ABSTRACTS
of current literature on the platinum metals and their alloys

PROPERTIES

Problems of the Mechanism of Sublimation and Oxidation of Platinum, Palladium and its Alloys

E. I. RYTVIN and L. P. ULYBYSHEVA, *Izv. Akad. Nauk SSSR, Metally*, 1969, (1), 247–252

The thermodynamic characteristics of the sublimation and oxidation of Pt and Pd and the rate constants of these metals during heating in vacuum were calculated. The rates of sublimation of Pt, Pd and their alloys were measured at 1573, 1598, 1623, 1648, and 1673K in air.

The Low Temperature Heat Capacity of Platinum

W. T. BERG, *J. Phys. Chem. Solids*, 1969, **30**, (1), 69–72

Heat capacity γ for Pt at 2.6–20K is 6.59 J/g.atom deg C^2. Debye temperature at 0K is 240.1K.

The Magnetic Anisotropy of Ordered Equiatomic Platinum Cobalt

R. A. MCCURRIE and P. GAUNT, *Phil. Mag.*, 1969, **19**, (158), 339–347

A single crystal of tetragonal phase of 52 at.% Co-Pt with one predominant tetragonal orientation is strongly uniaxial with [001] as easy direction. Anisotropy energy at 298K is represented by $E = K_0 + K_1 \sin^2 \psi$, where K_0 is a constant, $K_1 = 2.83 \times 10^7$ erg/cm^3 and ψ is the angle between magnetisation vector and easy direction. K_1 increases with degree of long range order but saturation magnetisation decreases.

Internal Oxidation of Cu-Pd and Cu-Pt Alloys

C. WAGNER, *Corrosion Sci.*, 1968, **8**, (12), 889–894

When Cu-Pd and Cu-Pt alloys are heated in O_2 at 850–1000°C, Cu_2O is formed as external scale and also further in the alloy due to inward diffusion of O_2. Conditions under which this type of internal oxidation occurs are shown.

New Nonmagnetic Elinvar-type Alloy "Pallagold" in the Pd-Au System

H. MASUMOTO and S. SAWAYA, *J. Japan Inst. Metals*, 1969, **33**, (1), 121–125

Measurements of Young's and rigidity moduli and of thermal expansion of Pd-Au alloys after various heat treatments and cold working showed that the temperature coefficients of the moduli after annealing at 1000°C for 1 h have a minimum of -3.0×10^{-6} at 50% Au-Pd, which becomes -2.8×10^{-5} when heated at 360°C for 15 h after water quenching from 1000°C or cold

reducing of 96%. The thermal expansion coefficient has a minimum at 48% Au after annealing at 1000°C for 1 h. The hardness of the alloys heated at 360°C for 15 h after quenching or cold working is $\sim$2 times that of the annealed alloys and they are known as "Pallagold".

The Temperature Dependence of Young's Modulus of Single Crystals of Pd-50% Au Alloy "Pallagold"

H. MASUMOTO, H. SAITO and S. KADOWAKI, *Ibid.*, 126–129

Young's moduli of 50% Au-Pd single crystals in the $<100>$, $<110>$ and $<111>$ directions at 20°C are 5.76×10^5, 11.80×10^5 and 18.10×10^5 kg/cm^2 respectively. The modulus in the $<100>$ direction increases steadily with temperature and reaches a maximum at $\sim$400°C but the other moduli decrease continuously.

On Susceptibility Measurements on Diluted Palladium Alloys to Investigate the Effect of Impurity Scattering on the Electronic Density of States

A. HAHN and W. TREUTMANN, *Z. angew. Phys.*, 1969, **26**, (2), 129–135

Magnetic susceptibility data for dilute Ag-Pd, Rh-Pd and Ag-Rh-Pd solid solutions, when corrected for small Fe impurities and extrapolated to 0K show a characteristic deviation from rigid band behaviour. A model for this is discussed but the explanation has not yet been agreed.

Speed of Sound in Pd Alloys Doped with Transition Elements

J. ORTELLI, C. SUSZ, E. WALKER and M. PETER, *Helv. Phys. Acta*, 1969, **42**, (2), 284–298

Temperature dependence of the torsional speed of sound was measured in Rh_xPd_{1-x} and in Pd_xAg_{1-x} alloys doped with Mn, Fe, Ni, Co, Ru, Os, and Pt. Temperature variation of speed in undoped alloys shows an anomaly at $Pd_{95}Rh_5$. Decrease or increase of the anomaly is correlated with band susceptibility.

