

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Young's Modulus of Single Crystals of Palladium at High Temperatures

H. MASUMOTO, H. SAITO and S. KADOWAKI, *J. Japan Inst. Metals*, 1968, **32**, (6), 529-532

Measurements at 0-600°C using a dilatometer and a vibrator-controlled oscillator system showed that the Young's moduli of a Pd single crystal are 7.35, 13.77 and 19.44×10^8 kg/cm² at 20°C in the <100>, <110> and <111> orientations respectively. The modulus in the <100> and <110> orientations decreases with increasing temperature but in the <111> orientation increases to a maximum at $\approx 250^\circ\text{C}$ and then decreases. Calculated and measured values for a polycrystal are in good agreement.

A New Heat-treatment of Pt-Co Alloys of High-grade Magnetic Properties

H. KANEKO, M. HOMMA and K. SUZUKI, *Trans. Japan Inst. Metals*, 1968, **9**, (2), 124-129

Detailed studies of the magnetic properties of ≈ 50 at.% Co-Pt revealed that double ageing at 680-720°C and 600°C effectively increased the coercive force and gave a maximum energy product $(B.H)_{\text{max}} = 12.5 \times 10^6$ G.Oe.

Uniaxial Magnetic Anisotropy Induced in Pt-Co Alloy by Tempering under Stress

S. SHIMIZU and E. HASHIMOTO, *J. appl. Phys.*, 1968, **39**, (5), 2369-2371

Tempering under compressive stress induces uniaxial magnetic anisotropy in 50 at.% Pt-Co with its easy axis along the direction of stress but tempering under tensile stress induces anisotropy with the hard axis along the direction of stress. In the perfectly ordered state $K = 3.1 \times 10^8$ erg/cm³ in 20 kOe field. $4\pi I$ is 7.4 kG and 4.7 kG is 23 kOe along the easy and hard axes respectively. X-ray diffraction indicates a kind of fibre structure with <001> axes of the ordered tetragonal lattices oriented more to the compressive stress direction than to the cross directions.

Electronographic Investigation of Diffusion in Thin Gold-Palladium Films

B. T. BOIKO, L. S. PALATNIK and M. V. LEBEDEVA, *Fiz. Metall. Metalloved.*, 1968, **25**, (5), 845-848

Diffusion coefficients of vacuum-deposited 100-150 Å films of 0-50 at.% Au-Pd annealed at 400-600°C are given by $D = 1.2 \times 10^{-5} \exp(-11,000/RT)$ cm²/sec and are unrelated to solid solution concentration. D tends to decrease as annealing time increases.

The Electrical Resistivity of Palladium-Hydrogen and Palladium-Deuterium Alloys between 4 and 300°K

N. S. HO and F. D. MANCHESTER, *Can. J. Phys.*, 1968, **46**, (11), 1341-1345

Electrical resistivity measurements at 4-300°K, and 0-0.62 H/Pd, showed that an anomaly exists in the resistivity of Pd-D as well as that in Pd-H.

The Reaction of Hydrogen with Palladium-Nickel Alloys

A. A. RODINA, M. A. GUREVICH, N. I. DORONICHEVA and L. V. MEL'NIKOVA, *Zh. fiz. Khim.*, 1968, **42**, (4), 977-981

Studies of 2-50 wt.% Ni-Pd alloys at 300-500°C showed that at a pressure difference of 1 atm there is no significant decrease of permeability for H₂ up to 5.5 wt.% Ni but that there is above this Ni content. 2 and 3.5 wt.% Ni-Pd have poor stability in H₂ for 20-500°C heating-cooling cycles. No second phase was formed although the microstructure altered. 5-50 wt.% Ni-Pd are stable in H₂, even after 3000 temperature cycles. No second phase was formed in 5-8 wt.% Ni-Pd alloys and the microstructure remained unaltered.

The System Ag₂Te-Pd

I. I. CHERNYAEV, N. N. ZHELIGOVSKAYA, M. K. BORISENKOVA and N. A. SUBBOTINA, *Zh. neorg. Khim.*, 1968, **13**, (6), 1620-1625

X-ray and thermographic studies of the Ag₂Te-Pd system enabled its composition diagram to be built up as far as 1000°C and indicated the existence of a quasibinary layer at the boundary of Ag₂Te and Pd. (AgPd)₂Te is stable below 425°C and possesses a PbFCl-type tetragonal lattice with $a = 6.24$, $c = 11.56$ Å.

Thermal Expansion of Iridium from 4.2° to 300°K

H. F. SCHAAKE, *J. less-common Metals*, 1968, **15**, (1), 103-105

The coefficient of linear thermal expansion of Ir in this range, determined from lattice parameter measurements by X-ray diffraction, is reported for 13 temperatures and agrees well with previous data. An empirical equation for the lattice parameter of Ir as a function of temperature at 0-300°K is $a(T) = 3.8344 \pm 0.0004 - 3.3612 \times 10^{-8} T + 1.2265 \times 10^{-7} T^2 - 1.7956 \times 10^{-10} T^3$.

Brittle Fracture in Iridium Single Crystals

C. A. BROOKES, J. H. GREENWOOD and J. L. ROUTBORT, *J. appl. Phys.*, 1968, **39**, (5), 2391-2395

Scanning electron microscope studies of brittle

fracture of Ir showed that, except where macroscopic imperfections occur, cracks can be nucleated only after extensive work-hardening. Plastic relaxation of the crack is inhibited because impurities substantially increase the critical resolved shear stress. Thus brittle fracture in Ir is caused mainly by impurities.

