

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

New Applications of Platinum Materials in Chemistry and Glass Industry

G. REINACHER and H. ROTERS, *Metall.*, 1969, **23**, (6), 543-548

Uses of the Pt metals in chemical and electrochemical technology are tabulated. Suitable crucible materials for crystal pulling are listed. A variety of uses in the glass industry are described also. (39 references.)

On the Tensile Deformation of Platinum at Elevated Temperatures

A. R. CAUSEY, *J. Metals*, 1969, **21**, (3), 101A

True stress-true strain relationships were obtained at 750-1450°C for Pt sheet. Temperature dependence was determined for the proportional limit, 0.002 yield stress, flow stress, maximum stress, and strain to the maximum stress and to failure. The strain rate-initial flow stress relation was determined. Stress exponent and activation energy agreed well with data for other polycrystalline f.c.c. pure metals and with deformation theory.

Adhesion between Precious Metals

H. C. ANGUS, *Br. J. appl. Phys., J. Phys. D*, 1969, **2**, (6), 831-837

Adhesion between Au/Au, Pt/Pt and Au/Pt group metal contacts over the load range 1-10 mg is interpreted on the basis of simultaneous measurements of contact resistances. Adhesion between Au/Au contacts is higher than between Au/Pt group metal contacts. Adhesion of Au/Au increased above 90°C but Pt/Pt contacts required > 550°C before adhesion was accentuated.

The Resistivity of Fine Platinum Wires

R. H. FREEMAN, F. J. BLATT and J. BASS, *Phys. kondens. Mater.*, 1969, **9**, (3), 271-282

Resistivity of 16-0.3 mil Pt wires at 1.2-4.2 K was measured and the temperature dependent portion of the resistivity was predominant. The coefficient increased from 12×10^{-12} ohm. cm/K² for the thickest wire to 18×10^{-2} ohm. cm/K² for the thinnest.

Contribution to the Study of the Creep of Platinum and of its Alloys

R. LACROIX and P. MAGNIER, *Mém. sci. Rev. Mét.*, 1969, **66**, (2), 167-174

The creep of Pt and Rh-Pt and Ir-Pt alloys was studied, together with the effect of O₂ at high temperatures. Unless care is taken in use, Pt apparatus may become defective. (29 references.)

An X-ray Diffraction Analysis of Uniaxially Deformed Cu₃Pt

R. A. BUCHANAN, J. J. WERT and S. G. CUPSCHALK, *Trans. Metall. Soc. AIME*, 1969, **245**, (1), 11-18

X-ray studies of the uniaxial deformation of thermally ordered and disordered polycrystalline Cu₃Pt showed that after correction for extinction the long range order in the ordered alloy decreased at a slow constant rate with plastic strain and that the antiphase domain probability increased at a constant rate to 17.5% strain. Stacking fault energy is lower in ordered than in disordered Cu₃Pt. Ordered Cu₃Pt has a slightly lower yield point but a much higher work-hardening rate than disordered Cu₃Pt.

The Determination of the Solidus in the Co-Pt System by Solid Electrolyte Techniques

R. J. KING and G. R. FITTERER, *J. Metals*, 1969, **21**, (3), 129A

Solidus temperatures, determined from the integral free energy of mixing of solid disordered Co-Pt alloys by special solid electrolyte techniques with good reproducibility, were combined with liquidus temperature data to construct a phase diagram, which has a minimum at 0.67 at.% Co, 1460°C. Solidus and liquidus compositions were computed from free energy equations. Activities were measured at 800, 900, and 1100°C. Heat of mixing was determined quasichemically. Solid alloys have Ω of -9,188 with maximum heat of mixing -2,297 cal/g.atom. Liquid alloys have suggested Ω of -10,488.

Magnetic Anisotropy Induced in Pt-Co Alloy by Cold Rolling

S. SHIMIZU and E. HASHIMOTO, *J. Japan Inst. Metals*, 1969, **33**, (6), 711-715

Magnetic properties of 50 at.% Co-Pt specimens, disordered by H₂O quenching from 1000°C, cold rolled 15-80% reduction in thickness and aged at 300-750°C, were measured in the directions of rolling, width and thickness. Anisotropy is induced by the cold rolling but it can be eliminated by disordering, e.g. H₂O quenching from 1000°C, when the alloys become isotropic again.

A Thermodynamic Study of the γ Phase Solid Solutions Formed between Palladium, Platinum and Iron

C. B. ALCOCK and A. KUBIK, *Acta Metall.*, 1969, **17**, (4), 437-442

Thermodynamic properties of solid solutions of Pd and Pt with Fe are investigated between 700

and 1000°C using O₂ concentration cells with ThO₂-Y₂O₃ and ZrO₂-CaO solid electrolytes. Results are given for activities, entropies and heats of mixing. The Pd-Pt solid system conforms with Raoult's Law.

Investigation of the Fine Structure of Fe-Pt Alloys

E. N. VLASOVA and E. Z. VINTAIKIN, *Fiz. Metal. Metalloved.*, 1969, 27, (4), 631-635

The dispersion of X-rays in 32 at.% Pt-Fe was studied before and after annealing at 600, 700, 750, and 780°C along various lines of symmetry. The change of volume during ordering was characteristic of the Fe-Pt superstructure.

Magnetic Behaviour of the Pt-Fe System near Pt₃Fe

D. PALAITH, C. W. KIMBALL, R. S. PRESTON and J. CRANGLE, *Phys. Rev.*, 1969, 178, (2), 795-799

Mössbauer studies of complex magnetic behaviour of alloys near Pt₃Fe were made and temperature dependence of hyperfine field was measured for 24-34.5% Fe-Pt. Two magnetic phases exist in 26.7% Fe-Pt at low temperature. The transition occurring at the lower transition temperature is an order-order transition. All Fe moments are aligned.