Susceptibility Measurements on Palladium/Hydrogen

P. BRILL and J. VOITLÄNDER, *Z. Naturf.*, 1969, **24a**, (1), 1–6

Susceptibility and weight of sample were observed near equilibrium of PdH_2/H_2 as a function of pressure between 50 and 100°C. $P_{(n)}$ isotherms show hysteresis. $\chi_{(n)}$ isotherms for adsorption and desorption coincide and show no hysteresis. $\chi - n$ is independent of the $\alpha - \beta$ phase transition.

Some Observations on the Thermodynamic Properties of α–Phase Palladium-Cadmium Alloys

W. G. BUGDEN, J. D. FILBY and J. N. PRATT, *J. less-common Metals*, 1969, **17**, (3), 257–262

Vapour pressure and solid electrolyte e.m.f. techniques gave the activities of Cd and free energies of solution and formation of 0–28 at.% Cd-Pd. Entropies of formation were estimated by combining these data with reported rates of formation. All the thermodynamic properties exhibit strong negative deviations from ideal behaviour.

On the Enhancement of the Magnetic Susceptibility in the Iridium-Rhodium Alloy System

W. D. WEISS, *Z. angew. Phys.*, 1969, **26**, (2), 124–128

Specific magnetic susceptibility measurements on Ir, Rh and Ir-Rh alloys at 6–1850K are associated quantitatively with electronic specific heat. Increases in these quantities near Pd and Pt indicate a maximum in the density of states function, whereas all exchange parameters are constant. One of these parameters changes from constant low to a higher constant value in a narrow range near Ir and Rh.

The Crystal Structure of Rh_2Al_9 and Ir_2Al_9

L.-E. EDSHAMMAR, *Acta Chem. Scand.*, 1968, **22**, (9), 2822–2826

Rh_2Al_9 has a=6.352, b=6.428, c=8.721 Å, β=94.81°. Ir_2Al_9 has a=6.378, b=6.430, c=8.732 Å, β=94.77°.

The Copper-Iridium Alloys

E. RAUB and E. RÖSCHEL, *Z. Metallkunde*, 1969, **60**, (2), 142–144

Unlike Ag or Au, Cu is completely miscible with Ir in the liquid state. Peritectic crystallisation occurs at 1138±5°C between ~8 and ~97 at.% Ir.

Dilatometric Investigation of Phase Conversion in Iron-Iridium Alloys

E. A. PLEKHANOVA, S. KH. KURUMCHINA and V. F. EGOLAEV, *Fiz. Metall. Metalloved.*, 1969, **27**, (3), 473–477

The kinetics of $\gamma \rightleftarrows \alpha$ and $\gamma \rightleftarrows \varepsilon$ transformations in 30, 40 and 50 wt% Ir-Fe were studied by dilatometric methods. The stability of the Fe-Ir austenite : martensite ratio was examined after the $\gamma \rightleftarrows \alpha$ and $\gamma \rightleftarrows \varepsilon$ transformations.

CHEMICAL COMPOUNDS

Synthesis and Crystal Structure of Mg_2PtO_4 and Zn_2PtO_4

O. MULLER and R. ROY, *Mater. res. Bull.*, 1969, **4**, (1), 39–44

Mg_2PtO_4 and Zn_2PtO_4, synthesised at 850–900°C,

p_{O_2}=150–200 atm, are inverse spinels with unit cell constants a_0=8.521 Å and a_0=8.549 Å respectively.

Platinum Compounds: a New Class of Potent Antitumour Agents

B. ROSENBERG, L. VANCAMP, J. E. TROSKO and V. H. MANSOUR, *Nature*, 1969, **222**, (Apr. 26), 385–386

cis-Pt(IV)(NH₃)₂Cl₄, cis-Pt(II)(NH₃)₂Cl₂, Pt(II) (NH₃CH₂CH₂NH₂)Cl₂ and Pt(IV)(NH₂CH₂CH₂ NH₂)Cl₄ injected interperitoneally inhibit sarcoma 180 and leukaemia L1210 in mice.

Synthesis of β-Alkyl and β-Aryl π-Allylic Palladium Halide Complexes and its Mechanistic Aspects

H. C. VOLGER, *Rec. Trav. chim. Pays-bas*, 1969, **88**, (3), 225–240

π-Allylic Pd halide complexes, substituted by alkyl or aryl groups at the centre C atom, were obtained in high yields in one-step synthesis by introducing the appropriate olefin into Na chloropalladite solution in glacial CH₃COOH in the presence of Na acetate at 85°C. Reaction proceeds via a π-olefinic Pd complex, which is in equilibrium with small amounts of π-allylic complex.