Reactions of Uranium with the Platinide Elements. I. The Uranium-Ruthenium System

J. J. PARK, *J. Res. NBS, Sect. A, Phys. Chem.*, 1968, **72A**, (1), 1-10

Thermal analysis, metallography and X-ray diffraction revealed five intermetallic compounds: U_2Ru , formed peritectically at $\approx 937^\circ C$; "URu," melting congruently at $\approx 1158^\circ C$; U_3Ru_{11} , formed peritectically at $\approx 1163^\circ C$; U_3Ru_6 , formed peritectically at $\approx 1182^\circ C$; URu_3 , formed peritectically at $\approx 1850^\circ C$. "URu" undergoes solid-state transition at $\approx 795^\circ C$. Eutectics occur at $\approx 886^\circ C$, 18.5 at.% Ru and $\approx 1148^\circ C$, 49 at.% Ru. Maximum solid solubilities are ≈ 7.5 at.% Ru in U, and ≈ 1.3 at.% U in Ru. Ru lowers the γ -U transformation to $\approx 691^\circ C$, and the β -U transformation to $\approx 625^\circ C$.

II. The Uranium-Rhodium System

Ibid., 11-17

Similar studies revealed four intermetallic compounds: U_4Rh_3 , formed peritectically at $\approx 1155^\circ C$ with a solid state transformation at $\approx 720^\circ C$; U_3Rh_4 , formed peritectically at $\approx 1450^\circ C$; U_3Rh_5 , formed peritectically at $\approx 1550^\circ C$; URh_3 , melting congruently at $\approx 1700^\circ C$. Eutectics occur at $\approx 865^\circ C$, 24.5 at.% Rh and $\approx 1393^\circ C$, 87 at.% Rh. Maximum solid solubility of Rh in U is ≈ 8 at.%, and of U in Rh is ≈ 3 at.%.

III. The Uranium-Iridium System

J. J. PARK and L. R. MULLER, *Ibid.*, 19-25

Similar studies revealed five intermetallic compounds: U_3Ir formed peritectically at $\approx 945^\circ C$ and decomposing eutectoidally at $\approx 758^\circ C$; U_2Ir_2 , formed peritectically at $\approx 1121^\circ C$; UIr , melting congruently at $\approx 1470^\circ C$; UIr_2 , formed peritectically above $1850^\circ C$; UIr_3 with congruent m.p. above $1950^\circ C$. U_3Ir_2 has a solid state transition at $\approx 898^\circ C$. Eutectics occur at $\approx 914^\circ C$, ≈ 15 at.% Ir; at $\approx 1450^\circ C$ between UIr and UIr_2 ; at $\approx 1950^\circ C$ between UIr_3 and Ir. Solid solubility of Ir in γ -U is ≈ 5.5 at.%, of U in Ir is < 3 at.%. Ir reduces the γ - β U transformation to $\approx 681^\circ C$, and the β - γ transformation to $\approx 565^\circ C$.

Activities in Solid Iridium-Iron and Rhodium-Iron Alloys at $1200^\circ C$

K. SCHWERTFEGGER and L. ZWELL, *Trans. Metall. Soc. AIME*, 1968, **242**, (4), 631-633

The equilibria between Ir-Fe or Rh-Fe, Fe oxide (wüstite or magnetite), CO_2 and CO at $1200^\circ C$ were studied by X-ray and thermodynamic analysis. Lattice parameters and activities are presented.

The Effect of Ruthenium, Rhodium and Palladium on the Heat of Expansion of Iron-Nickel and Iron-Nickel-Cobalt Alloys

N. A. SOLOV'EVA, M. I. YUDKEVICH, I. I. PASTERNAK and V. Z. POGOSOV, *Metalloved. Term. Obrabot. Metal.*, 1968, (4), 45-46

Additions of Ru or Rh to Fe-Ni and to Fe-Ni-Co alloys raised their coefficients of thermal expansion but had no effect on their Curie points. Additions of 5% or 20% Pd to Fe-Ni-Co at the expense of Fe and Ni raised both factors but the more intensive rise occurred for the coefficient of thermal expansion, which rose $5.0 \times 10^{-6} \text{ deg}^{-1}$ at 20- $700^\circ C$.

CHEMICAL COMPOUNDS

Complex Sulphates of the Platinum Metals

S. I. GINZBURG and N. N. CHALISOVA, *Zh. neorg. Khim.*, 1968, **13**, (5), 1239-1244

A review of the electrochemical and other properties of the Pt metal sulphates. (46 references.)

High Pressure Synthesis of Pyrochlore-type Oxides of Tetravalent Platinum

H. R. HOEKSTRA, S. SIEGEL and F. GALLAGHER, *Abstr. Papers, 155th Mtg, Am. Chem. Soc.*, 1968, (Mar.), M76

Fifteen $A_2^{III}Pt^{IV}_2O_7$ pyrochlore oxides, where $A = Sc, In, Y$, or rare earth, synthesised from binary oxides at 30-50 kbar, 100-1500 $^\circ C$, possess cell parameters 9.85-10.42 \AA and are stable to $\approx 1000^\circ C$ at ambient pressure.

Synthesis and Properties of Two New Members of the Rutile Family RhO_2 and PtO_2

R. D. SHANNON, *Solid state Commun.*, 1968, **6**, (3), 139-143

A tetragonal rutile form of RhO_2 and an orthorhombic distorted form of PtO_2 were made from commercial oxides at $700^\circ C$, 3000 atm. These compounds have room-temperature resistivities $< 10^{-4}$ ohm cm respectively and ionic radii $r(Pt^{4+}) = 0.63\text{\AA}$ and $r(Rh^{4+}) = 0.62\text{\AA}$. Both are thermally unstable.

Phase Relations between Palladium Oxide and the Rare Earth Sesquioxides in Air

C. L. MCDANIEL and S. J. SCHNEIDER, *J. Res. NBS, Sect. A, Phys. Chem.*, 1968, **72A**, (1), 27-37

Equilibrium phase relations were determined in air between PdO and each of La_2O_3 , 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 , and Lu_2O_3 .

The Ruthenium Dioxide-Oxygen-Ruthenium Tetroxide Equilibrium

B. D. PENMAN and R. R. HAMMAR, *USAEC Rept IN-1013*, 1968, (Jan.), 7 pp

Partial pressure of RuO_4 over RuO_2 as a function

of p_{O_2} at 453–723°C enabled new values of $H^{\circ}_{f,298}$, $F^{\circ}_{f,298}$ and C_p for oxides of Ru to be recommended. It is suggested that during calcining of nuclear waste there is volatilisation of Ru as RuO_4 and also as either nonequilibrium concentrations of $RuO_4(g)$, very fine particles, or as another Ru vapour species.