Heterometallic Phenomena in the Platinum-Mercury System

M. BARLOW and J. P. PLANTING, *Z. Metallkunde*, 1969, 60, (4), 292-297

Kinetic data obtained at 25-300°C during chemical attack by Hg on Pt and Pt alloys show that the activation energy is 8000 cal/mole for surface amalgamation to form mostly PtHg₄. Sn, Cu, and Zn additions inhibit the attack by forming various intermetallic compounds at the Pt-Hg interface but Ag, Au and Pd are ineffective. The intermetallic compounds act by forming diffusion barriers. The suggested mechanism is analogous to passivation in aqueous solutions.

The Variation of Lattice Parameter with Carbon Concentration in Palladium

R. H. SILLER and R. B. MCLELLAN, *J. Metals*, 1969, 21, (3), 60A

Lattice parameters of Pd were measured as function of interstitial C concentration up to ~0.6 wt% C and by using simple elastic considerations the equilibrium thermodynamic parameters were deduced for the Pd-C system and were compared with those for Ni-C, Co-C and austenite.

On the Thermal Expansion Coefficient and the Temperature Coefficient of Young's Modulus of Cobalt and Palladium Alloys

H. MASUMOTO and S. SAWAYA, *J. Japan Inst. Metals*, 1969, 33, (6), 685-687

Studies at 0-990°C showed that the mean linear

thermal expansion coefficient (0-40°C) is greatest in the α -phase 90% Pd-Co with ferromagnetic Curie point of 150°C and mean temperature coefficient of Young's modulus (0-40°C) positive at 90.5-95% Pd with largest positive value $+59.78 \times 10^{-5}$ in 94% Pd-Co.

Influence of Size Difference and Band Structure on the Thermodynamic Properties of Palladium Alloys

H. A. BRODOWSKY and H.-J. SCHALLER, *J. Metals*, 1969, 21, (3), 130A

Activity measurements on solid solutions of Cd, In and Sn in Pd show marked negative deviations from Raoult's Law. Partial molar excess free energies of dilute solutes are roughly \propto (valency of solute atoms)². These effects are interpreted by the "semi-rigid band" hypothesis. Size effects are less prominent than in Pd-Ag and Pd-H because of large electronic excess functions.

Thermodynamics of Nonstoichiometric Interstitial Alloys. I. Boron in Palladium.

H. A. BRODOWSKY and H.-J. SCHALLER, *Trans. Metall. Soc. AIME*, 1969, 245, (5), 1015-1020

Deviations from ideal behaviour, when determining activity coefficients of B in Pd at concentrations up to PdB_{0.23} by reducing B₂O₃ at 870-1050°C in a controlled H₂-H₂O stream and measuring the gain in weight, closely resemble those of Pd-H and suggest that solute atoms occupy octahedral interstitial positions, that they donate their valence electrons to the 4d and 5s bands of Pd, raising its Fermi energy, and that lattice strain energy is lower for two nearest-neighbour interstitial particles than for two farther separate ones.

Tetrapalladium Sulphide and Tetrapalladium Selenide. Heat Capacities and Thermodynamic Properties from 5° to 350°K

F. GRØNVOLD, E. F. WESTRUM and R. RADEBAUGH, *J. chem. engng Data*, 1969, 14, (2), 205-207

Heat capacities of Pd₄S and Pd₄Se, determined by adiabatic calorimetry, are sigmoidal without transitions or anomalies. Values of heat capacity, entropy and Gibbs energy functions at 298.15K are 27.48, 43.18, and 23.16 cal. mole⁻¹K⁻¹ for Pd₄S and 32.75, 47.83 and 24.84 cal. mole⁻¹K⁻¹ for Pd₄Se. Heat capacity of Pd₄Se exceeds the classical limit near 200K due to 4d electron excitations in Pd.

Close-packed Ordered AB₃ Structures in Binary Transition Metal Alloys

A. K. SINHA, *Trans. metall. Soc. AIME*, 1969, 245, (2), 237-240

CrRh₃ and WPt₃ were revealed during AB₃ studies. The Ti_xPt_{3-x} phase is close to Ti₂₃Pt₇. The alloy chemistry of AB₃ alloys is reviewed by electron concentration considerations. Relative volume contraction in these structures increases with the difference in volume of the components.

Magnetic Properties of h.c.p. Fe-Ru Alloys

H. FUJIMORI and H. SAITÔ, *J. Phys. Soc. Japan*, 1969, **26**, (5), 1115-1119

The magnetic susceptibility χ in the ϵ phase of 13-100 at. % Ru-Fe alloys shows Pauli paramagnetic temperature dependence at high temperatures with small negative and positive temperature coefficients for alloys with $<$ and $>$ 30 at. % Ru respectively. χ at room temperature increases with increasing concentration of Fe. χ for ϵ_{Fe} by extrapolation is $10^{-3}/\text{Oe}/\text{mole}$. Variation of χ with Fe concentration is attributed to change in density at the Fermi level due to change in width of the d band.

CHEMICAL COMPOUNDS

The Palladium-Bromine System. The Molecular Composition of Palladium Bromide Vapour

R. C. WILLIAMS and N. W. GREGORY, *J. phys. Chem.*, 1969, **73**, (3), 623-631

The reactions: (a) $\text{PdBr}(s) = \text{Pd}(s) + \text{Br}_2(g)$, for which at 760-790 K, $\log K = -19840 T^{-1} - 3.02 \log T + 40.124$; (b) $\text{Pd}(s) + \text{Br}_2(g) = \text{PdBr}_2(g)$, at 1090-1155 K, $\log K = -17386 T^{-1} - 1.006 \log T + 13.278$; (c) $x\text{PdBr}_2(s) = (\text{PdBr}_2)_x(g)$; (d) $x\text{Pd}(s) + x\text{Br}_2(g) = (\text{PdBr}_2)_x(g)$, have been studied by the transpiration method. Simplest molecular mixture consistent with equilibrium data for (d) is a combination of monomer, tetramer and hexamer. Principal molecular forms in the saturated vapour phase above solid PdBr_2 , equilibrium (c) are the tetramer and hexamer. Thermodynamic properties of $\text{PdBr}_2(s)$ and $\text{PdBr}_2(g)$ were evaluated.