Thermodynamic Investigations of Anhydrous Iridium Tribromide

N. I. KOLBIN and V. M. SAMOILOV, *Zh. neorg. Khim.*, 1969, **14**, (3), 631–635

Studies of the dissociation of $IrBr_3$ at 716–973K and constant pressure measurements at 377–742K showed that its specific heat is $99.39 + 20.35 \times 10^{-3}T$ J/mole. deg. When forming $IrBr_3$ from metallic Ir and gaseous Br the change of enthalpy is $\Delta H°_{298.15} = -(223.0 \pm 3.0).10^{-3}$ J/mole, the change of entropy is $\Delta S°_{298.15} = -274.0 \pm 4.0$ J/mole. deg and the standard entropy of solid $IrBr_3$ is $S°_{298.15}$=130.5 J/mole. deg.

Substitution Reactions of $Ru_3(CO)_{12}$

J. P. CANDLIN and A. C. SHORTLAND, *J. organometall. Chem.*, 1969, **16**, (2), 289–299

Kinetics of substitution of $Ru_3(CO)_{12}$ using Group V donor ligands yielding complexes of the type $Ru_3(CO)_9L_3$ were studied. Rate determining step for substitution is reversible dissociation of CO yielding intermediate $Ru_3(CO)_{11}$.

Inorganic Nitrogen Fixation. Nitrogen Compounds of the Transition Metals

A. D. ALLEN and F. BOTTOMLEY, *Accounts chem. Res.*, 1968, **1**, (12), 360–365

Preparation and properties of nitrogenpentaammineruthenium(II) complexes are described. Bonding and nitrogen fixation by inorganic systems are discussed. N_2 acts as ligand towards appropriate transition metal centres in a similar manner to isoelectronic CO. The Os(II) com-

pound is very air-stable; the Co(I) compound is very air-sensitive.

Reactions of Complexes of Ruthenium and Osmium Halides with Ammonia, Amines and Hydrazine

J. CHATT, G. J. LEIGH and R. J. PASKE, *J. chem. Soc., A, inorg. phys. theor.*, 1969, (5), 854–859

NH_3 and primary amines (am) react with $[MX_3(PR_3)_3]$ (M=Ru or Os, X=Cl or Br, PR_3=tertiary phosphine) in C_2H_5 OH at 20°C to form *mer*-$[MX_2am(PR_3)_3]$ and CH_3CHO, whereas secondary and tertiary amines with $[MX_3PMe_2Ph)_3]$ cause reduction to the alcohol complex $[MX_2(C_2H_5OH)(PMe_2Ph)_3]$, possibly via a hydride complex intermediate. When C_2H_5OH contains a little H_2O then $(C_nH_{2n+1})_2NH$ is dealkylated to form the corresponding $[MX_2am(PR_3)_3]$. N_2H_4 in small amounts forms $[MCl_2(N_2H_4)(PMe_2Ph)_3]$ or more commonly $[M_2X_4(N_2H_4)_2(PR_3)_4]$. N_2, H_2 and $N_2H_4.HCl$ are produced also. $[Ru(NH_3)_5N_2]^{2+}$ is formed under more vigorous reaction conditions.

Investigation of the Polymorphism of Osmium Tetrachloride

P. MACHMER, *Z. Naturf.*, 1969, **24b**, (2), 200–205

High temperature phase OsO_4 of orthorhombic unit cell has a=12.08, b=11.96, c=11.68 Å. The cubic lattice constant a=9.95 Å is deduced from low temperature phase OsO_4. High temperature phase OsO_4 is temperature independent; magnetic susceptibility $\chi_{mole} = +1080 \times 10^{-6}$ c.g.s. units. The low temperature value of $\chi_{mole} = +880 \times 10^{-6}$ c.g.s. units at 300K, and susceptibility is temperature dependent.

ELECTROCHEMISTRY

The Electrochemical Oxidation of Adsorbed Hydrogen and Carbon Monoxide on Noble Metals and their Alloys

R. J. ROETHLEIN and H. J. R. MAGET, *J. Electrochem. Soc.*, 1969, **116**, (1), 37–40

Electrochemical oxidation of H_2-CO mixtures was investigated on Pt, Rh, Ru and on Pt-Rh and Pt-Ru. Relative coverage of adsorbed H_2 in the presence of CO was found to be 5% for Pt-Rh alloys and total surface coverage was dependent on alloy surface area. H_2 coverage is a function of Ru content in Pt-Ru alloys.

The Solubility of Hydrogen in Alloys of the Nickel-Palladium System

T. V. LIPETS, ZH. L. VERT and I. P. TVERDOVSKII, *Elektrokhimiya*, 1969, **5**, (1), 71–74

Solubility of H_2 in Ni-Pd alloys was studied by cathodic saturation of $p_{H_2} > 1$ atm and results were compared with those for $p_{H_2} > 0.03$ atm. The solubility of H_2 depends on the presence of 3*d* and 4*d* vacancies in the alloys. There are analogies between the sorption and magnetic properties of the systems.