The Oxidising Properties of the Third Transition Series Hexafluorides and Related Compounds

N. BARTLETT, *Angew. Chem. internat. Ed. En.*, 1968, 7, (6), 433–439

Electron affinity E increases regularly by 20 kcal/mole for each unit increase in atomic number over the series $WF_6 < ReF_6 < OsF_6 < IrF_6 < PtF_6$, while affinity for F^- decreases. PtF_6 , ($E > -156$ kcal/mole), oxidises O_2 and Xe. IrF_6 is more effective in oxidative fluorination of ONF to ONF_3 .

ELECTROCHEMISTRY

Mechanism of Electrolytic Perchlorate Production

M. P. GROTHEER and E. H. COOK, *Electrochem. Technol.*, 1968, 6, (5–6), 221–224

Smooth bright Pt is the most efficient anode for the electrochemical oxidation of $NaClO_3$. The effects of current density, $NaClO_3$ concentration and anode polarisation on perchlorate production are analysed and a mechanism is suggested whereby $d(ClO_4^-)/dt$, the rate of production, is equal to $K_3(ClO_3^-)_i$, where K_3 is proportional to the true current density and $(ClO_3^-)_i$ is the concentration of chlorate ion at the anode surface.

Electrochemical Determination of the Specific Surface and the Activity of Porous Platinum

H. BINDER, A. KÖHLING, K. METZELTHIN, G. SANDSTEDTE and M.-L. SCHRECKER, *Chem.-Ing.-Tech.*, 1968, 40, (12), 586–591

The specific surface area of Raney Pt depends on Al content and decreases with use. Results were obtained from measurements of cathodic adsorption and anodic desorption of H atoms by potentiostatic sweep methods and were compared with those obtained from BET surface area measurements.

The Effect of Surface-active Cations on the Catalytic Activity and Selectivity of Pt Black

F. M. TOKTABAEVA, G. D. ZAKUMBAEVA and D. V. SOKOL'SKII, *Kinet. Kataliz*, 1968, 9, (3), 690–692
Studies at 20 and 30°C showed that increasing concentrations of the surface-active cations Cd, Zn, Pb, Sn, In, Tl, Mn, and Re decreased the rate of hydrogenation of propargyl alcohol on Pt black. A decrease in selectivity for the hydrogenation of triple bonds was connected with the changed mechanism due to certain adsorbed

cations suppressing atomisation of H_2 . Activation of H_2 was mainly by formation of Pt- H_2 dipoles, it was assumed.

On the Activity of Platinum Catalysts in Solution. III. Facets on Flame-formed Platinum Spheres

T. B. WARNER, *J. Electrochem. Soc.*, 1968, 112, (6), 615–616

Pt beads melted with an oxyhydrogen flame and cooled slowly develop flat regions corresponding to {111} and {100} crystal faces, which increase catalytic activity.

Surface Oxidation and Reduction of Platinum Electrodes: Coverage, Kinetic and Hysteresis Studies

D. GILROY and B. E. CONWAY, *Can. J. Chem.*, 1968, 46, (6), 875–890

Polarisation and hysteresis effects were used to study the nature and extent of surface oxidation on three sorts of Pt surface. The quantity of reducible oxide depends on potential and time of anodic polarisation. Galvanostatic and potential sweep techniques were compared.

Adsorption and Oxidation of Carbon Monoxide on Platinised Platinum Electrodes

M. W. BREITER, *J. phys. Chem.*, 1968, 72, (4), 1305–1313

Anodic oxidation mechanisms of the two types of CO adsorbed on platinised Pt at open circuit are discussed. Saturation coverage of H atoms decreases linearly with CO coverage and the H-adsorption isotherms change.

Interactions of Adsorbed Organic Layers with Hydrogen Atoms on Platinum Electrodes

S. B. BRUMMER and K. CAHILL, *US Rept AD 663,903*, 1968, (Jan.), 28 pp

Studies in 1 M H_2SO_4 at 40°C of H atom coverage of smooth Pt foils indicate that the presence of CO leads to repulsive H-CO interaction at all potentials in terms of sites occupied and at >0.15 V versus R.H.E. Interaction of H- CO_2 is repulsive above 0.20 V but attractive below 0.20 V. Results are discussed. The cathodic method of H-atom charging for estimating organic coverage on Pt seems least suspect. Interactions with H on Pt show that the species CO_{ads} and “reduced CO_2 ” are different.

On the Activity of Platinum Catalysts in Solution. Part I. Effects of Thermal Treatment and Chemical Etching on the Pt-O/Hydrogen Specific Reaction Rate

T. B. WARNER, S. SCHULDINER and B. J. PIERSMA, *US Rept AD 664,490, NRL Rept 6622*, 1967, (Dec.), 11 pp

This reaction is very sensitive to pretreatment of

the Pt and is a responsive test for cleanliness of electrode and electrolyte. H was present in electrochemically clean 1 M H₂SO₄ and in the derma of the Pt. Reaction of H with Pt-O on Pt beads was usually faster where their heating to m.p. had been more uniform and their recrystallisation on cooling had been slower. The specific rate of chemical reaction of chemisorbed O₂ with H was lower on Pt wires than on Pt beads, due to differences of crystallite size and drawing defects, but results on both were variable.

Oxygen Overvoltage on Bright Rhodium

J. P. HOARE, *Electrochim. Acta*, 1968, 13, (3), 417-428

Anodic evolution and cathodic reduction of O₂ on bright Rh electrodes were studied galvanostatically and by potentiometry. O₂ is absorbed above 1400°C to give Rh₂O₃, which produces a higher overvoltage than do Pt electrodes. Rh has a poor surface for decomposition of H₂O₂.