Physico-chemical Investigation of Aqueous Solutions of Rhodium(III) Perchlorate

O. A. EFREMNKO, V. I. SHELNSKAYA and I. P. ALIMARIN, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, (4), 740-745

The properties of an aqueous solution of Rh perchlorate prepared by a new method were studied by absorption spectroscopy and ion exchange, and the predominant Rh complex ion was shown to possess charge 3+. The solution is stable at 20°C. Chloro- and hydroxy- complexes may be formed at 90°C.

On a Rhodium Complex with Carbon Dioxide

Y. IWASHITA and A. HAYATA, *J. Am. Chem. Soc.*, 1969, **91**, (10), 2525-2528

$\text{Rh}_4(\text{CO})_{12}$ reacted with $\text{P}(\text{C}_6\text{H}_5)_3$ to form $\text{Rh}_2(\text{CO})_4(\text{P}(\text{C}_6\text{H}_5)_3)_4$, which was easily oxidised by O_2 in aromatic solvents to form $\text{Rh}_2(\text{CO})_2(\text{CO}_2)(\text{P}(\text{C}_6\text{H}_5)_3)_3\text{L}_n$, where L is C_6H_6 , $\text{C}_6\text{H}_5\text{CH}_3$, o -, m -, and p -xylene, or mesitylene. The reaction was studied using $^{18}\text{O}_2$. The coordinated CO_2 appears to be bent.

Kinetics and Mechanism of the Formation and Decomposition of Complexes of Molecular Nitrogen with Divalent Ruthenium

A. K. SHILOVA and A. E. SHILOV, *Kinet. Kataliz.*, 1969, **10**, (2), 267-272

N_2 complexes, or nitrogenyls, form during reduction of RuCl_3 and RuOHCl_3 as N_2 reacts with unsaturated RuL_5 derivatives, where L is a ligand. Exchange of N_2 with N of the coordination sphere of Ru, which occurs during thermal decomposition of Ru nitrogenyls, also involves RuL_5 intermediates. The ratio of rate constants of reactions of RuL_5 with N and H_2O is 3:1. Activation energy of thermal decomposition of $\text{RuN}_2\text{Cl}_2(\text{H}_2\text{O})_2$ -tetrahydrofuran is 22 kcal/mole, the Ru- N_2 bonding energy.

Complexes of Molecular Nitrogen

YU. G. BOROD'KO and A. E. SHILOV, *Uspekhi Khim.*, 1969, **38**, (5), 761-796

N_2 forms complexes with Ni, Pd and Pt and also forms nitrogenyl compounds with compounds of Fe(II), Ru(II), Os(II), Co(I), Rh(I), Ir(I), and Ni(O). The syntheses of these compounds and their structures are surveyed. (121 references.)

Formation of the Molecular Nitrogen Complex Cation of Pentammineruthenium(II) from Nitrous Oxide

A. A. DIAMANTIS and G. J. SPARROW, *J. Chem. Soc., D, Chem. Commun.*, 1969, (9), 469-470

N_2 complexes of pentammineruthenium(II) were prepared by reducing chloropentammineruthenium(III) in the presence of N_2O .

Phase Relations in the Ru-Ir-O₂ System in Air

C. L. MCDANIEL and S. J. SCHNEIDER, *J. Res. NBS, Sect. A, Phys. Chem.*, 1969, **73A**, (2), 213-219

RuO_2 , formed by Ru oxidising in air, dissociates at 1405°C and IrO_2 dissociates at 1020°C. A binary representation of the Ru-Ir-O₂ system in air is given. Up to 1020°C RuO_2 reacts with IrO_2 to form a complete solid solution series with rutile-type structure. At 1345°C three solid phases, rutile_{ss}, Ru_{ss}, and Ir_{ss}, exist in equilibrium for compositions between 2 and 45 mole % IrO_2 . Above 1405°C dissociation is complete for all compositions. At 1500°C a solid solution of Ru and Ir occurs with addition of up to 45 mole % Ir and up to 44 mole % Ru.

ELECTROCHEMISTRY

Potentiodynamic Examination of Electrode Kinetics for Electroactive Adsorbed Species: Applications to the Reduction of Noble Metal Surface Oxides

P. STONEHART, H. A. KOZLOWSKA and B. E. CONWAY, *Proc. R. Soc.*, 1969, **310A**, (1503), 541-563

Model cases are distinguished by examination of

the dependence of reaction rate with time and the effect of potential scan rate on maximum reaction rate and the potential at which it occurs. The significance of hysteresis and time effects in the processes of electrochemical formation and reduction of surface oxides at Pt, Rh, Ir and Pd is investigated.

Electrochemical Processes of the Chlorine-Chloride System on Platinum-Iridium-coated Titanium Electrodes

G. FAITA, G. FIORI and J. W. AUGUSTYNSKI, *J. electrochem. Soc.*, 1969, **116**, (7), 928-932

Anodic Cl_2 evolution follows the same scheme for both 30% Ir-Pt/Ti and Pt/Ti electrodes. Pt/Ti electrodes undergo passivation when $\eta_{\text{an}} > 0.2\text{V}$. Passivation on Ir-Pt/Ti electrodes is important only for overvoltages $> 0.5\text{V}$. There are similar differences in passivation in the cathodic process.

The Problem of the Catalytic Role of Electrodes during the Electroreduction of Cinnamic Acid on Platinised Platinum

I. V. KUDRYASHOV and V. L. KOCHETKOV, *Zh. fiz. Khim.*, 1969, **43**, (5), 1312-1315

Limiting step in both electroreduction and catalytic hydrogenation of cinnamic acid solutions in 0.1 N H_2SO_4 on platinised Pt is the chemical reaction occurring on the electrode catalyst. The effect of gelatine additions was studied. The rates of both processes depend on the number of active centres on the catalyst surface. The catalytic role of the electrodes during electroreduction of cinnamic acid on platinised Pt is confirmed.