LABORATORY APPARATUS AND TECHNIQUE

Continuous Measurement of Lining Wear in Steel Furnaces with Radioisotopes

S. BERGH, H. SANDBERG and N. STAHL, *J. Metals*, 1969, **21**, (2), 19–22

Lining wear in a rotating steel furnace is measured by determining the activity of the steel bath when ^{192}Ir wire placed in the bricks is continuously dissolved at a rate proportional to the lining wear. This simple, rapid, reliable, and cheap method does not interfere with production and is reproducible to $\pm 5\%$. A statistically reliable relationship between metallurgical variables and lining wear is now possible.

HETEROGENEOUS CATALYSIS

Industrially Useful Characteristics of Platinum Metal Hydrogenation Catalysts

P. N. RYLANDER, *Abstr. Papers, 157th Mtg, Am. Chem. Soc.*, 1969, (Apr.), INDE 26

Decreasing activity series for olefin saturation is Pd>Rh>Pt≫Ir>Ru>Os, for double bond migration is Pd≫Ru>Rh>Pt>Ir, for selective hydrogenation of dienes is Pd>Rh>Ru∼Pt>Ir. The value of Pd in these respects makes it suitable for selective removal of dienes from pyrolysis gasolines. Pd has low tendency to hydrogenate aromatics. It is suitable for selective hydrogenation of aromatic ketones whereas Rh is useful for aromatic ring saturation with minimum hydrogenation or hydrogenolysis of aromatic carbonyl.

New Platforming Catalyst Found Exceptional

M. J. STERBA, P. C. WEINERT, A. G. LICKUS, E. L. POLLITZER and J. C. HAYES, *World Petroleum*, 1969, **40**, (1), 32–34

Pilot plant trials and commercial operation using R-16 catalyst demonstrated its unusual stability characteristics which make it superior to all previous Platforming catalysts. Maximum benefit of using R-16 occurs in units designed specifically for low pressure operation with high yields of Platformate and H_2. See also *Oil gas J.*, 1968, **66**, (53), 143–146.

Selective Reduction of Nitrogen Oxides by Ammonia

M. MARKVART and V. POUR, *Chem. Prumysl*, 1969, **19**, (1), 8–12

1% Pt/Al_2O_3 is the best catalyst for reduction of N oxides by NH_3 in tail gas from HNO_3 production. Reduction of 1:1 $NO:NO_2$ has 90% conversion at 240–250°C. Pure NO is reduced at 170°C. ∼50% more NH_3 than predicted by theory is required to reduce the mixture and

Prediction of Platinum Losses during Ammonia Oxidation

E. J. NOWAK, *Chem. engng Sci.*, 1969, **24**, (2), 421–423

Oxidation rate calculations for infinite Pt cylinders in forced convective flow show that the rate is controlled by the PtO_2 transport rate at 500–1400°C, 1 atm. Commercial losses can be predicted by applying a constant factor of $\sim$4 to the rate equation. This factor may be due to the roughness of the gauze. The rate equation is $\bar{R} = (k_b \cdot K_{eq} \cdot P_{O_2})/(1 + k_b/k_m)$, where $\bar{R}$ is the rate, k_b is the rate constant of the reverse reaction, K_{eq} is the equilibrium constant P_{PtO_2}/P_{O_2} for reversible oxidation, k_m is the mass transfer coefficient.

Chlorided Platinum-Alumina Low Temperature Isomerisation Catalysts

J. P. GIANNETTI and R. T. SEBULSKY, *Abstr. Papers, 157th Mtg, Am. Chem. Soc.,* 1969, (Apr.), PETR 60

Paraffin isomerisation catalysts can be prepared by chloriding Pt/Al_2O_3 with thionyl chloride, sulphuryl chloride, sulphur monochloride and a SO_2-Cl_2 mixture at high temperatures. HCl treatment before sulphur chloride treatment gives increased activity. The Al_2O_3 and the Pt content are also important to catalyst activity.

The Structure and Activity of Supported Metal Catalysts. III. Desorption of Carbon Monoxide-^{14}C from Platinum/Silica Impregnated Catalysts

D. CORMACK and R. L. MOSS, *J. Catalysis*, 1969, **13**, (1), 1–11

Studies of desorption of CO labelled with ^{14}C from Pt/SiO_2 showed that the percentage of readily desorbed CO was greatest on small Pt crystallites occurring in catalysts with low Pt content. Quantitative measurements of the relative amounts of the two types of desorbed CO, which are correlated with linear and bridged species, enable calculation of the number of exposed Pt atoms. The shape and size of the Pt crystallites may be the reason for the variation in the relative amounts of the two types of CO.