Oxygen Overvoltage on Bright Iridium

J. P. HOARE, *J. electroanal. Chem. interfac. Electrochem.*, 1968, 18, (3), 251-259

Galvanostatic and potentiostatic studies of bright Ir bead electrodes in O₂-saturated H₂SO₄ indicated that the O₂-reduction mechanisms on Ir and Pt cathodes are similar. Although IrO₂ is formed, the O₂-evolution mechanism is that of H₂O-discharge. The adsorbed O₂ layers on Ir are believed to be good electronic conductors. Adsorbed O₂ on Ir cathodes hinders reduction of O₂ to H₂O₂ but promotes reduction of H₂O₂ to H₂. Intermediate H₂O₂, which is stable, forms during the O₂-reduction process.

Electrooxidation of Methanol on Pt+Ru and Ru Electrodes at Various Temperatures

V. S. ENTINA and O. A. PETRII, *Elektrokhimiya*, 1968, 4, (6), 678-681

Stationary polarisation curves were obtained for the electrooxidation of CH₃OH on Ru, platinised Pt, 10 and 25% Pt-Ru, and 10, 25 and 40% Ru-Pt electrodes in 2N H₂SO₄+2M CH₃OH at various fixed temperatures. Products were analysed for HCHO, HCOOH and CO₂.

ELECTRODEPOSITION AND SURFACE COATINGS

High-speed Hard Chromium Plating. Part I. Etch-free Plating

R. D. BEDI, *Plating*, 1968, 55, (3), 238-246

Etching frequently occurs while hard Cr plating steel or steel alloys from fluoride-catalysed baths at unprotected low current density areas, thus contaminating the bath. It is due to homogeneous electrochemical corrosion, depending on the passivating properties of the electrolyte, the degree of cathodic activation of the passive film,

and the stability of the complex formed between passive film cations and solution anions. An immersion deposit of Pt or another Pt metal inhibits cathodic reduction of the passive film, so protecting recessed areas from etching, and increasing the range of hard Cr plating by giving high-speed, smoother harder deposits.

Part II. A New Stop-off Procedure

Ibid., 246-249

The surface to be stopped off is coated with an immersion deposit of a low H₂ overvoltage noble metal such as Pt or Pd. This procedure prevents plating where not desired and yet gives uniform hard Cr deposits with smooth, rounded edges, which can be put in service with no further finishing.

Platinised Titanium Anodes Permit Plating of "Unplatable" Parts

E. JOLLIFF, *Plating*, 1968, 55, (5), 508

Auxiliary anodes of Pt/Ti enabled awkward angles of wheel covers to be Ni- and Cr-plated. Their life is more than 100 times that of a similar design in Ni.

Electrodeposition of Ductile Palladium

J. M. STEVENS, *Trans. Inst. Metal Finish.*, 1968, 46, (1), 26-31

An electrolyte based on [Pd(NH₃)₄]Br₂ can be used under a range of conditions to provide Pd coatings with up to 20% ductility. Under the preferred conditions for vat plating the cathode efficiency is >90% and the rate of deposition is 1μ/min. Regeneration of the electrolyte is simple and incorporates purification. Impurity effects and wear characteristics are studied.

The Corrosion Resistance of Electroplated Rhodium Deposits on Nickel

K.-E. BECKER, H. SCHLEGEL and A. KUBAT, *Metall-oberfläche*, 1968, 22, (5), 145-153

Measurements of corrosion current density and of current density-potential curves for Ni and Rh show that contact corrosion in the pores of electroplated Rh deposits on Ni is determined by reactions on the Rh. Corrosion is accelerated at low pH but is still detectable at pH9. This indicates that the standard Rh electrodeposit on Ni may not stand up to such severe conditions as are met with in the food industry.

LABORATORY APPARATUS AND TECHNIQUE

Initial Field Evaporation of Platinum Surfaces in the Field Ion Microscope

C. A. SPEICHER and W. T. PIMBLEY, *Surface Sci.*, 1968, 10, (3), 470-473

Two methods of obtaining atomically smooth Pt tip surfaces are described. Rough surfaces resulting from etching may be treated by field evapora-

tion at 78°K or by field evaporation at 10°K while stress cycling the tip.

Versatile and Rapid Trace Nitrogen Analysis of Petroleum Materials by Microcoulometry

D. R. RHODES, J. R. HOPKINS and J. C. GUFFY, *Abstr. Papers, 155th Mtg, Am. Chem. Soc.*, 1968, (Mar.), R37

10 to 20 times the sensitivity of the Dohrmann N₂ analyser was obtained by modifications, including the use of Pd instead of Pt pH-sensing electrodes. The range was extended to 0.1 ± 0.02 ppm, 600°C with ±5% reproducibility.

Production of Ruthenium Targets [Foil] for Nuclear Research and a Study of Ruthenium, Rhodium, and Palladium Deposits

C. N. MEDYANIK and L. I. KADANER, *Ukr. fiz. Zh.*, 1968, 13, (1), 127-129

Electrolytic production of ≥3μ Ru foils is described. The dependence of the internal stress of Ru, Rh and Pd foils on electrolyte concentration and current density was studied.

BRAZING

Joining Dissimilar Metals by Gas Tungsten-Arc Braze-Welding

D. E. SOLOMON, *Welding J.*, 1968, 47, (3), 181-191
Brazing alloys for the tungsten arc technique of joining dissimilar metals were evaluated by tests on welding an annular disc around a pipe. The eutectic alloys Pd-Au, m.p. 1190°C and Pd-Co, m.p. 1220°C were used successfully in a number of cases, e.g. Pd-Au: discs of carbon steel to stainless steel pipe, Ni-Fe-Co alloy to stainless steel, stainless steel to carbon steel, Mo, Ni-Fe-Co, and W; Pd-Co: discs of carbon steel to carbon steel and Ni-Fe-Co pipes, Ni-Fe-Co to carbon steel and Ni-Fe-Co, stainless steel to Mo, stainless steel and W.

HETEROGENEOUS CATALYSTS

Atomisation of Oxygen on Platinum

J. FUSY, B. WEBER, A. CASSUTO and P. LE GOFF, *J. Chim. phys.*, 1968, 65, (6), 1192-1193

Studies of O₂ atomisation between 10⁻⁹ and 10⁻⁴ torr on Pt at 1370-1640°K show that the reaction is first order at low pressures with the probability of atomisation of a molecule during one collision at 0.12 ± 0.015. As the pressure rises the reaction becomes half order with frequency factor ≈ 10²⁵.

