentration. Rates and degrees of polymerisation, solvent effect, and the effect of CO addition are discussed.

The Mechanism of Hydrogenolysis of Cyclopropanes at Platinum and Palladium

W. J. IRWIN and F. J. MCQUILLIN, *Tetrahedron Lett.*, 1968, (18), 2195–2198

The rate of fission of cyclopropanes with single substituents and the nature of the products both depend on the nature of the substituent and on the catalyst used, Pd being much more active than Pt. Hydrogenolysis by electrophilic polarisation of the chemisorbed cyclopropane is postulated as the rate-determining step, followed by H₂ transfer.

Isomerisation of α -Olefins in Palladium Chloride Solutions

I. I. MOISEEV, A. A. GRIGOR'EV and S. V. PESTRIKOV, *Zh. org. Khim.*, 1968, 4, (3), 354-359

KMnO₄, K₂Cr₂O₇, H₂O₂, CuCl₂, and *n*-benzoquinone inhibit positional and geometric isomerisation of butenes, hexene-1, and 4-methylpentene-1 by PdCl₂ by oxidising the reduced form of Pd. Anhydrous PdCl₂ does not cause isomerisation but addition of H₂O or alcohol causes reductive decomposition of Pd(II) π -complexes and inhibits isomerisation.

The Isomerisation of *n*-Phenylbutenes Catalysed by Palladium Complexes

N. R. DAVIES, A. D. DI MICHEL and V. A. PICKLES, *Aust. J. Chem.*, 1968, 21, (2), 385-395

Isomerisation of 4-phenylbut-1-ene to a mixture of *cis*- and *trans*-1-phenylbut-2-ene and *trans*-1-phenylbut-1-ene in the presence of bis(benzonitrile)dichloropalladium(II) proceeds both by consecutive reactions and by direct conversion. The kinetics of this reaction are similar to those observed for allylbenzene.

Organic Syntheses by Means of Noble Metal Compounds. XXXIV. Carbonylation and Decarbonylation Reactions Catalysed by Palladium

J. TSUJI and K. OHNO, *J. Am. Chem. Soc.*, 1968, 90, (1), 94-98

PdCl₂ is more efficient than metallic Pd for decarbonylation of acyl halides to form olefins. Pd(NO₃)₂, PdO, Pd(acetylacetonate)₂, RhCl₃, and Rh₂O₃ are also active for this reaction but Pt/C, PtCl₄, ReCl₃, ReCl₅, and IrCl₃ are inactive. Pd/C catalyses decarbonylation of aldehydes in gaseous phase at 200°C.

XXXV. Novel Decarbonylation Reactions of Aldehydes and Acyl Halides Using Rhodium Complexes

K. OHNO and J. TSUJI, *Ibid.*, 99-107

Aldehydes are decarbonylated by RhCl(PPh₃)₃ under mild conditions and acyl halides are decarbonylated also to give olefins. Five-coordinate acyl-Rh complexes were isolated as intermediates of the latter reaction. RhCl(CO)(PPh₃)₂ catalyses decarbonylation of acyl halides and aldehydes, e.g. aromatic acid halides give aromatic halides. The complex also catalyses carbonylation of alkyl to acyl halides.

Dimerisation of Acrylonitrile to 1,4-Dicyano-1-butene with Ruthenium Complexes

J. D. MCCLURE, R. OWYANG and L. H. SLAUGH, *J. organometal. Chem.*, 1968, 12, (1), P8-P12.

The mechanism of this reaction was studied using RuCl₂(CH₃-CHCN)₃ and similar Rh complexes. A Rh hydride intermediate was postulated with the insertion of π -bonded acrylonitrile into the σ -2-cyanoethylruthenium bond followed by elimination of the Rh complex.

Conversions of Acetylene Compounds in Solutions of Palladium and Rhodium Salts

S. M. BRAILOVSKII, O. L. KALIYA, O. N. TEMKIN and R. M. FLID, *Kinet. Kataliz.*, 1968, 9, (1), 177-179

Studies of the reaction of acetylenes, vinylacetylenes and phenylacetylenes with PdCl₂ and RhCl₃ in aqueous and non-aqueous solutions at various temperatures show that in all cases compounds are formed with general formula Cl_mM(-CR₁=CR₂)_n-X, where m, n, and X depend on the metal, the solubility and the temperature. Where M is Pd, m=1, n varies from 2 to 14, and X is OH or Cl. When M is Rh, n varies from 4 to 20. An organic residue in the reaction of RhCl₃ with phenylacetylenes is low molecular weight polyphenylacetylene.

Homogeneous Catalytic Hydrogenation of Aldehydes with Rhodium Carbonyl Catalysts. II

B. HEIL and L. MARKÓ, *Acta Chim. Acad. Sci. Hung.*, 1968, 55, (1), 107-116

Reaction kinetics at 160°C, p_{CO} ≥ 80 atm obey the equation d(alcohol)/dt = k[aldehyde][Rh]^{1/6}(P_{H₂})^{0.5}(P_{CO})^{-0.3}. Rh₈(CO)₁₈ was the principal Rh complex in the mixture. CO-deficient HRh(CO)¹⁶ was also active. Rh₂(CO)₈ and HRh(CO)₄ were not detected.

