

# ABSTRACTS

## of current literature on the platinum metals and their alloys

### PROPERTIES

#### Presence of Depleted Zones in Platinum

M. J. ATTARDO and J. M. GALLIGAN, *Phys. Rev. Letters*, 1966, **17**, (4), 191-193

Field ion microscopy of annealed Pt before and after irradiation by neutrons revealed large disturbances of the lattice apparently introduced by isolated damage events.

#### A Field Ion Microscope for Operation at 4.2°K

M. J. ATTARDO, J. M. GALLIGAN and J. SADOFSKY, *J. Sci. Instrum.*, 1966, **43**, (8), 607-608

A field ion micrograph of Pt with the tip at 4.2°K shows striking uniformity of intensity over the specimen surface, generally increased intensity and better resolution. Details of the liquid He and N cooling system for the instrument are described.

#### The Activity of Oxygen in the Liquid Fe-Pt Alloy System

E. S. TANKINS and W. A. SIPES, *A.S.M. Trans. Q.*, 1966, **59**, (3), 535-543

Equilibrium studies of  $H_2(g) + O = H_2O(g)$  at 1500-1700°C in liquid 10 and 30% Pt-Fe alloys enabled measurement of the standard free-energy changes when the standard state was 1% dissolved  $O_2$  solution. The equilibrium constant was determined for compositions up to 60 wt.% Pt at 1550°C. The interaction parameter  $\epsilon = +0.004$  is valid for compositions up to 20 wt.% Pt.

#### Nonstoichiometric A15-type Phases in the Systems Cr-Pt and Cr-Os

R. M. WATERSTRAT and E. C. VAN REUTH, *Trans. Met. Soc. A.I.M.E.*, 1966, **236**, (8), 1232-1233

Nonstoichiometric A15-type phases were observed in the Cr-Pt and Cr-Os systems. X-ray and metallographic studies established that they occur at  $21 \pm 1$  at.% Pt after vacuum annealing for a week at 1200°C and at  $28 \pm 1$  at.% Os after annealing for a day at 1400°C.

#### The Rate of Diffusion of Hydrogen through Palladium

A. A. RODINA and N. I. DORONICHEVA, *Zh. Fiz. Khim.*, 1966, **40**, (7), 1450-1456

Rate of  $H_2$  diffusion through Pd  $\propto \sqrt{(\text{incident } H_2 \text{ pressure})}$ .  $\log(\text{permeability}) \propto 1/T$  at 300-500°C, but not always at lower temperatures. Pd permeability is highly dependent on its surface area and preparation. It is greatest and most reproducible when the Pd foil is sealed by clamping between Cu gaskets. Soldering or welding the foil in air or in a poor vacuum sharply reduces its

permeability, which only recovers after repeated heating in  $H_2$ . Permeability of Pd foil produced by rolling pure Pd monocrystals differs by 20% from that of commercial grade Pd.

#### Investigation of Changes of the Properties of Palladium and Some of its Alloys during Reactions with Hydrogen

A. A. RODINA, M. A. GUREVICH, V. A. STROEVA and N. I. DORONICHEVA, *Ibid.*, (9), 2046-2052

Except for 50 wt.% Ag-Pd, the permeability for  $H_2$  of the alloys tested is greater than that of Pd above 300°C. The permeability of 18.5 wt.% Ag-Pd increased with use. Greatest stability after repeated heating and cooling in  $H_2$  was obtained with 5 wt.% Ni-10 wt.% Ag-Pd, 10 wt.% Au-Pd and 35 wt.% Ag-Pd. X-ray analysis showed that the low stability of 18.5 wt.% Ag-Pd after similar treatment is due to increase of  $\alpha$ -phase lattice spacing, and to  $\alpha \rightleftharpoons \beta$  phase conversion, which reduced the contact between the alloy and  $H_2$  during heating and cooling.

#### Stabilising a Spacecraft by Sunlight

R. L. SOHN, *New Scientist*, 1966, **31**, (510), 425-426

A suggested stabiliser consists of solar sails with an honeycomb steel core and Pd plate surfaces.  $H_2$  is contained in the core under pressure and diffuses through the Pd surfaces at a rate dependent on the heat from solar radiation. The gas diffusion creates a reaction which maintains the spacecraft in the desired attitude.