The Role of the Metal Solution Interface Layer on the Mechanism of Dissolution of Hydrogen in Palladium

L. STOICOVICIU and R. V. BUCUR, *J. electroanal. Chem. interfac. Electrochem.*, 1969, **21**, (2), 307-310
A Pd black layer acts as a barrier, reducing the rate of absorption of H_2 in Pd, and can absorb larger amounts of H_2 than smooth Pd, resulting in H/Pd being higher than the theoretical equilibrium value.

ELECTRODEPOSITION AND SURFACE COATINGS

Addition Agent for Platinum Plating

K. S. INDIRA, S. SAMPATH and K. S. G. DOSS, *Metal Finish.*, 1969, **67**, (5), 44-49

In the presence of cetylammmonium bromide (CTAB) the cathode surface was covered by an adsorbed film of the wetting agent. Adsorption equilibrium was dynamic; CTAB was adsorbed and desorbed continuously. Pt deposition took place through vacant sites which changed position continuously, leading to a highly uniform deposit over the whole surface.

Electrodeposition of Palladium and Platinum from Aqueous Electrolytes

S. D. CRAMER and D. SCHLAIN, *Plating*, 1969, **56**, (5), 516-522

Techniques are described for thick, adherent and coherent deposits from aqueous electrolytes of Pd and Pt on Mo, Ni, Nb and W, and of Pd on Ti. Cathodic pretreatment in a fused salt bath containing Pt group metal salts was needed to plate on refractory metals. Microhardness and electron probe tests determined the effect of heat treatment up to 1250°C on deposit/substrate specimens.

Electrodeposition of Palladium-Cobalt Alloys

P. M. VYACHESLAVOV, N. P. FEDOT'EV, G. K. BURKAT and N. L. SEMENOVA, *Zashchita Metal.*, 1969, **5**, (3), 348-349

Pd-Co alloys were deposited from solutions of $\text{K}_6[\text{Co}(\text{P}_2\text{O}_7)_2]$ with PdCl_2 in HCl at 20°C and current density $0.3\text{ A}/\text{dm}^2$. $\text{K}_6[\text{Co}(\text{P}_2\text{O}_7)_2]$ was formed from $\text{K}_4\text{P}_2\text{O}_7$ and Co sulphate and the Pd content of the alloy dropped from 50% to 20% as the $\text{K}_4\text{P}_2\text{O}_7$ content of the solution rose from 200 to 500 g/l. Solution content of Pd+Co was 7 g/l.

LABORATORY APPARATUS AND TECHNIQUE

Bimetal Strip Hydrogen Gas Detectors

P. J. SHAVER, *Rev. sci. Instrum.*, 1969, **40**, (7), 901-905

50 ppm H_2 in N_2 have been detected with bimetal strips using Pd-Ag as the part which expands in the presence of H_2 . There is fast response at $200-300^\circ\text{C}$.

HETEROGENEOUS CATALYSIS

Catalyst Costs Are Tumbling down

Chem. W., 1969, **101**, (21, May 24), 81-82, 86

Chevron Research Corp. have developed a series of Pt-Re/ Al_2O_3 reforming catalysts which have given good results over long periods. Economics of the process are claimed to be good. See also: R. L. JACOBSON, H. E. KLUKSDAHL, C. S. MCCOY and R. W. DAVIS, *34th Midyear Mtg. Am. Petrol. Inst. Div. Refining, Chicago*, 1969, (May), Preprint 37-69

On Results from the Development of New Reforming Catalysts

K. BECKER, H. BLUME and H. KLOTZSCHE, *Chem. Tech.*, 1969, **21**, (6), 348-353

New catalysts for reforming petroleum fractions have been developed consisting of Pt compounds homogeneously distributed on Al_2O_3 . A fibrous catalyst with a particle diameter of 1.5 or 2 mm and a base of $\mu\text{-Al}_2\text{O}_3$ or $\gamma\text{-Al}_2\text{O}_3$ was used. Such

a fibrous catalyst, 8813/S, on γ - Al_2O_3 gave higher activity and selectivity than the spherical variety. The catalyst 8815 on μ - Al_2O_3 was more efficient for aromatisation of light petroleum fractions.

Hydroisomerisation of Normal Paraffins over Fluorided Platinum-Alumina Catalysts

B. A. ORKIN, *Ind. engng Chem., product Res. Dev.*, 1969, 8, (2) 154-159

Reducing total pressure of H_2 from 1000 to 50 p.s.i.g. increased isomerisation from 37 to 88%. At 300 p.s.i.g. a 0.6% Pt/ Al_2O_3 5% fluorided catalyst was more selective than the 10% fluorided catalyst or a fluoride-free catalyst.

Study of the Regularity of Crystallisation of Platinum on Supports. II. Effects of Thermal Treatment on the Dispersion and Activity of Platinum on Aluminium Oxide

N. M. ZAIDMAN, V. A. DZIS'KO, A. P. KARNAUKHOV, L. M. KEFELI, N. P. KRASILENKO, N. G. KOROLEVA and I. D. RATNER, *Kinet. Kataliz*, 1969, 10, (2), 386-391

Studies on the effect of heat treatment at 300-700°C on the dispersion and activity of 0.1-2 wt% Pt/ Al_2O_3 indicated a linear relation between surface concentration and inverse size of dispersion. The amount of Pt aggregation at each temperature is characterised by the slope of this graph, or crystallisation constant. Crystallisation constants are related exponentially to temperature. The mechanism of forming Pt on the support surface is explained satisfactorily by experiment. Specific activity is constant and unrelated to heat treatment in H_2 , to surface concentration or to dispersion of Pt.