Structure and Activity of Platinum-Silica Catalysts Prepared by a Combustion Process

H. SCHACHNER, W. BOLLMANN and B. BAUMBERGER, *J. appl. Chem.,* 1969, **19**, (3), 68–72

37–90% Pt/SiO_2 catalysts, prepared by combustion of silicone oil with H_2PtCl_6 and organic solvents and tested statically for activity in C_6H_6 hydrogenation, show special structural characteristics due to the method, i.e. small Pt particles with smooth round surfaces separated by SiO_2 ensure good resistance to deactivation at high temperatures and in high humidity at low temperatures.

Hydrogenation of o-Nitrophenol on Platinum/Polyvinyl Alcohol Catalyst

O. A. TYURENKOVA, *Zh. fiz. Khim.,* 1969, **43**, (1), 135–138

Aqueous colloidal Pt/polyvinyl alcohol catalyst has more activity but less selectivity than the powdered form in alcoholic medium. *o*-Nitrophenol is reduced on the latter catalyst faster in neutral or slightly alkaline media; in stronger alkali the rate decreases. Both catalysts are poisoned by *o*-nitrophenol and by its reduction products. The poisoning is less noticeable at higher catalyst : substrate ratios.

Catalysis of Hydrogen Transfer by Methods Supposedly Similar to Fermentation. Part 8. Catalytic Systems of Hydrogenation of Carbonyl Compounds

V. V. ABALYAEVA, A. S. ASTAKHOVA, E. N. BAKHANOVA and M. L. KHIDEKEL', *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1969, (1), 89–95

The catalytic system for hydrogenation of fluorenone and benzophenone comprised Rh/Al_2O_3 or PtO_2, H_2 and $ZnCl_2$. The latter acts by complex formation with ketones. The mechanism of reactions is described in terms of the bonding of protons in the carbonyl groups.

Catalytic Properties of Binary and Ternary Alloys of the Pd-Ni-Cu System

T. V. LIPETS, ZH. L. VERT and I. P. TVERDOVSKII, *Kinet. Kataliz,* 1969, **10**, (1), 206–208

Studies of Pd-Ni, Pd-Cu, Ni-Cu, and Pd-Ni-Cu catalysts for decomposition of alkaline N_2H_4 hydrate solutions showed the relation of rate constants and resistivity to alloy constitution. N_2H_4 may take some of the alloy outer electrons during decomposition.

The Kinetics of the Hydrogenation of Cycloalkenes on Palladium-Alumina Catalysts

A. S. HUSSEY and G. P. NOWAK, *J. org. Chem.,* 1969, **34**, (2), 439–444

Hydrogenation rates, reported for bicyclo-[2.2.1]-heptene, cyclopentene, cyclohexene, cycloheptene, and cyclooctene in cyclohexane solution on Pd/Al_2O_3 at 25°C, 1 atm, are first order in catalyst but have fractional order dependence on p_{H_2} and on cycloalkene concentration. Apparent activation energy for cyclohexene is 5.7 ± 0.5 kcal/mole.

Hydrogenation of Acetylenic Alcohols on Palladium/Polyethyleneterephthalate Catalyst

S. F. LANKIN and O. A. TYRENKOVA, *Zh. fiz. Khim.,* 1969, **43**, (1), 150–154

Reduction products of dimethylethynylcarbinol on Pd/polyethyleneterephthalate do not poison the

catalyst significantly but adsorbed products hinder the reduction of methylethylethynyl-carbinol on this catalyst. Initial amount of carbinol has no effect on reaction rate. Growth of hydrocarbon radicals at one group – CH_2 – leads to reduced reduction rate and more product adsorption. Increased acidity cuts the reaction rate. The catalyst is 5–6 times more active than Pd black for hydrogenations of acetylenic alcohols.

Hydrogenation of Salicylic Acid and its Derivatives with Rhodium and Ruthenium Catalysts

G. FERRARI and A. ANDREETTA, *Chim. e Ind.*, 1969, **51**, (1), 38–40

Rh and Ru on C or Al_2O_3 catalyse hydrogenations of salicylic acid, its Na salt and its methyl ether selectively and minimise hydrogenolysis and decarboxylation. The support used affects the reaction rate and product distribution. Satisfactory yields of cyclohexane-2-one-carboxylic acid or its derivatives are obtained in the presence of Rh. *cis-* and *trans-*2-OH-cyclohexanecarboxylic acids are obtained in the presence of Ru.