#### Hydrogen in Palladium Alloys

H. BRODOWSKY and H. HUSEMANN, *Ber. Bunsengesell. Phys. Chem.*, 1966, **70**, (6), 626-630

$H_2$  absorption isotherms of 4.78 at.% Sn-Pd, 5 at.% Pb-Pd, 5 at.% Rh-Pd and 16.7 at.% Ni-Pd at 30-175°C, 1-800 Torr were measured gas-volumetrically. Thermodynamic excess functions of these systems are discussed. The effect of alloy additions suggests that the four outer electrons of Sn and Pb compete with electrons of  $H_2$  in filling the  $4d$ -band but that Rh increases the number of vacancies in that band. Strain energy for proton entry into octahedral holes is reduced by alloy additions with relatively large atomic volume, and vice versa.

#### Speed of Sound in the Alloys Pd-Rh and Pd-Ag

O. BELMAHI, M. MERCK, E. PERRÉARD, M. PETER, E. WALKER and J. R. SCHRIEFFER, *Helv. Phys. Acta*, 1966, **39**, (4), 338-354

Impulses from piezoelectric and magnetostrictive transducers were used to measure the transverse, torsional, longitudinal and extensional speeds of

sound at 77 and 300°K as a function of the mean atomic number  $\bar{M}$  of Rh-Pd and Ag-Pd alloys. 5% Rh-Pd shows maxima in the electronic contribution of the specific heat  $\gamma$  and in the susceptibility  $\chi_d$ , and its bulk modulus  $\alpha$  shows a slight minimum.  $\Delta\alpha = \alpha(300^\circ\text{K}) - \alpha(77^\circ\text{K})$  shows a broad maximum. Temperature increment of the shear modulus  $\Delta G = G(300^\circ\text{K}) - G(77^\circ\text{K})$  shows a narrow peak which correlates with the temperature increment  $\Delta\chi_d$  of the susceptibility.

#### Ordering Effects in Equiatomic Au-Pd Alloys

V. I. IVERONOVA and A. A. KATSNEL'SON, *Kristallografiya*, 1966, **11**, (4), 576-580

Ordering of equiatomic Au-Pd alloy samples increased during successive 0.5 h annealings at temperatures up to 500°C and analogously affected the Hall effect and electrical conductivity of specimens. Plastic deformation sharply decreased ordering.

#### The Effect of Periodic Antiphase Domain Structure on the Mechanical Properties of Copper-Palladium Alloys

V. I. SYUTKINA and E. S. YAKOVLEVA, *Fiz. Tverd. Tela*, 1966, **8**, (9), 2688-2694

The presence of periodic antiphase domain structures strongly affects the behaviour of Cu-Pd alloys under stress. Strengthening mechanisms are discussed.

#### Magnetic Susceptibility of Iron-rich Face-centred Cubic Iron-Palladium Alloys

S. ARAJS, *Phys. Status Solidi*, 1966, **15**, (2), 501-506

Mass magnetic susceptibilities of 1.0, 3.0, 4.9, 7.9, 10.0, 11.9, and 15.3 at.% Pd-Fe f.c.c. alloys and of pure f.c.c. Fe, measured at 1500°K, do not follow the Curie-Weiss law.  $1/\chi T$  plotted against  $1/T$ , where  $\chi$  is magnetic susceptibility and  $T$  is absolute temperature, indirectly reveals the antiferromagnetic nature of Fe, which is gradually reduced by alloying with Pd.

#### Close Order and K-Effect in the Pd-W and Pd-Co Alloys

SH. A. ALIMOV and A. A. KATSNEL'SON, *Fiz. Met. Metalloved.*, 1966, **22**, (3), 468-470

Ordering in 11.3 at.% W-Pd and in 15 and 25 at.% Co-Pd was studied. Annealing of the alloys increases the effect and also, for 25 at.% Co-Pt, the electrical resistivity  $\rho$ . Raising the annealing temperature from 700 to 900°C causes no noticeable change of resistivity. The  $K$ -effect occurs in the Co-Pd as well as in W-Pd alloys.

#### X-ray Diffraction and Thermo-analytical Investigation of the Palladium-Phosphorus System

L. O. GULLMAN, *J. Less-Common Metals*, 1966, **11**, (3), 157-167

X-ray diffraction and differential thermal analysis

of the Pd-P system at 300-1100°C revealed the phases Pd<sub>8</sub>P, Pd<sub>6</sub>P, Pd<sub>4.8</sub>P, Pd<sub>3</sub>P, Pd<sub>2</sub>P<sub>23</sub>, Pd<sub>7</sub>P<sub>3</sub> and PdP<sub>2</sub>. Pd<sub>4.8</sub>P, Pd<sub>3</sub>P and probably PdP<sub>2</sub> melt congruently; the others decompose peritectically on heating. On cooling, Pd<sub>4.8</sub>P decomposes eutectoidally into Pd<sub>6</sub>P and Pd<sub>3</sub>P. Limits of the homogeneity region, cell parameter/composition curves and density/composition data were determined for Pd<sub>3</sub>P. Pd<sub>4.8</sub>P is monoclinic with  $a = 5.0059 \pm 0.0003 \text{ \AA}$ ,  $b = 7.6082 \pm 0.0005 \text{ \AA}$ ,  $c = 8.4199 \pm 0.0005 \text{ \AA}$ ,  $\beta = 95.640 \pm 0.005^\circ$ .