III. Dispersion and Activity of Platinum in the Range of High Dilution

N. M. ZAIDMAN, V. A. DZIS'KO, A. P. KARNAUKHOV, N. P. KRASILENKO and N. G. KOROLEVA, *Ibid.*, (3), 652-656

Studies of 0.025-0.25 wt% Pt/ Al_2O_3 catalysts after heat treatment in H_2 at 300-700°C showed that the adsorption capacity of Pt at high dilution is unrelated to roasting temperature and amounts to H:Pt=2, i.e. the amount on individual atoms. An empirical equation was derived for the crystallisation of highly dispersed Pt. Catalytic activity during dehydrogenation of cyclohexane is unrelated to the surface concentration of Pt, the dispersion, and the roasting temperature.

Measurement of the Electron Work Function of Platinum/Alumina Catalysts during the Adsorption of Hydrocarbons, Hydrogen and their Mixtures

YU. E. SMOL'NIK, I. A. MAKAROV and A. V. KRYLOVA, *Ibid.*, (2), 446-449

Electron work function of industrial Pt/ Al_2O_3 catalysts decreases during their reduction by H_2 but increases after use in processes. The

positively charged form occurred during adsorption of H_2 and C_6H_6 , C_6H_{12} , n - C_8H_{18} , and methylcyclopentane. Charging is additive for adsorption of mixed hydrocarbons.

Effect of the Pressure of Hydrogen on the Selectivity of Platinum Catalysts in the Hydrogenolysis of Methylcyclopentane

V. V. VORONIN, I. I. LEVITSKII and KH. M. MINACHEV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, (4), 832-837

Studies on the effect of H_2 pressure on the selectivity of Pt/ Al_2O_3 , Pt/ SiO_2 and Pt/C catalysts in hydrogenolysis of methylcyclopentane showed that as p_{H_2} increased more molecules of methylcyclopentane underwent hydrogenolysis to n - C_6H_{14} . The effect was much greater on 0.3% Pt/ Al_2O_3 than on 1% Pt/ SiO_2 or 4% Pt/C. The ratio of 2-methylpentane to 3-methylpentane formed during hydrogenolysis of methylcyclopentane decreased as p_{H_2} increased.

Effect of Hydrogen Pressure on the Kinetics of Hydrogenolysis of Methylcyclopentane over Platinum-Alumina Catalyst

KH. M. MINACHEV, I. I. LEVITSKII and V. V. VORONIN, *Ibid.*, 1283-1287

Activation energies for hydrogenolysis of branched C-C bonds of methylcyclopentane over 0.3% Pt/ Al_2O_3 under 10 atm H_2 are 25 kcal/mole for tertiary double bonds and 38 kcal/mole for secondary double bonds when the catalyst is first treated at 550°C with H_2 free from O_2 or H_2O but are both 39 kcal/mole after catalyst treatment at 350°C with H_2 containing some O_2 .

The Structure and Activity of Supported Metal Catalysts. IV. Ethylene Hydrogenation on Platinum/Silica Catalysts

T. A. DORLING, M. J. EASTLAKE and R. L. MOSS, *J. Catalysis*, 1969, 14, (1), 23-33

Pt/ SiO_2 catalysts with crystallite sizes 13-200 Å were prepared in various ways and their specific activity for C_2H_4 hydrogenation was measured. An apparent effect of crystallite size on specific activity occurred in catalysts with low Pt content or fired at high temperatures because of poisoning or self-poisoning of the small Pt areas. When the reduction temperature of impregnation catalysts was varied there was a change in the amount of residual Cl_2 , which promoted the catalysis. Specific activity was constant when apparent crystallite-size effects were eliminated.

Investigation of Liquid Phase Hydrogenation. VI. Influence of Structure on the Reactivity of Olefins in Catalytic Hydrogenation on Platinum Catalysts

L. CERVENY and V. RUZICKA, *Coll. cz. chem. Commun.*, 1969, 34, (5), 1570-1579

The influence of structure on the reactivity of

Pt/SiO₂ and Pt/C in C₂H₅OH was greatest for hydrogenation of C₆-C₈ olefins with linear or branched chains.

Hydrogenation of Unsaturated Compounds on Mixed Platinum-Palladium Catalysts Supported on Polyvinyl Alcohol

D. V. SOKOL'SKII, O. A. TYURENKOVA and L. A. CHIMAROVA, *Zh. fiz. Khim.*, 1969, **43**, (5), 1168-1172

Studies of 10-60% Pt-Pd/polyvinyl alcohol catalysts in hydrogenations of unsaturated compounds showed that selectivity was in the order methylethylenylcarbinol > dimethylethylenylcarbinol > phenylacetylene. Maximum rates of hydrogenation occurred for two catalyst contents for the first and third compounds; a maximum occurred at 20% Pt for the second compound. Phenylacetylene hydrogenation products did not poison the catalyst. A small Pt content reduced the rate below that on Pd/polyvinyl alcohol but 10-20% Pt addition helped promote the reaction.

Palladised Pd Wire as a Hydrogenation Catalyst. I. Rate and Mechanism of Hydrogen Transport

F. NAGY, S. SZABÓ and I. TELCS, *Acta Chim. Acad. Sci. Hung.*, 1969, **59**, (3-4), 359-371

An unambiguous linear relationship in the interval $0.08 \leq H/Pd \leq 0.45$ exists between the relative resistance of the wire and the H₂ content. The rate of H₂ transport from a smooth Pd wire at 20-25°C is given and the effect of different solutions on this is discussed.