Hydroisomerisation of *n*-Paraffins over Fluorided Platinum on Alumina Catalysts

B. A. ORKIN, *Abstr. Papers, 155th Mtg, Am. Chem. Soc.*, 1968, (Mar.), R57

Selectivity of Pt/Al₂O₃ catalyst with 5% fluoride for isoparaffin formation from C₁₁-C₁₄

n-paraffins was greater than with 10% fluoride or no fluoride at 300 psig H₂. Effects of PH₃, type of Al₂O₃, S compounds, N compounds, and aromatic compounds were studied. Reduced PH₂ from 1000 to 50 psig increased isomerisation from 37 to 88%.

Dehydrocyclisation of 2-*n*-Butylnaphthalene on Alumina-Platinum Catalyst

L. A. ERIVANSKAYA, G. A. SHEVTSOVA, N. L. KOMISSAROVA and A. F. PLATE, *Neftekhimiya*, 1968, 8, (2), 192-197

Studies of the effects of temperature, volume rate, test duration and concentration of Pt in Pt/Al₂O₃ catalyst during C₆-dehydrocyclisation of 2-*n*-butylnaphthalene showed that the phenanthrene:anthracene product ratio depends on the reaction temperature. The reaction is accompanied by cracking, by isomerisation and by dehydrogenation of alkyl groups. The chief mechanism leading to the predominant formation of phenanthrene at 400-510°C is the intermediate formation of 2-(buten-1-yl)naphthalene.

The Surface Transport of Various Gases on a Platinum-Alumina Catalyst

D. GELBIN, *Chem. engng Sci.*, 1968, 23, (1), 41-49

Permeation measurements of the surface transport rates of C₃H₈, *n*-C₄H₁₀, *n*-C₆H₁₄ and Kr in a Pt/Al₂O₃ pellet showed that surface transport of hydrocarbons is related to the dissociative adsorption of the migrating gas. Surface mobility decreases with increasing molecular length. Activation energies, which increase from C₃H₈ to C₆H₁₂, are rather larger than the corresponding heats of adsorption. The behaviour of Kr is different and a mechanism for it is proposed.

On the Role of C₅-Dehydrocyclisation in the Aromatisation of *n*-Paraffins in the Presence of Platinum on Alumina Catalysts

YU. V. FOMICHEV, I. V. GOSTUNSKAYA and B. A. KAZANSKII, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, (5), 1112-1117

Microreactor studies of the aromatisation of *n*-C₆H₁₄ and of *n*-C₇H₁₆ over 0.6% Pt/Al₂O₃ at 450-540°C, 1 atm H₂ indicated a C₅-dehydrocyclisation mechanism involving alkylcyclopentane intermediates, the hydrogenation of which is accompanied by dehydrogenation with some isomerisation to the aromatic compound.

C₅- and C₆-Dehydrocyclisation of *n*-Paraffins in the Presence of a Platinum on Alumina Catalyst

Ibid., *Dokl. Akad. Nauk SSSR*, 1968, 180, (2), 383-385

Tests at 450-540°C over Pt/γ-Al₂O₃ showed that aromatisation of *n*-hexane and *n*-heptane can proceed via C₆-dehydrocyclisation with subsequent dehydrogenation in which all the cyclohexane and methylcyclohexane are converted to

the respective aromatic compounds, as well as by C_6 -dehydrocyclisation with subsequent dehydroisomerisation.

Competitive Hydrogenations on Platinum

A. S. HUSSEY, R. H. BAKER and G. W. KEULKS, *J. Catalysis*, 1968, **10**, (3), 258-265

Results of competitive hydrogenations of 14 pair combinations of 10 cycloalkenes from solution in cycloalkane solvents on 0.52% Pt/Al₂O₃ at 25°C, 1 atm agreed with both equilibrium and rate-controlled chemisorption models, the latter being preferred. Stereochemical and product ratio problems are discussed and factors affecting chemisorption of cycloalkenes on Pt surfaces are considered.

Catalytic Dehydrogenation of Cyclohexane: a Transport-controlled Model

R. R. GRAHAM, F. C. VIDAURRI and A. J. GULLY, *AIChE J.*, 1968, **14**, (3), 473-479

Kinetics of the dehydrogenation of cyclohexane with excess H₂ over Pt/Al₂O₃ at 400-500°C, 21-41 atm and at Reynold's numbers 20-65 indicate a rapid overall reaction influenced by external concentration, temperature gradient and reverse reaction.

The State of Platinum in Promoted Platinum Catalysts and the Nature of the Activity of Metallic Catalysts in the Dehydrocyclisation of Paraffin Hydrocarbons

N. R. BURSIA, S. B. KOGAN and Z. A. DAVYDOVA, *Kinet. Kataliz*, 1968, **9**, (3), 661-667

Additions of Li, Na and Cs to Pt/Al₂O₃ and Pt/SiO₂ promote the catalysts by stabilising the active centres containing Pt ions both in air and H₂. A suggested model contains complex active centres incorporating Pt⁴⁺ ions. Its action during dehydrocyclisation of paraffins is discussed.

Hydrogenation of Ethylene on Platinised Silica Gel

I. NICOLAU, *Rev. roumaine Chim.*, 1968, **13**, (1), 71-75

The rate of hydrogenation of C₂H₄ on 0.1% Pt/SiO₂ at 30-90°C, 1 atm is dependent on H₂ concentration but is independent of C₂H₄ concentration. An apparent activation energy of 4.2 kcal/mole is reported.

Kinetics of Isomerisation of Cyclohexane on Pt Zeolite Catalyst in a Gradientless System under Pressure of Hydrogen

U. M. KURKCHI, V. I. GARANIN and KH. M. MINACHEV, *Kinet. Kataliz*, 1968, **9**, (3), 571-576

The rate of isomerisation of C₆H₁₂ on a Pt zeolite catalyst was studied in relation to the size of the catalyst granules, the rate of circulation of the gas mixture, and the temperature and partial pressure of C₆H₁₂ and H₂. At 288-318°C, as

$P_{C_6H_{12}}$ increases, the order of the reaction with respect to C₆H₁₂ changed from first to zero order. Increasing P_{H_2} retards the reaction. Apparent activation energy was 32 kcal/mole.