#### The Magnetic Susceptibilities of Pd-Cd, Pd-Sb, and Pt-Cu Binary Alloys

D. J. LAM and K. M. MYLES, *J. Phys. Soc. Japan*, 1966, **21**, (8), 1503-1507

Magnetic susceptibilities of Pd-Cd, Pd-Sb and Pt-Cu alloys were measured at 300-4.2°K and plotted against their compositions. Factors contributing to the susceptibility were assessed. Spin paramagnetic susceptibility is discussed in terms of the rigid-band model of alloying.

#### Nitrogen Adsorption on Iridium and Rhodium

V. J. MIMÉAULT and R. S. HANSEN, *J. Phys. Chem.*, 1966, **70**, (9), 3001-3003

No N<sub>2</sub> adsorption occurred during flashing of Ir and Rh filaments previously dosed with N<sub>2</sub> for 15 min at 300°K,  $4 \times 10^{-7}$  Torr but some did occur after thermal excitation of N<sub>2</sub> at >2000°K on W filaments in an ionisation gauge. A model of this is based on dissociation of N<sub>2</sub> to atomic N on W with subsequent adsorption rate proportional to atomic N concentration.

#### On Intermediate Phases in Alloys of Titanium with Iridium, Rhodium and Osmium

V. N. EREMENKO, T. D. SHTEPA and V. G. SIROTKENKO, *Poroshkovaya Met.*, 1966, (6), 68-72

Studies of the Ti-Ir, Ti-Rh and Ti-Os systems throughout the range of concentrations revealed the existence of  $\gamma$ ,  $\delta$  and  $\epsilon$  phases in the Ti-Ir system,  $\gamma$ ,  $\delta$  and  $\epsilon$  phases in the Ti-Rh system, but only  $\delta$  phase in the Ti-Os system. Ti<sub>3</sub>Ir is  $\gamma$  phase, TiIr is  $\gamma$  phase and TiIr<sub>3</sub> is  $\epsilon$  phase. The  $\delta$  phase in the Ti-Rh is monoclinic with  $a = 2.96 \pm 0.03$ ,  $b = 2.86 \pm 0.03$ ,  $c = 3.41 \pm 0.02 \text{ \AA}$ ,  $\beta = 90^\circ 37'$ .

#### Magnetic Properties of Rh-rich FeRh Alloy

E. M. HOFER and P. CUCKA, *J. Phys. Chem. Solids*, 1966, **27**, (9), 1552-1555

Magnetic moment per alloy atom decreases from 1.73  $\mu_B$  for 51% Rh-Fe to 0.18  $\mu_B$  for 63% Rh-Fe. The transition temperatures rise from 26° to 78°C over the same composition range. The paramagnetic Curie point remains almost steady around  $367 \pm 3^\circ\text{C}$ . The decrease in paramagnetic Curie point remains almost steady around  $367 \pm 3^\circ\text{C}$ . The decrease in magnetic moment is probably due to increasing content of paramagnetic  $\gamma$  phase.

### Elastic Properties of Polycrystalline Sc, Re, Ru and Pt-21 Ir

H. L. BROWN, P. E. ARMSTRONG and C. P. KEMPTER  
*J. Less-Common Metals*, 1966, **11**, (2), 135-140  
Polycrystalline Sc, Re, Ru and 21% Ir-Pt tested at 23°C have Young's moduli 0.770, 4.63, 4.47 and  $2.18 \times 10^6$  kg/cm<sup>2</sup> respectively; shear moduli 0.294, 1.78, 1.73 and  $0.899 \times 10^6$  kg/cm<sup>2</sup>; bulk moduli 0.672, 3.78, 3.65 and  $1.25 \times 10^6$  kg/cm<sup>2</sup>; Poisson's ratios 0.31, 0.30, 0.30 and 0.21; specific electrical resistivities 86.6, 17.4, 7.06 and 29.9  $\mu\Omega$ cm at 20°C.