Hydrogenation of *cis*- and *trans*-Cyclododecenes over Pt and Pd Blacks

V. I. ALEKSEEVA, E. S. BALENKOVA, G. I. KHROMOVA and S. I. KHROMOV, *Neftekhimiya*, 1969, **9**, (2), 180-183

Studies of liquid-phase hydrogenation of *cis*- and *trans*-cyclododecenes over Pd and Pt blacks at 50°C show that *cis*-cyclododecene is reduced rather faster than the *trans* isomer. The rate constants are 3.10^{-2} and $2.68. 10^{-2} \text{ min}^{-1}$, respectively. Rates of hydrogenation and isomerisation of *trans*-cyclododecene over Pd are equal but the initial rate of isomerisation of *cis*-cyclododecene is greater than its rate of hydrogenation. Pd is a better isomerisation catalyst for cyclododecenes than Pt. Hydrogenation of both isomers takes place at the same sites on the catalyst surface.

Influence of Ring Size on the Rate of Hydrogenation of Cyclenes

Ibid., 184-187

Studies of liquid-phase hydrogenations of *cis*-cyclooctene and of cyclohexene over Pt and Pd blacks indicate that the rate of hydrogenation varies with ring size. Rate constants over Pt black decrease during transition from cyclo-

hexene to *cis*-cyclooctene but rise again for *cis*-cyclododecene.

Isomerisation and Dehydrogenation of Butene Catalysed by Noble Metals and their Alloys

S. H. INAMI, B. J. WOOD and H. WISE, *J. Catalysis*, 1969, **13**, (4), 397-403

Au catalyses isomerisation of C₄H₈-1 to C₄H₈-2 at 300-400°C in the absence of H₂ but, with H₂, Pd and Pd-Au alloy cause some isomerisation. Small additions of O₂ completely suppress isomerisation and butadiene forms with <60 at. % Au-Pd catalysts. The rate of isomerisation exceeds that of hydrogenation; both processes depend on surface density of H atoms. Mechanism of isomerisation may be H atom addition followed by H abstraction.

The Influence of the Substrate on the Behaviour of Graphite-supported Palladium Catalysts

I. C. BROWNLIE, J. R. FRYER and G. WEBB, *Ibid.*, **14**, (3), 263-269

Studies of the reaction parameters of hydroisomerisation of 1-C₄H₈ catalysed by 1 wt% Pd/C showed that "decoration" of the graphite surface by Pd increased the rates of both hydrogenation and isomerisation. The Pd is mobile on the substrate surface, thereby increasing the particle size of the Pd and reducing the catalytic activity.

Palladium-catalysed Reactions of Triorganosilicon Hydrides with Halocarbons

J. D. CITRON, J. E. LYONS and L. H. SOMMER, *J. org. Chem.*, 1969, **34**, (3), 638-640

Si-H bonds react over Pd with many halocarbons to produce high yields of silicon halides, except fluorides. 10% Pd/C was used generally but Pd black and PdCl₂ were used sometimes.

Catalytic Hydrogenation of Phenol over Pd-C Catalyst

M. MATSUMOTO, T. SUZUKI and S. SUZUKI, *Kogyo Kagaku Zasshi*, 1969, **72**, (4), 881-884, A43

Cyclohexanone in high yields was obtained during hydrogenation of C₆H₅OH at 1 atm H₂, 30-60°C over catalyst 0.1 g Pd/2 g C, and yield rose with increased temperature. Rate of cyclohexanone formation was zero order with respect to C₆H₅OH concentration, first order with respect to p_{H₂} and directly proportional to the amount of Pd dispersed on C. Activation energy of the reaction is 15 kcal/mole.

Selective Hydrogenation of 2-Ethyl-2-hexenal on Palladium in Gaseous Phase

V. MACHO and M. POLIEVKA, *Chem. Průmysl*, 1969, **19**, (5), 215-217

Supported Pd is a highly selective catalyst for hydrogenation of C=C up to 150°C, but is

practically inactive for hydrogenation of C=O in unsaturated organic compounds. Selectivity is evident for high p_{H_2} . Selectivity drops rapidly above 150°C, especially for α , β -unsaturated compounds, because of hydrogenolytic reactions.

Hydrogenation of Methyleneethynylcarbinol on Palladium/Polyacrylonitrile Catalyst

O. A. TYURENKOVA and E. I. SELIVERSTOVA, *Kinet. Kataliz*, 1969, 10, (2), 439-443

Studies of methyleneethynylcarbinol hydrogenation on Pd/polyacrylonitrile in various solutions and media showed that the rate of reaction depends on the amount of coverage of polymer by metal.

Catalytic Properties of Ruthenium in the Hydrogenation of Monosaccharides

N. A. VASYUNINA, G. S. BARYSHEVA and A. A. BALANDIN, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, (4), 848-854

Tests confirmed the theoretical selection of Ru for highly active catalysis of the hydrogenation of monosaccharides. Ru has greater activity than Pd and Pt. It is active for reduction in neutral or acid media and can be compared with Ni in these respects.

Catalytic Oxidation of Methane over Noble Metals

J. G. FIRTH and H. B. HOLLAND, *Trans. Faraday Soc.*, 1969, 65, (4), 1121-1127

Complete oxidation of CH₄ over Pd, Pt, Rh and Ir was studied. CH₄ is adsorbed on two types of reaction site; one also adsorbs O₂. Activation energies are proportional to Pauling bond energies of the O₂-metal bond in the region where the order in O₂ is low.

Dealkylation of Toluene on Platinum Group Metals

G. V. DYDYKINA, G. L. RABINOVICH, G. N. MASLYANSKII and M. I. DEMENT'eva, *Kinet. Kataliz*, 1969, 10, (3), 607-612

Pt group metals on γ -Al₂O₃ catalyse demethylation of toluene both in the presence of H₂ and without it. Studies of activity at 300-500°C showed that in He medium the order of activity is Rh > Pt > Pd > Ru \approx Ir \approx Os but that in H₂ the order is Rh > Ir > Ru \approx Os > Pt > Pd, i.e. H₂ inhibited dealkylation with Pt and Pd but assisted it for Rh, Ir, and Os. A relation was established between the catalytic activities of the metals and their rates of sublimation.