Dehydrocyclisation of *n*-Hexane on Palladised Tape

V. M. GRYAZNOV, K. MALDONADO, E. KHAZHZHAR and D.-K. OLUOCH OKEIO, *Kinet. Kataliz*, 1968, **9**, (2), 435-437

Mass-spectrometric studies of *n*-C₆H₁₄ vapour conversion on palladised tape at $\approx 10^{-6}$ mm Hg indicated slight dehydrocyclisation at 20°C, intensifying with increased temperature. At 200°C there is almost complete conversion into C₈H₆.

Palladium Areas in Supported Catalysts. Determination of Palladium Surface Areas in Supported Catalysts by Means of Hydrogen Chemisorption

P. C. ABEN, *J. Catalysis*, 1968, **10**, (3), 224-229

Hydrogen chemisorption proved suitable for determination of Pd surface areas in Pd/Al₂O₃ and Pd/SiO₂ when the chemisorption conditions were chosen carefully. It was also suitable for particle size determination in cases where interference by the support caused other methods to fail. Combined surface area and H₂ chemisorption measurements on Pd black showed that 1 H atom was adsorbed on each exposed Pd atom, as confirmed by electron microscopy.

Heterogeneous Catalysis by Metal Chelates - Isomerisation of Butenes

M. MISONO, Y. SAITO and Y. YONEDA, *Ibid.*, (2), 200-202

[Pd(acac)₂] mounted on silica gel is an efficient catalyst for isomerisation of C₄H₈. Rate constant at 61.5°C for *cis*-2-C₄H₈ isomerisation was $4.3 \times 10^{-8} \text{g}^{-1} \text{min}^{-1}$, far higher than with Ni or Pt as the central metal ion and also far higher than with dmg as chelate.

On the Mechanism of 1-Butene Isomerisation on Supported Palladium

S. CARRA and V. RAGAINI, *Ibid.*, (3), 230-237

Studies of double-bond migration of 1-butene on 0.484% Pd/Al₂O₃ in the absence of H₂ indicated stereoselectivity towards *cis*-2-butene. Kinetic studies by both integral and differential reactor techniques at 160-240°C suggested two mechanisms for isomerisation: the former with two atomic centres and stereospecific towards *cis* isomer; the latter tending towards equilibrium of *trans*- and *cis*-2-butene.

The Hydroisomerisation of *n*-Butenes. I. The Reaction of 1-Butene over Alumina- and Silica-supported Rhodium Catalysts

J. I. MACNAB and G. WEBB, *J. Catalysis*, 1968, **10**, (1), 19-26

Studies of the reaction of 1-C₄H₈ with H₂ over

5%Rh/Al₂O₃ or 5%Rh/SiO₂ at -20 to +80°C gave the kinetics and apparent activation energies for hydrogenation and isomerisation. The initial *cis* : *trans* ratio in 2-C₄H₈ is greater than the thermodynamic equilibrium value but it decreases with increasing temperature. The support has little effect. A suggested isomerisation mechanism is via a 1-methyl-π-allyl intermediate.

Catalytic Activity of Rhodium and Ruthenium in the Hydrogenolysis of Ethane

G. K. STAROSTENKO, T. A. SLOVOKHOTOVA, A. A. BALANDIN and K. A. EL KHATTIB, *Vest. Moskov. Univ., Ser. II, Khim.*, 1968, (2), 52-55

Activities of Rh/SiO₂ for hydrogenolysis of C₂H₆ were measured at 155-190°C and activation energies were calculated for various H₂/C₂H₆ mixtures.

Modification of Raney Catalysts by Addition of Transition Metals. VIII. Electrooxidation of Hydrogen and Catalytic Hydrogenation on Raney Nickel-Ruthenium Alloys

A. B. FASMAN, A. ISABEKOV and B. K. ALMASHEV, *Zh. fiz. Khim.*, 1968, 42, (4), 903-908

Studies of the effect of the composition of Raney Ni-Ru catalysts on the kinetics of hydrogenations of potassium maleate, *o*-nitrophenol, and α -naphthoquinone, and of anodic oxidations of H₂ and alkaline electrolytes showed that new phases were formed in the initial Ni-Ru-Al alloys and that the Ru addition leads to growth of the crystal lattice parameters of Raney Ni.

Structures of Olefins and their Simultaneous Hydrogenation on Ru Catalyst

L.KH. FREIDLIN, E. F. LITVIN and S. K. TILYAEV, *Neftekhimiya*, 1968, 8, (2), 155-161

Studies with 5% Ru/C show that it possesses high selectivity during simultaneous hydrogenation of olefins with various structures. The H₂ is added in positions depending on the alkyl groups to be substituted, the structures and the position of the double bonds.

Stereoisomeric Conversion of Individual *cis*- and *trans*-3-Methylpentene-2 in the Presence of Group VIII Metals

M. ABUBAKER, Z. S. KHRUSTOVA, I. V. GOSTUNSKAYA and B. A. KAZANSKII, *Vest. Moskov. Univ., Ser. II, Khim.*, 1968, (2), 148-152

The activity and selectivity of C-supported catalysts for *cis*-, *trans*-isomerisation of *cis*- and *trans*-3-methylpentene-2 are in the order Pd > Rh > Ru > Os > Ir > Pt.

Catalytic Hydrogenation of Methylacetylene over Group VIII Metals

R. S. MANN and S. C. NAIK, *Indian J. Technol.*, 1968, 6, (2), 57-58

Studies of the reaction between methylacetylene

and H₂ over pumice-supported catalysts in a static system showed that the initial rates of reaction depended only on the initial p_{H₂}, except for Pt/pumice where the pressure of methylacetylene was also important. Apparent activation energies for pumice-supported Fe, Co, Ni, Rh, Pd, Ir, and Pt were 14, 13.3, 16.8, 8.6, 10.3, 9.2, and 12.9 kcal/mole respectively and the activities were in order Pt > Pd > Ni > Ir > Rh > Co > Fe > Ru, Os.