Hydrogenation of Dimethylethynylcarbinols on Ruthenium-Palladium Catalysts Supported on Al_2O_3

D. V. SOKOL'SKII, K. K. DZHARDAMALIEVA and T. M. DUKHOVNAYA, *Zh. fiz. Khim.*, 1969, **43**, (2), 505–507

Tests during the hydrogenation of dimethyl-ethynylcarbinols in H_2O at 20, 40 and 60°C with 1% (Ru-Pd)/Al_2O_3 catalysts show that the most active contains 20.8 at.% Ru-Pd. Slight changes in potential ($\sim$100mV) and low activation energies ($\sim$5 kcal/mole) show that the catalyst surface is charged significantly with H_2 and that adsorption of unsaturated compounds limits the rate.

The Hydrogenation of Acetylene. V. The Reaction of Acetylene with Hydrogen and Deuterium Catalysed by Alumina-supported Ruthenium and Osmium

G. C. BOND, G. WEBB and P. B. WELLS, *J. Catalysis*, 1968, **12**, (2), 157–165

Studies of the kinetics, activation energies and selectivities of the reaction of C_2H_2 with H_2 and D_2 over 1 wt% and 5 wt% Ru/Al_2O_3 at 92–192°C and over 1 wt% and 5 wt% Os/Al_2O_3 at 144–202°C showed that in comparable conditions Ru is always more selective than Os for C_2H_4 production. The reaction with D_2 indicated that acetylene exchange and deuteration occur separately. Chances of adsorbed species acquiring D atoms rather than H atoms are about the same on both Ru and Os but vinyl is less likely to be hydrogenated rather than dehydrogenated on Ru than on Os. The mechanism may be successive addition of two "H" atoms to adsorbed C_2H_4.

Liquid-phase Hydrogenation of Some Aromatic Acids on Ruthenium Catalysts

A. A. PONOMAREV, L. M. RYZHENKO and N. S. SMIRNOVA, *Zh. org. Khim.*, 1969, **5**, (1), 75–77

3- and 4- amino-cyclohexanecarboxylic acids, 2-methylhexahydroterephthalic acid and related acids were produced using RuO_2 and Ru/C catalysts.

Hydrogenation of Methylacetylene. IV. The Reaction of Methylacetylene with Hydrogen Catalysed by Palladium, Platinum, Iridium, Rhodium, and Ruthenium Catalysts

R. S. MANN and K. C. KHULBE, *Can. J. Chem.*, 1969, **47**, (2), 215–222

Activation energies for pumice-supported and unsupported Pd, Pt, Ir, Rh were 10.5, 9.5; 12.4, 14.7; 8.6, 6.2; 10.7 and 11.7 kcal/mole respectively.

Hydrogenation of Cycloheptene and *cis-*Cyclooctene on Group VIII Metals

V. I. ALEKSEEVA, E. S. BALENKOVA, L. E. MARININA and S. I. KHROMOV, *Vest. Moskov. Univ., Ser. II, Khim.*, 1969, **24**, (2), 102–104

Studies of the liquid phase hydrogenations of cycloheptene on Pd black, Pt black, Ir black, and 5% Pd/C and of *cis-*cyclooctene on Ir black and on 5% Pd/C at 50°C show that *cis-*cyclooctene is hydrogenated more slowly than cycloheptene.

Radiochemical Studies of Chemisorption and Catalysis. VIII. The Behaviour of ^{14}C-Ethylene and Tritium Adsorbed on Alumina-supported Palladium, Rhodium and Platinum Catalysts

G. F. TAYLOR, S. J. THOMSON and G. WEBB, *J. Catalysis*, 1968, **12**, (2), 191–197

Studies of the nature and reactivity of adsorbed species on 5 wt% Pd/Al_2O_3, 5 wt% Rh/Al_2O_3 and 5 wt% Pt/Al_2O_3 at 20–200°C showed that injection of ^{14}C-ethylene on to freshly reduced catalyst causes formation of a strongly adsorbed species which is inactive in molecular exchange, hydrogenation and displacement by C_2H_2; the relative abilities of the metals to promote C_2H_4 self-hydrogenation are Rh>Pt>Pd. The same catalysts differ in their degree of surface heterogeneity for different hydrocarbon molecules.

Lignin and Related Compounds. I. A Comparative Study of Catalysts for Lignin Hydrogenolysis

J. M. PEPPER and Y. W. LEE, *Can. J. Chem.*, 1969, **47**, (5), 723–727

10% Pd/C, 5% Rh/C, 5% Rh/Al_2O_3, 5% Ru/C, 5% Ru/Al_2O_3, and Raney Ni were studied as catalysts for hydrogenolysis of spruce wood lignin. Rh, Pd and a limited amount of Raney Ni produce similar results to Ru and an excess of Raney Ni but with the latter two catalysts the

degradation is more severe. Rh/C and Pd/C are advantageous.