HOMOGENEOUS CATALYSIS

Homogeneous Hydrogenation

M. E. VOL'PIN and I. S. KOLOMNIKOV, *Uspekhi Khim.*, 1969, 38, (4), 561-592

The Pt metals take part in many homogeneous

hydrogenations as complex catalysts. (282 references.)

The Homogeneous Platinum(II)-catalysed Exchange of Hydrogen in Polycyclic Aromatic Hydrocarbons and Heterocyclic Molecules

R. J. HODGES and J. L. GARNETT, *J. phys. Chem.*, 1969, 73, (5), 1525-1539

The rate of exchange of several classes of polycyclic aromatic hydrocarbons in CH₃COOH media catalysed by Na₂PtCl₄ and by K₂PtCl₄ increases with decreasing double-bond localisation energy for the condensed polycyclics. Polyphenyl compounds mainly exchange multiply but polycyclic condensed compounds exchange stepwise. Heterocyclic molecules and polycyclic hydrocarbons with delocalised double bonds exchange more slowly and inhibit exchange in C₆H₆ due to strong complex formation. The exchange is not acid-catalysed. Catalyst stability is discussed.

Reduction of Olefins by Means of an HA-Platinum(II) Hydride System

M. GIUSTINIANI, G. DOLCETTI, R. PIETROPAOLO and U. BELLUCO, *Inorg. Chem.*, 1969, 8, (5), 1048-1051

Hydrogenation of linear and/or cyclic unsaturated hydrocarbons in the presence of *trans*-Pt(P(C₂H₅)₃)₂HCl and HCl or HClO₄(HA) in C₂H₅OH under ambient conditions leads to saturated hydrocarbons and *trans*-Pt(P(C₂H₅)₃)₂Cl₂. The pseudo first-order rate constants depend on the concentrations of olefin, mineral acid and Cl⁻. Possible reaction mechanisms are discussed. Electronegatively substituted olefins, e.g. acrylonitrile and *trans*-C₂H₂Cl₂, do not react under these conditions.

Catalytic Hydration of Acetylene in Sulphuric Acid Solution in the Presence of Pd^{II} Ammoniates

D. V. SOKOL'SKII, YA. A. DORFMAN, S. S. SEGIZ'AEVA and I. A. KAZANTSEVA, *Kinet. Kataliz*, 1969, 10, (3), 659-662

[PdNH₃(H₂O)₅]²⁺ complexes were observed to have the most catalytic activity of Pd(II) ammoniates for C₂H₂ hydration in H₂SO₄ solutions. The activity of the complexes fell as the number of NH₃ molecules in the coordination sphere of the metal increased but as the acidity of the medium rose so did the rate of hydration.

Catalytic Properties of Palladous Salts in Glacial Acetic Acid. V. Synthesis of Vinyl Acetate from Ethylene in Liquid Phase

M. TAMURA and T. YASUI, *Kogyo Kagaku Zasshi*, 1969, 72, (2), 561-567

The oxidation of CuCl formed during the one-step synthesis of vinyl acetate from C₂H₄ using palladous salt-cupric salt catalyst was in some cases the rate-determining step of the overall

reaction. The rate of the overall reaction was dependent on Li chloride concentration and on the $C_2H_4:O_2$ ratio. Reactivities of the palladous salts to C_2H_4 were affected by the nature of the palladous salt.

VI. Synthesis of Ethylene Glycol Monoacetate from Ethylene with Palladous Salt-Cupric Salt Catalyst System

Ibid., 568-571

VII. Synthesis of Vinyl Acetate from Vinyl Chloride by Means of Palladous Salt Catalyst

Ibid., 572-574

VIII. Reactions of Palladous Salts with Metal Salts and Ethylene in N,N-Dimethylformamide

Ibid., 605-606

IX. Behaviours of Various Nitrogen Containing Oxidants in Acetic Acid

Ibid., 575-578

X. Reaction of Ethylene with Palladous Salt-Nitrate Catalyst in Acetic Acid

Ibid., 578-580

XI. Rate and Mechanism of Glycol Monoester Formation

Ibid., 581-585

XII. Synthesis of Ethylene Glycol Monoacetate from Ethylene in Presence of Oxygen

M. TAMURA, M. TSUTSUMI and T. YASUI, *Ibid.*, 585-589

Catalysis of Hydrogen Transfer by Methods Supposedly Similar to Fermentation. Part 10. Dynamic Stabilisation of the Active Centres of Complex Catalysts during Hydrogenation of Aromatic Compounds

O. N. EFIMOV, O. N. EREMenKO, A. G. OVCHARENKO, M. L. KHIIDEKEL' and P. S. CHEKRII, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, (4), 855-858

Rh complex catalysts catalyse hydrogenation of polycyclic organic compounds in mild conditions, e.g. anthracene is reduced to 1,2,3,4-tetrahydroanthracene.

A New and Highly Active Catalyst for Homogeneous Hydrogenation

I. JARDINE and F. J. MCQUILLIN, *J. Chem. Soc., D, chem. Commun.*, 1969, (9), 477

$[py_3RhCl_3]$ treated with $NaBH_4$ in dimethylformamide gives the complex $[py_2(dmf)Rh-Cl_2(BH_4)]$, which is a highly active homogeneous hydrogenation catalyst.

The Protonation of Metal Carboxylates; New Homogeneous Hydrogenation Catalysts

P. LEGZDINS, G. L. REMPEL and G. WILKINSON, *Ibid.*, (14), 825

Rh, Ru and Mo carboxylates were protonated by

non-complexing strong acids. In the presence of a stabilising ligand such solutions as those of the complexes $Rh_2(CO_2Me)_4$, $Ru_2(CO_2Me)_4Cl$ and $Mo_2(CO_2Me)_4$ catalyse hydrogenation of $C=C$ and $C\equiv C$ bonds.