Homogeneous Hydrogenation of Olefinic Substrates Using Rhodium Complexes Containing Sulphur Ligands

B. R. JAMES, F. T. T. NG. and G. L. REMPEL, *Inorg. nucl. chem. Lett.*, 1968, 4, (4), 197-199

RhCl₃(SEt₂)₃ catalyses hydrogenation in N,N'-dimethylacetamide solution with excess of the substrate. Kinetics and mechanism of the hydrogenation of maleic acid were studied. The reaction is first order in both Rh and H₂.

Kinetic Study of Iridium(I) Complexes as Homogeneous Hydrogenation Catalysts

B. R. JAMES and N. A. MEMON, *Can. J. Chem.*, 1968, 46, (2), 217-223

Hydrogenations catalysed by IrX(CO)(PPh₃)₂, where X=Cl, Br or I, were found to be between zero and first order in each of the concentrations of Ir, substrate and H₂. The reaction rate was enhanced by a co-ordinating solvent and by traces of O₂, and followed the order I > Br > Cl for the different halogens.

Osmium Tetroxide-catalysed Oxidation of Olefins

J. F. CAIRNS and H. L. ROBERTS, *J. Chem. Soc., C, org.*, 1968, (6), 640-642

The catalytic activity of OsO₄ in alkaline solution is dependent on pH. A wide range of olefins and partially oxidised compounds were oxidised by O₂ at 1 atm, 80°C, pH 8.5-12.5. The products and the stability of the reaction depended on pH.

FUEL CELLS

Ammonia - Oxygen Fuel Cell

E. J. CAIRNS, E. L. SIMONS and A. D. TEVEBAUGH, *Nature*, 1968, 217, (5130, Feb. 24), 780-781

An $\text{NH}_3\text{-O}_2$ fuel cell uses 54 wt. % aqueous KOH electrolyte and Teflon-bonded Pt black electrodes with 51 mg Pt/cm². Total cell resistance was 0.03 ohm, the cathode curve showed no limiting current density up to at least 1000 mA/cm² at 140°C and the anode voltage rose sharply at current density >700 mA/cm². For current densities between 20 and 200 mA/cm² the anode performance improved by almost 75 mV between 109 and 191°C. Performance level of these cells exceeds those of all fuels other than H₂ or N₂H₄.

TEMPERATURE MEASUREMENT

Practical Temperature Scales between 11K and 273K

H. PRESTON-THOMAS and R. E. BEDFORD, *Metrologia*, 1968, 4, (1), 14-30.

The reproducibility of proposed scales, which might replace four national scales below 90.18°K, is analysed and the scales are related to best estimates of the thermodynamic scale. Lack of reproducibility below 50°K may be tolerated or the thermometer characteristics must be restricted. The proposed scales have systematic variation in degree size with temperature. All this work is based on the Pt resistance thermometer.

NEW PATENTS

METALS AND ALLOYS

Manufacture of Precious Metal Spheres and Spheroids

INTERNATIONAL NICKEL LTD.
British Patent 1,103,396

Small spheres or spheroids of alloys of Ru, Rh, Os and Ir are used for points of moving elements, e.g. in compasses, and fountain pen nibs. They are produced by heating a powder of one of these four metals with a matrix mixture of Pd or Pt with Au or Ag above the melting point of the matrix but below that of the four metals, forming the product into spheres, cooling and leaching out the matrix.

Niobium Alloys

BIRMINGHAM SMALL ARMS CO. LTD.
British Patent 1,103,724

The strength of Nb-W alloys, with or without Ta, is improved by the addition of one or more of Ru, Os and Ir. The range claimed is at least 30% Nb, 10-25% W, 0-40% Ta and 0.1-10% Pt metal. Small amounts of Hf and Zr may also be present.

Preparation of Finely Divided Metals

INTERNATIONAL NICKEL LTD.
British Patent 1,109,890

Finely divided Ir or Ru is produced by thermally decomposing a halogen-free Ir or Ru compound at up to 400°C in non-oxidising conditions, the Ir or Ru atom being in a complex with NH₃ and/or oxalate groups, the other groups in the compound leaving no residue on decomposition. A typical compound is $(\text{NH}_4)_3[\text{Ru}(\text{CO})_3(\text{C}_2\text{O}_4)]$.

Manufacturing Non-Magnetic, Elastic Metallic Materials

ZAIDAN HOJIN DENKI JIKI ZAIRYO KENKYUSHO
British Patent 1,110,045

These materials are produced from metallic Pd or an alloy of 30-100 wt% Pd and 70-0 wt% Au by heating the metal or alloy at above 600°C but below its melting point for more than one minute and then slowly cooling it to achieve annealing. It is permissible for 0-5% of a variety of other alloying elements to be present.

Reorientation of Stabilised Platinum

JOHNSON, MATTHEY & CO. LTD.
Italian Patent 787,630
French Patent 1,504,716

Mechanical properties of a strengthened metal or alloy are improved by cold-working and annealing. The cold-working causes recrystallisation during annealing with a grain structure elongated in the direction of working. Pt and Rh-Pt are strengthened prior to treatment by the inclusion of a dispersed carbide.

Platinum Claddings for Refractory Metals

JOHNSON, MATTHEY & CO. LTD.
Italian Patent 794,340

Articles comprise refractory metal cores, such as Nb, Ta, Cr, or an alloy thereof, or Mo, which do not form volatile oxides at the operating temperature nor form alloys with the Pt or Pt alloy cladding at melting points below this temperature. A barrier layer between core and cladding consists of a compatible refractory carbide, silicide, boride, sulphide, nitride, or oxide, e.g. a rare