## CHEMICAL COMPOUNDS

### Acetylenic Complexes of Palladium

E. O. GREAVES and P. M. MAITLIS, *J. Organomet. Chem.*, 1966, **6**, (1), 104-106  
Rapid polymerisation of acetylenes by Pd(II) compounds prevents the formation of complexes of the type  $RC_2R'PdCl_2X$ , where X=Cl, amine, etc., but it has proved possible to replace two phosphines in  $(Ph_3P)_4Pd$  by acetylenes bearing strongly electron-withdrawing substituents.

### Chlorination of Rhodium and Thermal Conversion of the Trichloride

YA. I. IVASHENTSEV and R. I. TIMONOVA, *Zh. Fiz. Khim.*, 1966, **11**, (10), 2189-2192  
Reactions of Rh with Cl<sub>2</sub>, HCl and CCl<sub>4</sub> were studied at 500°C. Dilution of Cl<sub>2</sub> by O<sub>2</sub> to > 20% Cl<sub>2</sub> prevented formation of RhCl<sub>3</sub>. RhCl<sub>3</sub> melted in a stream of Cl<sub>2</sub> and partially sublimated and dissociated. Its crystal hydrate can be dehydrated in one stage at 105-140°C. H<sub>2</sub> reduced anhydrous RhCl<sub>3</sub> to Rh but air decomposed it to oxide.

### Production and Properties of Osmium Heptafluoride

O. GLEMSER, H. W. ROESKY, K.-H. HELLBERG and H.-U. WERTHER, *Chem. Ber.*, 1966, **99**, (8), 2652-2662  
Pale yellow OsF<sub>7</sub>, formed by heating Os with F<sub>2</sub> at 350-400 atm, 500-600°C, is extremely hygroscopic and F<sub>2</sub> begins to separate above 100°C.  $OsF_7 \rightarrow OsF_6 + \frac{1}{2}F_2$  occurs slowly at room temperature. Mass spectra, magnetic susceptibility measurements, ESR measurements and Ir spectra indicate the possible existence of OsF<sub>8</sub> and show that OsF<sub>7</sub> has the configuration D<sub>5h</sub>, that of a pentagonal bipyramid.

### High Pressure Synthesis of Arsenopyrite-type Ternary Compounds

M. D. BANUS and M. C. LAVINE, *Mat. Res. Bull.*, 1966, **1**, (1), 3-12  
OsSbSe, OsSbTe, OsBiSe and RuBiSe were synthesised for the first time at 35-50 kbar. The Os compounds are monoclinic. Resistivity measurements on OsSbSe and on OsSbTe suggest that they are extrinsic semiconductors.

### Structural Investigations of $\beta$ -RuCl<sub>3</sub>, RuBF<sub>3</sub> and RuI<sub>3</sub>

H. G. VON SCHNERING, K. BRODERSEN, F. MOERS, H. K. BREITBACH and G. THIELE, *J. Less-Common Metals*, 1966, **11**, (4), 288-289  
The three compounds are of the TiI<sub>3</sub> structural type with hexagonal crystals and the following lattice parameters:  $\beta$ -RuCl<sub>3</sub>, a=6.12<sub>6</sub>, c=5.65<sub>3</sub>Å, c/a=0.923; RuBr<sub>3</sub>, a=12.924, c=5.860 Å, c/a=0.453; RuI<sub>3</sub>, a=6.982, c=6.231, c/a=0.892.

### Metalocene Polymers. XV. Polymers Containing the Ruthenocene System

E. W. NEUSE, *J. Organomet. Chem.*, 1966, **6**, (1), 92-95  
Ruthenocene-containing polymers with a structure in which 1,2-, 1,3-, and 1,1'-C<sub>10</sub>H<sub>8</sub>Ru groups are interlinked in a random sequence distribution by CH<sub>2</sub> or variously substituted methinyl bridges have been obtained by ZnCl<sub>2</sub>-catalysed melt condensation of ruthenocene with aldehydes, as previously done with ferrocene-aldehyde condensations, but more rigorous reaction conditions were required.

## ELECTROCHEMISTRY

### The Reversible Oxygen Electrode

J. P. HOARE, *Nature*, 1966, **211**, (5050), 703-705  
A review of the mechanisms occurring at the Pt surface of the reversible O<sub>2</sub> electrode. (17 refs.)