Catalytic Hydroformylation of Unsaturated Compounds Using Hydridocarbonyltris(tri-phenylphosphine)rhodium(I)

C. K. BROWN and G. WILKINSON, *Tetrahedron Lett.*, 1969, (22), 1725-1726

Relative rates of hydroformylation of alkenes for several substrates are presented. Using hex-1-ene the ratio of straight to branched aldehydes increases linearly with catalyst concentration. An increase occurs with pH_2 at 15 mM catalyst concentration, 25°C, 1 atm.

FUEL CELLS

Hydrogen-Oxygen Ion-exchange Membrane Fuel Cells

F. R. FOULKES and W. F. GRAYDON, *Can. J. chem. Engng*, 1969, 47, (2), 171-176

A H_2-O_2 cationic ion-exchange membrane fuel cell operated at various pressures, temperatures and electrolyte concentrations with Pt electrodes. Open circuit and discharge characteristics of the cell were explained in terms of the O_2 poly-electrode theory. Discharge was limited by internal resistance but pressurisation reduced polarisation.

Electrocatalysts for Hydrogen/Carbon Monoxide Fuel Cell Anodes. IV. Platinum-Nickel Combinations

D. W. MCKEE and M. S. PAK, *J. Electrochem. Soc.*, 1969, 116, (4), 516-520

The behaviour of a series of Pt-base metal binary catalysts as anodes for the oxidation of H_2-CO fuel mixtures was studied at 85 and 100°C with 85% H_3PO_4 electrolyte. Pt-Ni catalysts showed best tolerance for CO. Performance of catalysts with <25 wt% Ni is superior to that of Pt black. Effect is related to strength of bonding of chemisorbed CO to alloy surface.

CATHODIC PROTECTION

Influence of Imposed Currents on the Corrosion of Platinised Titanium

R. YUKHNEVICH and V. BOGDANOVICH, *Zashchita Metallov*, 1969, 5, (3), 259-264

Considerable corrosion of Pt/Ti anodes in NaCl aqueous solution occurs when the a.c. component of the imposed d.c. exceeds 70.7%. The corrosion is intercrystalline and pitting occurs. Increasing the frequency of the a.c. component from 20 to 100 Hz decreased the rate of corrosion and the amount of H_2 evolved at the anode also dropped.

ELECTRICAL AND ELECTRONIC ENGINEERING

Investigation of Electrolytically Deposited Ohmic Contacts of Palladium on Silicon

A. P. DOSTANKO, G. V. DUDKO, V. I. MAKHOV and O. V. MITROFANOV, *Zh. prikladnoi Khim.*, 1969, **42**, (5), 1109-1113

Pd, electrodeposited on p- and n-type Si with specific resistance 0.0004-20.0 ohm.cm, forms ohmic contacts with linear voltage current characteristics. Deposits adhere well and consist uniformly of fine crystals. Factors which reduce

the resistance of the ohmic contacts are decreasing the specific resistance of the Si, the separation of the blocks and the voltage of the latter.

Platinum-base Alloys for Elastic-sensitive Elements of Electrical Measuring Instruments

S. N. PAVLOVA, *Izv. Vysshikh Ucheb. Zaved., Tsvet. Metall.*, 1969, **12**, (2), 132-134

Tests on various Ag-Pd-Pt alloys showed that 20% Ag-10% Pd-Pt is better than any other tested for elastic-sensitive elements of electrical instruments. It is superior to 20% Ag-Pt used hitherto in its physical and mechanical properties.

NEW PATENTS

METALS AND ALLOYS

Improvements in and Relating to Alloys Containing Platinum Group Metals

JOHNSON MATTHEY & CO. LTD

French Patent 1,570,312

The alloys contain at least one of the Pt metals, especially Rh, Ir, Pt and Pd, and up to 20% of one of the transition elements Sc, Ti, V, Y, Zr, Nb, Hf, Ta or a lanthanide. The Pt metal is melted under inert conditions, the apparatus is evacuated, the transition element is added, and the alloy is cast.

(e.g. Fe, Co, Ni, Mn, etc.) dried and heated at 500-1,500°C to produce an intimate mixture of Pt and the second metal. A major amount of the second metal is then removed to increase the internal surface area of the electrode.

Reference Electrode

JENAER GLASWERK SCHOTT & GEN.

German Patent 1,498,827

An electrode for electrochemical potential measurements is equipped with a noble metal diaphragm, e.g., a Pt sintered diaphragm.

CHEMICAL COMPOUNDS

Preparation of Palladium Sulphate Solution

DOW CHEMICAL CO.

U.S. Patent 3,425,801

Metallic Pd is contacted with aqueous H₂SO₄ (concentration 9-60 wt%) at 80-150°C in the presence of O₂ to yield stable aqueous solutions of Pd sulphate.

ELECTRODEPOSITION AND SURFACE COATINGS

Coating of Refractory Materials

JOHNSON MATTHEY & CO. LTD

British Patent 1,150,074

A protective metallic coating is applied to a refractory material by introducing the latter (below 400°C) into an atmosphere of vaporised Pt group metal oxide (or other reducible compound) maintained at about 1400°C. A coating of the reducible compound is deposited on the material and this is reduced to metal by further heat treatment. In preferred embodiments the oxide is PtO₂.

Manufacture of Palladous Halide

FARBWERKE HOECHST A.G.

U.S. Patent 3,427,123

Metallic Pd having a large surface area is treated with O₂ in the presence of carboxylic acids, metal halide and ammonium halide to produce palladous halides.

Metal Plating Polymers

TOKYO SHIBARA ELECTRIC CO. LTD

British Patent 1,155,257

Polymer articles are roughened by bombarding them with activated ions generated by glow discharge. The roughened surface is immersed in aqueous solutions of HCl/SnCl₂ and HCl/PdCl₂. The Pd is electrolessly plated on the surface and subsequently electrolytically plated on the coated surface.

ELECTROCHEMISTRY

Improved Platinum Electrode

STANDARD OIL CO.

U.S. Patent 3,429,750

An electrically conducting inert support is impregnated with salts of Pt and a second metal