Consecutive Hydrogenation of Double Bonds of Cycloheptatriene over Palladium, Platinum and Rhodium Catalysts

B. D. POLKOVNIKOV, O. M. NEFEDOV, E. P. MIKOS and N. N. NOVITSKAYA, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, (6), 1240-1245

Hydrogenation of conjugated double bonds of cycloheptatriene-1,3,5 proceeded consecutively on borided Pd catalyst, with less selectivity on borided Rh, and with no selectivity on borided Pt. Consecutive hydrogenation of unsaturated bonds of cycloheptadiene-1,3 also occurred on borided Pd catalyst.

HOMOGENEOUS CATALYSIS

Organic Syntheses by Means of Noble Metal Compounds. XXXVI. Reactions of Carbanions with Cyclooctadienepalladium and -platinum Halide Complexes and Tetraphenylcyclobutadienepalladium Chloride Complex

H. TAKAHASHI and J. TSUJI, *J. Am. Chem. Soc.*, 1968, 90, (9), 2387-2392

Studies of C-C bonding by the reaction of diene-palladium and -platinum halide complexes with carbanions showed that malonate and acetoacetate react smoothly at room temperature with cyclooctadienepalladium and -platinum complexes to give new complexes with σ and π bonds with metals. Reaction of these with methylsulphinyl carbanion produced bicyclo[6.1.0]-nonene derivatives. Malonate attacked the complexes to give 2,6-disubstituted bicyclo[3.3.0]-octane rings.

Palladium-catalysed Reactions of Unsaturated Compounds in Non-aqueous Solvents

C. F. KOHLL and R. VAN HELDEN, *Rec. Trav. chim. Pays-bas*, 1968, 87, (5), 481-500

The formation of vinyl acetate is first order in catalyst and in acetate concentration. Acetate is thought to displace chloride via a π -olefin-Pd(II) complex. Effects of chloride ion, solvent and various transition metal salts are discussed.

Polymerisation of Allene with a Soluble Palladium Catalyst

G. D. SHIER, *Abstr. Papers, 155th Mtg, Am. Chem. Soc.*, 1968, (Mar.), T25

1 : 1 mole ratio of Pd(NO₃)₂ : triarylphosphine in

glacial CH_3COOH catalysed head-to-head polymerisation of allene. Chemical and spectral tests indicated that the polymer contained repeating conjugated diene units.

The Dimerisation of Butadiene by Palladium Complex Catalysts

S. TAKAHASHI, T. SHIBANO and N. HAGIHARA, *Bull. Chem. Soc. Japan*, 1968, **41**, (2), 454-460

$\text{Pd}(\text{Ph}_3\text{P})_2(\text{C}_4\text{H}_2\text{O}_3)$ catalysed linear dimerisation of butadiene to form 1,3,7-octatriene in aprotic solvents and 1-alkoxy-2,7-octadiene and/or 1,3,7-octatriene in alcohols, depending on the nature of the solvent. Dimerisation in $\text{C}_6\text{H}_5\text{OH}$, CH_3COOH or amines produced solvent-dimer adducts.

Carbonylation of Olefins under Mild Temperature Conditions in the Presence of Palladium Complexes

K. BITTLER, N. VON KUTEPOW, D. NEUBAUER and H. REIS, *Angew. Chem. internat. Ed. En.*, 1968, **7**, (5), 329-335

L_mPdX_n complexes, (where L is a ligand such as phosphine, nitrile, amine, or olefin; where X is acid; where $m+n=3$ or 4) are efficient catalysts for both ester and acid production below 100°C . Polyunsaturated olefins were carbonylated selectively.

Transition Metal Catalysis Exemplified by Some Rhodium-promoted Reactions of Olefins

R. CRAMER, *Accounts chem. Res.*, 1968, **1**, (6), 186-191

The Rh ion catalysed syntheses $\text{C}_2\text{H}_4 \rightarrow \text{C}_4\text{H}_8$, $\text{C}_3\text{H}_4 + \text{C}_4\text{H}_8 \rightarrow 1,4\text{-C}_6\text{H}_{10}$, $1\text{-C}_4\text{H}_8 \rightarrow$ isomeric linear C_4H_8 , and the effect of thermodynamic or kinetic control on the products are discussed. Coordination of Rh with the reactant molecules causes orientation and reduces energy barriers to the reaction.

Dimerisation of Acrylonitrile by Ruthenium Chloride

A. MISONO, Y. UCHIDA, M. HIDAI, H. SHINOHARA and Y. WATANABE, *Bull. Chem. Soc. Japan*, 1968, **41**, (2), 396-401

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ under H_2 atmosphere catalysed the formation of *cis*- and *trans*-1,4-dicyano-1-butene by end-to-end coupling of acrylonitrile. Effects of temperature, p_{H_2} and addition of various salts were considered.

Patterns of Organometallic Reactions Related to Homogeneous Catalysis

J. P. COLLMAN, *Accounts chem. Res.*, 1968, **1**, (5), 136-143

A review of reaction patterns involved in homogeneous catalysis by transition metal complexes, including those of Ru, Ir, Rh, and Pt.

FUEL CELLS

Activation of Nickel Fuel Electrodes with Platinum Catalysts

D. M. DRAZIC, A. R. DESPIC and N. D. KOSELJ, *Electrochem. Technol.*, 1968, **6**, (3-4), 98-100

The activity of porous Ni fuel cell electrodes, activated by chemical plating with a solution of H_2PtCl_6 , $\text{Pb}(\text{CH}_3\text{COO})_2$ and NaCl, depended on the concentrations of Pt and of the neutral salt, on the flow rate of the solution through the electrode, and on the amount of Pt deposited. With 1 mg Pt/cm^2 , 100 mA/cm^2 the best H_2 electrodes had overpotential 65 mV . It appears from Pt distribution measurements that, whatever the overall electrode thickness, the active layer is $\approx 0.3 \text{ mm}$.