### Some Effects of Nitric Acid on Pt/O<sub>2</sub> Cathodes

J. P. HOARE, S. G. MEIBUHR and R. THACKER, *J. Electrochem. Soc.*, 1966, **113**, (10), 1078-1082  
O<sub>2</sub> and not N<sub>2</sub> causes the improved polarisation characteristics of Pt/O<sub>2</sub> cathodes treated with HNO<sub>3</sub>. It is dissolved in the surface layers of the metal as an alloy of Pt and O atoms several layers deep. This surface is a good catalyst for O<sub>2</sub> reduction and H<sub>2</sub>O<sub>2</sub> decomposition. It retains its activity for O<sub>2</sub> reduction over extended periods. Attempts to make a porous electrode of this type by similar techniques as for bright Pt failed.

### The Rate of Ionisation of Hydrogen on Semi-immersed Platinum Electrodes in Alkaline Solutions

E. A. OSTROVIDOV and A. L. ROTINYAN, *Zh. Prikladnoi Khim.*, 1966, **39**, (8), 1742-1747  
Studies showed that, for high polarisation, ionisation of H<sub>2</sub> is not a film mechanism. Results indicated kinetic problems and suggested that ionisation of H<sub>2</sub> only occurs at active centres on the Pt electrode depending on the amount reaching them.

### Area Changes of Electrodeposited Platinum Black

R. THACKER, *Nature*, 1966, **212**, (5058), 182-183  
Measurements of area changes of Pt black

deposited on Pt wires in 5M  $O\text{-H}_3\text{PO}_4$  at 25 and 80°C demonstrated the effects of time, temperature and electrode composition, including additives, on the sintering properties of Pt black electrodeposits in aqueous solution. Recrystallisation of unsupported Pt blacks occurs slowly at ambient temperatures but more quickly at enhanced temperatures.

### The Permeation of Electrolytic Hydrogen through Platinum

E. GILEADI, M. A. FULLENWIDER and J. O'M. BOCKRIS, *J. Electrochem. Soc.*, 1966, **113**, (9), 926-930

Absorption and permeation of electrolytic  $H_2$  through Pt foils was observed directly by an electrochemical method at 50-80°C. Diffusion coefficient at 70°C was  $3.4 \times 10^{-9}$  cm<sup>2</sup>/sec.; apparent energy of activation was 9.6 kcal/g atom. Concentration of absorbed  $H_2$  just below the cathode surface was  $2.7 \times 10^{-5}$  g atom/cm<sup>3</sup>. Atomic H tended to concentrate in areas of high strain within the metal where it could be in a lower energy state.  $H_2$  permeation was detectable only when the cathodic surface of the membrane became poisoned.  $H_2$  embrittlement phenomena resembled those in Fe and steel. Variation of cathodic overpotential with time was related to the change in  $H_2$  concentration in the metal near the cathodic surface.

### Electrode Kinetics of Oxygen Evolution and Dissolution on Rh, Ir, and Pt-Rh Alloy Electrodes

A. DAMJANOVIC, A. DEY and J. O'M. BOCKRIS, *Ibid.*, (7), 739-746

Determinations of electrode kinetics of Rh, Ir and Pt-Rh electrodes showed that each possesses two regions of constant  $\delta(\ln i_{\text{anodic}})/\delta V$ . Catalytic activity above  $\sim 1.4$ V (versus NHE) was  $i_{\text{Pt}} < i_{\text{Pt-Rh}} < i_{\text{Rh}} < i_{\text{Ir}}$ . The anodic side of the alloy behaved like Rh; the cathodic side like Pt. Time decay was conventional except that the anodic side of Pt-Rh behaved like Pt. Stoichiometric numbers were  $\sim 2$ . After anodic polarisation, Pt-Rh electrodes behaved as if the substrate was an individual area of Pt and Rh oxides.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Kinetics of Pd<sup>II</sup> Cementation on Sheet Copper in Perchlorate Solutions

E. A. VON HAHN and T. R. INGRAHAM, *Trans. Met. Soc. A.I.M.E.*, 1966, **236**, (8), 1098-1103

Studies on cementation rates of Pd<sup>II</sup> in 0.02-0.1 mM concentration in aqueous  $HClO_4$  on electropolished Cu cylinders, rotated at various high speeds to minimise thickness of the diffusion layer, showed that in 0.1 M  $HClO_4$  the cemented Pd is dense, adherent and shiny. First stage of this cementation is first order with respect to

Pd<sup>II</sup> concentration but the second stage is much slower. In 0.001 M  $HClO_4$  only the first stage is evident and the cementation rate is faster, due to  $(PdOH)^+$  ions predominating over unhydrolysed Pd<sup>II</sup>. This deposit is porous and loose. Pd-Cu alloys rather than pure Pd constitute the deposits. Activation energies are 9.5 kcal/mole in 0.1 M  $HClO_4$ , 7.4 kcal/mole in 0.001 M  $HClO_4$ .