HOMOGENEOUS CATALYSIS

The Direct Oxidation of Ethylene to Acetaldehyde

J. SMIDT, W. HAFNER, J. SEDLMEIER, R. JIRA and R. RÜTTINGER, *Chem. et Ind.*, 1969, **101**, (3), 291–297

A general review of the direct oxidation of C_2H_4 to CH_3CHO using $PdCl_2$-$CuCl_2$ aqueous solution catalyst, which is now an important industrial process. (20 references).

Kinetics of Isomerisation of Butene-1 in Aqueous Solutions of Palladium Chloride

S. V. PESTRIKOV, I. I. MOISEEV and L. M. SVERZH, *Kinet. Kataliz*, 1969, **10**, (1), 74–82

Kinetic studies of $C_4H_8 - 1$ isomerisation in aqueous $PdCl_2$ solution enabled the rate equation to be derived. Isomerisation rate fell as the ionic strength of solution increased. It was 3.4 times less in D_2O containing 15% H_2O than in pure H_2O. These data and data on inhibition by oxidants explained the isomerisation mechanism, including the formation of π complexes of Pd with olefins and their subsequent conversion.

A Novel Carboxyvinylation of Aromatic Compounds by Palladium(II) Chloride

S. NISHIMURA, T. SAKAKIBARA and Y. ODAIRA, *J. Chem. Soc., D, chem. Commun.*, 1969, (6), 313–314

C_6H_6 and substituted benzenes are converted into cinnamic acid derivatives by carboxyvinylation by $PdCl_2$ in the presence or absence of aliphatic acid anhydrides.

Novel Hydrosilylation of Butadiene Catalysed by a Palladium Complex

S. TAKAHASHI, T. SHIBANO and N. HAGIHARA, *Ibid.*, (4), 161

Low valent Pd-phosphine complexes are shown to catalyse a novel hydrosilylation of butadiene on addition of Si hydrides to butadiene dimer.

Isomerisation of Vinylphenylglycol by Homogeneous Catalysis on *cis*-Dichlorobis-(triphenylphosphine)palladium(II)

A. MARBACH and Y. L. PASCAL, *C.r., Sér. C*, 1969, **268**, (11), 1074–1076

Homogeneous solution of *cis*-$PdCl_2(Ph_3P)_2$ complex in different solvents was used for the isomerisation of phenyl-1-butene-diol-1.

Selective Reduction of Butadiene in the Presence of Bisdimethylglyoximato Complex of Rhodium

B. G. ROGACHEV and M. L. KHIDEKEL', *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, (1), 141–142

Bis(dimethylglyoximato)triphenylphosphine-butene-2-rhodium is believed to act as an intermediate in the catalytic reduction by H_2 or $NaBH_4$ of butadiene with bis(dimethylglyoximato) triphenylphosphinerhodium as catalyst.

Hydrogenations of Cycloalkenes Using Tris-(triphenylphosphine)chlororhodium(I)

A. S. HUSSEY and Y. TAKEUCHI, *J. Am. Chem. Soc.*, 1969, **91**, (2), 672–675

Homogeneous hydrogenations in C_6H_6 and in $C_6H_6 - C_2H_5OH$ solutions at $25 \pm 0.1°C$, 1 atm H_2 using $RhCl(PhP)_3$ catalyst are much slower for 1-methylcyclohexene, 1,4-dimethylcyclohexene and 1-methyl-4-isopropylcyclohexene than for cyclohexene or 4-methylmethylenecyclohexane.

Hydration of Acetylenes Catalysed by Rhodium(III) Chloride Complexes

B. R. JAMES and G. L. REMPEL, *Ibid.*, (4), 863–865

$[Rh(H_2O)_{6-n} Cl_n]^{(n-3)-}$ catalyses acetylene hydration under mild conditions. Substitution inert cationic species are completely inactive. Activity then increases with substitution lability up to a maximum at $n = 5$, while the hexachloro complex is inactive. Thus a ligand H_2O molecule is necessary for hydration to occur. The system is similar to one with Ru (III) and its kinetics and mechanism are discussed.

Oxidative Coupling of Aromatic Compounds in Systems Incorporating Ruthenium Complexes

N. F. GOL'DSCHLEGER and M. L. KHIDEKEL', *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, (3), 675–682

$RuOHCl_3$ and CH_3COONa in CH_3COOH are agents for oxidative coupling of phenols. H_2O_2 oxidises various phenol derivatives by oxidative coupling in the presence of $RuOHCl_3$.