Electrocatalysts for Hydrogen/Carbon Monoxide Fuel Cell Anodes. III. The Behaviour of Supported Binary Noble Metals

D. W. MCKEE and A. J. SCARPELLINO, *Electrochem. Technol.*, 1968, **6**, (3-4), 101-105

Practical CO-tolerant anode electrocatalysts were prepared from Pt and Ru on inert substrates such as B_4C . Catalyst activity depends strongly on the preparation and composition of the metal phase. Using reformer gas as fuel with up to 10% CO at 85°C , satisfactory results were obtained with as little as 3 mg/cm^2 metal in 5N H_2SO_4 . The high performance of Rh-Pt or of Ir-Pt blacks is largely lost when these are supported, perhaps because the mechanism of anodic oxidation is different.

CATHODIC PROTECTION

Internal Cathodic Protection of Salt Water Pipelines with the Aid of Platinised Titanium Anodes

J. W. KÜHN VON BURGSDORFF, *Werkstoffe Korrosion*, 1968, **19**, (6), 473-478

Continuous partly platinised Ti wire anodes were used to protect long pipelines. A current density of $\approx 150 \text{ mA/m}^2$ was required but could be reduced considerably by coating the pipeline with a passive protective coating.

CHEMICAL TECHNOLOGY

Electrolysed Seawater Plays Big Role in Sewage Disposal Method

R. EALES, *Chem. Engng*, 1968, **75**, (13, June 17), 172-174

Vertical electrolytic cells for the purification of sewage by electrolysis with sea water have platinised Ti anodes and plain steel cathodes. The cells operate at 6 V dc. CJB have constructed one plant on Guernsey and another is under construction at Capenhurst in Cheshire.

TEMPERATURE MEASUREMENT

A Platinum Resistance Thermometer Calibration between 2 and 273.15°K

CHAN YET-CHONG and A. M. FORREST, *J. sci. Instrum., J. Phys. E.*, 1968, 1, (8), 839-842

Selected Pt resistance thermometers were calibrated approximately at 2-273.15°K using only the b.p. of He, the ice point, and temperatures at 2-4.2°K from He vapour pressure thermometer measurements. Interpolation for 4.2-273.15°K used a table of Z functions and for 2-16°K used a polynomial equation in T against R.

Comparison between Gas Thermometer, Acoustic, and Platinum Resistance Temperature Scales between 2 and 20°K

J. S. ROGERS, R. J. TAINSH, M. S. ANDERSON and C. A. SWENSON, *Metrologia*, 1968, 4, (2), 47-59

The NBS Pt resistance thermometer scale of 1955 at 2-16°K was used in determining the resistance versus temperature relation of Ge thermometers to ± 3 mdeg against a constant volume gas thermometer.

Temperature Measurements with Metal Ribbon High-temperature X-ray Furnaces

W. OSTERTAG and G. R. FISCHER, *Rev. sci. Instrum.*, 1968, 39, (6), 888-889

Thin Pt and Rh-Pt thermocouple wires were welded to the Pt ribbon of a high-temperature X-ray diffractometer attachment. The temperature profile of the specimen stage, determined as functions of temperature, heater position and heater shape, showed improved accuracy of temperature measurement.

Protective Devices for Thermocouples Used in Glass-melting Furnaces

V. M. OBUKHOV, *Steklo Keram.*, 1968, 25, (4), 12-14
Four types of protective casings for 6%Rh-Pt: 30% Rh-Pt thermocouples are described. Pro-

tection against flame above 1450°C is given by a three-layer cover of corundum, ZrO₂ and corundum. Protection against molten glass up to 1200°C may be afforded by corundum, or at temperatures $\pm 1200^\circ\text{C}$ by a three-layer cover of corundum, steel and corundum. Protection against molten glass above 1250°C consists of corundum sheathed with Pt. In each case the thermocouple itself is supported in a twin-bore corundum tube.

Determination of Temperature According to the Thickness of the Clinker Deposit

V. V. PUZANKOV, YU. P. SHCHUKIN and M. L. VISHNEVETSKII, *Stal'*, 1968, (4), 304-305

To eliminate errors of temperature measurement with Rh-Pt thermocouples due to clinker build-up on the sheath a probe has been developed at the Karaganda works which extends telescopically so that the hot junction projects beyond the point of clinker build-up.

Calibration and Stability of Miniature Resistance Thermometers

G. W. LINDBERG and W. V. JOHNSTON, *Abstr. Papers, 155th Mtg, Am. Chem. Soc.*, 1968, (Mar.), V9

Miniature Pt resistance thermometers 0.5 in. long, 0.156 in. diameter, weighing 1 g were calibrated at -182 to +100°C by comparison with capsule-type Pt resistance thermometers and at -262 to -182°C by interpolation data. The resistance at 0°C was reproducible to 10 ppm for six months.

The Accuracies of Calibration and Use of I.P.T.S. Thermocouples

T. P. JONES, *Metrologia*, 1968, 4, (2), 80-83

Uncertainty expressed as 99% confidence limits from precise calibration of Pt : 10% Rh-Pt thermocouples at 630.5-1063°C is $\approx \pm 1.0 \mu\text{V}$, based on five replicates at each of the three primary calibration points and subsequent accuracy of a calibrated thermocouple with systematic errors eliminated is $\pm 0.2^\circ\text{C}$.

NEW PATENTS

METALS AND ALLOYS

An Improved Alloy

JOHNSON, MATTHEY & CO. LTD
British Patent 1,112,766

A new alloy, especially suitable for spinnerette production, consists of 50-80% Au, 0.04-0.5% Ir, and the remainder Pt with the usual impurities.

Producing Iron-Rhodium Base Alloys Having Improved Magnetic Transition Properties

GENERAL ELECTRIC CO. (NEW YORK)
British Patent 1,117,727

An alloy with a CsCl-type ordered crystal structure and an antiferro-magnetic-ferromagnetic transition is obtained from an Fe-Rh alloy, optionally containing small amounts of Pd or Pt,