### Investigation of the Mechanism of Anodic Dissolution and Electrodeposition of Palladium in Chloride Electrolytes

V. I. KRAVTSOV and M. I. ZELENSKII, *Elektrokhimiya*, 1966, **2**, (10), 1138-1143

Studies on 3M  $H_2SO_4$  solutions of Pd containing various amounts of  $Cl^-$  and  $PdCl_4^{2-}$  showed that the orders of the processes are:  $Cl^-$ (cathodic) 2.6;  $Pd^{2+}$ (cathodic), 0.91;  $Cl^-$ (anodic), 2.14. The results partially explain the electrochemical reactions which occur on Pd surfaces and in Pd complexes. The mechanism of slow electrochemical reactions is discussed.

## LABORATORY APPARATUS AND TECHNIQUE

### Gases in Underground Plants and Their Detection

J. O. COLYER, R. THARBY and R. C. SENIOR, *Post Off. Elect. Eng. J.*, 1966, **59**, (2), 80-84

Indicator, Gas, No. 5 is sensitive to the common property of flammability of gases which are dangerous in underground spaces. Samples of the atmosphere to be tested are passed over a heated Pt filament forming part of a Wheatstone bridge circuit. Catalytic action in the presence of flammable gases raises the filament temperature and unbalances the bridge. This method is faster than the older sodium-chloropalladite tester.

### Negative Staining with Osmium Tetroxide Vapour

P. BARLAND and M. ROJKIND, *Nature*, 1966, **212**, (5057), 84-85

Collagen fibres to be studied by electron microscopy were stained negatively by  $OsO_4$ , which gave delicate outlines of better contrast than other techniques.

## CATALYSIS

### Surface Catalysis of the Hydrogen-Oxygen Reaction on Platinum at Low Temperatures

F. LEDER and J. B. BUTT, *Am. Inst. Chem. Eng. J.*, 1966, **12**, (4), 718-721

Data from low-temperature  $H_2\text{-}O_2$  conversions over dilute  $Pt/Al_2O_3$  indicated a strong effect of product  $H_2O$  on reaction rate and second-order dependence of rate on  $p_{H_2}$  in the presence of excess  $O_2$ . Stable activity levels lower than previously reported were consistent with a chemi-

sorbed O<sub>2</sub> mechanism and with reaction conditions at a dilute catalyst. Activation energy at 100°C was 10 ± 2 kcal/mole.

### Catalytic Oxidation of Hydrogen – Intrapellet Heat and Mass Transfer

J. A. MAYMO and J. M. SMITH, *Ibid.*, (5), 845–854

High rates of oxidation of H<sub>2</sub> over 1.86 cm pellets of Pt/Al<sub>2</sub>O<sub>3</sub> particles mixed with Al<sub>2</sub>O<sub>3</sub> showed temperature differences > 300°C between centre and surface of pellets and also large temperature variations at their surfaces, depending on position. Intrapellet heat and mass transfer resistance were both important but only heat transfer resistance was significant between pellet and gas. A new method was devised for measurement of effective diffusivity under reaction conditions. Predictions gave results 7% greater than the experimental effectiveness factor.

### The Mechanism of Hydrogenolysis and Isomerisation of Hydrocarbons on Metals. II. Mechanisms of Isomerisation of Hexanes on Platinum Catalysts

Y. BARRON, G. MATRE, J. M. MULLER and F. G. GAULT, *J. Catalysis*, 1966, 5, (3), 428–445

Isomerisation of *n*-hexane, 2-methylpentane and 3-methylpentane over Pt films, Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/pumice, when compared with hydrogenolysis of methylcyclopentane, indicated that a common cyclopentane intermediate was involved in both reactions and was adsorbed on metal sites of the catalysts. Formation of 2,3-dimethylbutane from hexanes and of C<sub>6</sub>H<sub>6</sub> from methylcyclopentane also occur on Pt films. Only aromatisation occurs when 1,1,3-trimethylcyclopentane reacts with H<sub>2</sub> on Pt film at 300°C.

### Chemisorption and Catalytic Properties of Supported Platinum

J. A. CUSUMANO, G. W. DEMBINSKI and J. N. SINFELT, *Ibid.*, 471–475

Chemisorption studies for H<sub>2</sub> on Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> showed that Pt dispersion is greater on Pt/Al<sub>2</sub>O<sub>3</sub>. Catalysts were prepared by impregnation of the supports by H<sub>2</sub>PtCl<sub>6</sub> followed by reduction in H<sub>2</sub>. The rate of dehydrogenation of cyclohexane on these catalysts is also higher on Pt/Al<sub>2</sub>O<sub>3</sub> which is attributed to the greater Pt dispersion. Adsorption of H<sub>2</sub> on Pt at 70% surface coverage is 7–8 kcal/mole exothermic for Pt/Al<sub>2</sub>O<sub>3</sub>.