FUEL CELLS

Electrochemical Oxidation of Multicomponent Hydrocarbon Fuels. I. Studies with *n*-Octane Based Fuels Containing Aromatic, Olefin, and Naphthenic Components

E. LUKSHA and E. Y. WEISSMAN, *J. Electrochem. Soc.*, 1969, **116**, (1), 118–122

II. Long-term Performance Studies with *n*-Octane Based Fuels Containing Aromatic, Olefin, and Naphthenic Components

J. F. LENNON, E. LUKSHA and E. Y. WEISSMAN, *Ibid.*, 122–125

Using porous Pt black Teflon electrodes in 95 wt% H_3PO_4 at 150–200°C the performance of anodes operating on binary mixtures of *n*-octane and small amounts of hydrocarbon additives was found to depend on the nature of the additive. Increase in anode voltage resulted with increase in molecular weight or complexity of the aromatic molecules in aromatic additives. There was a relationship between types of olefins and per-

formance with olefin additives. Anode over-voltage decreased as the number of allylic H atoms increased. Gains in performance could be made by increasing cell operating temperature. Long-term performance was studied at 175°C. The effect of additives is not necessarily the same as in the short-term. When a certain total additive limit is exceeded, the decrease in anode performance can be severe over an extended period. Cycling characteristics associated with direct electrochemical oxidation of hydrocarbons are described in terms of distinct modes of performance fluctuation prior to establishment of steady-state conditions.

CHEMICAL TECHNOLOGY

High Current Density Chlorate Cell Using Platinised Anodes
J. R. NEWBERRY, W. C. GARDINER, A. J. HOLMES and R. F. FOGLE, *J. Electrochem. Soc.*, 1969, **116**, (1), 114-118
$NaClO_3$ was produced in a monopolar cell with platinised Ti anodes and steel cathodes. The 144A cell was tested continuously for 31 days and energy requirements were 6300 KWh d.c./ton $NaClO_3$. Replacement Pt was 5.3 g/ton $NaClO_3$. The cell was operated at 1 A/in², 110°C, 3.7V, pH 6.7. The feed contained 190 g/l NaCl and 330 g/l $NaClO_3$. Cell effluent was 110 g/l NaCl and 580 g/l $NaClO_3$. 1/8 in. electrode spacing was preferred with electrodes 3 ft high. The process is the subject of *U.S. Patent* 3,043,757.

ELECTRICAL AND ELECTRONIC ENGINEERING

Emission-Adsorption Properties of Films of Barium Oxide and of Barium Oxide Activated by Barium on Platinum Group Metals
V. V. NIKULOV and G. A. KUDINTSEVA, *Radiotekh. Elektron.*, 1969, **14**, (3), 516-521
The emission properties of Pt, Ir and Os were determined from their work functions by measuring their various contact potentials. BaO dust or BaO activated by Ba reduce the work functions. The high temperature stability of these films is good. The work functions of Pt and Ir can be reduced to ~1.4 eV at room temperature by this method.

The Reliability of Palladium-Silver Thick Film Resistors
R. C. HEADLEY, *NTZ*, 1969, **22**, (1), 53-56
Reliability testing of Pd-Ag thick film resistors enabled the optimum firing conditions to be established. Change of unloaded resistances after 1000 h was 0.1-1%. Drift values of loaded resistances were essentially lower.

TEMPERATURE MEASUREMENT

Stability and Calibration of Miniature Platinum Resistance Thermometers
W. V. JOHNSTON and G. W. LINDBERG, *Rev. sci. Instrum.*, 1968, **39**, (12), 1925-1928
Miniature Pt resistance thermometers weighing ~1g were evaluated as substitutes for capsule-type instruments. They were calibrated between 12 and 373K at fixed points and by comparison with a NBS standard instrument. Above 90K IPTS requirements were met but below 90K $R_T/R_{273.15}$ drops slower than for capsule-type thermometers, perhaps due to geometric strains in the Pt element. Interpolation allowed a table to be plotted with a smooth curve through the data to better than 0.002 deg K. R_0 for these thermometers over 12 months was reproducible to 10 ppm.

Precious-metal Thermocouples
D. W. RHYS, *Metals Mater.*, 1969, (Mar.), 47-60
A review of the development and applications of precious-metal thermocouples. A short appendix modifies the article in the light of the IPTS-68.

NEW PATENTS

METALS AND ALLOYS

Metallising Compositions
E. I. DU PONT DE NEMOURS & CO.
British Patent 1,144,930
A noble metal alloy metallising composition comprises a Pd-Au, Pt-Au, Ag-Au, Ag-Pt or Pd-Pt alloy in powder form (average particle size not greater than 40 μ). The alloy powder is dispersed in an organic vehicle (which may con-tain a vitreous binder) and constitutes 10-70 wt% of the metallising composition.

Finely Divided Metals of the Platinum Group
MONSANTO CO.   *British Patent* 1,146,530
A salt of a Pt metal is reduced in the presence of an alcohol, acetal, ketone, ether, carboxylic acid ester or olefine which complexes the metal formed. The complex is then decomposed.