### On the Specific Activity of Platinum Catalysts

M. BOUDART, A. ALDAG, J. E. BENSON, N. A. DOUGHARTY and C. G. HARKINS, *Ibid.*, 6, (1), 92–99

Cyclopropane hydrogenations at 0°C showed that specific activity is independent of Pt content in Pt/η-Al<sub>2</sub>O<sub>3</sub> and Pt/γ-Al<sub>2</sub>O<sub>3</sub>, and of whether the support is Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub>. It is almost the same in highly dispersed Pt catalyst samples as in Pt foil. Such samples were merely twice as active as

sintered, less dispersed or foil catalysts but their specific surface area varied by >4 orders of magnitude. They were also more susceptible to O<sub>2</sub> poisoning.

### The Mechanism of Heterogeneous Catalysis

R. L. BURWELL, *Chem. Engng. News*, 1966, 44, (36), 56–67

A review of present knowledge of heterogeneous catalysis in which the importance of the Pt metals is outstanding. (9 refs.)

### Some Agents Influencing the Surface Area of Platinum in Reforming Catalysts

Z. JAWORSKA-GALAS and J. WRZYSZCZ, *Chem. Stosowana, Ser. A*, 1966, 10, (1), 105–112

The specific surface of Pt/Al<sub>2</sub>O<sub>3</sub>, determined by H<sub>2</sub> reduction of O<sub>2</sub> chemisorbed on it, was 2.5–190 m<sup>2</sup>/g, depending on Al<sub>2</sub>O<sub>3</sub> preparation, method of Pt impregnation and calcination temperature. Pt surface area decreased in use but oxidising regeneration restored or even augmented the original area. Preparation included impregnation of dried or hydrated Al<sub>2</sub>O<sub>3</sub> with H<sub>2</sub>PtCl<sub>6</sub> or PtS<sub>2</sub> followed by drying and calcination for 2–4 h at 500–800°C. Cl content was 1–2%, depending on the preparation.

### On the Damaging of Platinum Catalysts in Their Large Scale Use

H. BLUME, C. SZKIBIK, F. PFEIFFER, H. KLOTZSCHE, E.-R. STRICH, K. BECKER and G. WEIDENBACH, *Chem. Tech.*, 1966, 18, (8), 449–454

Results are reported of a year-long study designed to increase the life of Pt reforming catalysts. Studied were ways in which catalysts are damaged during installation and by S-, N- and O-complexes and by inorganic components during use. The effect of the conditions during regeneration was studied also.

### The Role of Hydrogen in the Dehydrogenation of Cyclohexane on Platinum

V. A. DRUZ', N. I. UTEGULOV and D. V. SOKOL'SKII, *Zh. Fiz. Khim.*, 1966, 40, (7), 1483–1488

Potentiometric studies indicated that the degree to which the Pt catalyst surface is charged with H<sub>2</sub> increases with higher temperature and faster process rate. Dehydrogenation of cyclohexane on Pt occurs when the surface is comparatively highly charged with H<sub>2</sub> and when the potential variation is 20–80 mV. Increased H<sub>2</sub> adsorption on Pt displaces C<sub>6</sub>H<sub>6</sub> and restricts hydrogenation of C<sub>6</sub>H<sub>6</sub>.

### Catalytic Conversion of Dicyclopentylmethane on Pd-, Pt-, Co-Alumina Catalysts in Catalytic Reforming Conditions

N. I. SHUIKIN and I. I. VOZNESENSKAYA, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1966, (8), 1455–1456

Conversions of dicyclopentylmethane were carried out at 450°C, 30 atm H<sub>2</sub>, volume rate 0.3 h<sup>-1</sup>, H<sub>2</sub>: hydrocarbon = 5:1 over 0.5% Pd/Al<sub>2</sub>O<sub>3</sub>,

0.5% Pt/Al<sub>2</sub>O<sub>3</sub>, 10% Co/Al<sub>2</sub>O<sub>3</sub>. Isomerisation to decalin occurs most easily on the Pd catalyst. Hydrogenolysis of both rings to form C<sub>11</sub>H<sub>24</sub> isoalkanes occurs on the Pt catalyst together with the formation of methylcyclopentane and cyclopentane. Slight isomerisation occurs on the Co catalyst and formation of various alkylcyclopentanes.

### Study of Supported Catalysts by the Exoelectronic Emission Method. VI. Platinum on Magnesium Oxide and Chromium Oxide

A. S. SHASHKOV, V. M. MOZZHUKHINA, I. V. KRYLOVA and N. I. KOBOZEV, *Zh. Fiz. Khim.*, 1966, **40**, (8), 1965-1968

Increase of Pt concentration on the surface of the support in Pt/MgO and Pt/Cr<sub>2</sub>O<sub>3</sub> catalysts leads to increases in both catalytic activity and exoelectronic emission. The oxides have similar surface electronic properties. Exoelectronic emission is first order with respect to paramagnetism for these samples.

### The Modification of Raney Nickel Catalysts by Additions of Transition Metals. III. Electro-oxidation of Hydrogen and Catalytic Hydrogenation on Raney Nickel-Platinum Alloys

A. B. FASMAN, A. ISABEKOV, D. V. SOKOL'SKII, A. A. PRESNYAKOV and K. T. CHERNOUSOVA, *Ibid.*, (9), 2086-2093

Pt added to Raney Ni considerably increases its electrochemical activity as anode for the oxidation of H<sub>2</sub> and its catalytic activity for the hydrogenation of potassium maleate, *o*-nitrophenol and *n*-quinone. During manufacture Pt forms a solid solution with NiAl<sub>3</sub> and Ni<sub>2</sub>Al<sub>3</sub>, which leads to growth in the lattice parameters of the Raney Ni.

### The Isomerisation of Aliphatic Hydrocarbons over Evaporated Films of Platinum and Palladium

J. R. ANDERSON and N. R. AVERY, *J. Catalysis*, 1966, **5**, (3), 446-463

Paraffins reacted over Pd films are mainly hydrocracked whereas over Pt films on mica or on NaCl there is considerable isomerisation. The mechanisms of these reactions are discussed for oriented and unoriented films.

### Investigation of the Mechanism of Catalytic Decomposition of Formic Acid Vapour on Palladium

A. A. KHOMENKO, L. O. APEL'BAUM and M. I. TEMKIN, *Kinetika i Kataliz*, 1966, **7**, (4), 671-678  
Studies of HCOOH dehydrogenation on Pd membranes at 225-275°C,  $p_{\text{HCOOH}} = 0.01-0.1$  atm showed that reaction rate  $\propto p_{\text{HCOOH}}^{0.66}$ ; activation energy = 16.2 kcal/mole. Studies involving H<sub>2</sub> excluded a bond mechanism but a dissociative

mechanism applied to calculations for an heterogeneous surface explained the kinetic equation produced.

### Hydrogenation of Ethylene and Propylene over Palladium Hydride

R. J. RENNARD and R. J. KOKES, *J. Phys. Chem.*, 1966, **70**, (8), 2543-2549

Studies of the rate of C<sub>2</sub>H<sub>4</sub> hydrogenation as a function of H<sub>2</sub> concentration, temperature,  $p_{\text{C}_2\text{H}_4}$  and  $p_{\text{H}_2}$  over Pd hydride and deuteride show it to be nearly zero order in  $p_{\text{C}_2\text{H}_4}$  and  $p_{\text{H}_2}$  at 78°C but first order in hydride concentration. The first order rate constant decreases with hydride concentration but activity increases. An inverse isotope effect occurs with D<sub>2</sub>; the main deuterated product is C<sub>2</sub>H<sub>4</sub>D<sub>2</sub>. The slow step is probably addition of adsorbed H atoms to adsorbed C<sub>2</sub>H<sub>4</sub> or adsorbed ethyl radicals. Similar studies were carried out using C<sub>3</sub>H<sub>6</sub>.

### Catalytic Oxidation of Methane on Palladium-Gold Alloys

J. G. FIRTH, *Trans. Faraday Soc.*, 1966, **62**, (9), 2566-2576

A microcalorimetric method for the determination of rates, orders and apparent activation energies of heterogeneous catalytic reactions was applied to the complete oxidation of CH<sub>4</sub> on Pd-Au alloys and indicated that the *d*-orbitals of the catalyst take part in the reaction. A relatively stable adsorbed intermediate appears to be part of the reaction sequence. Changes in the apparent activation energies seem due partly to changes in the heat of formation of this intermediate. Two types of microcalorimeter were used: one consists of catalyst deposited on an Al<sub>2</sub>O<sub>3</sub> bead in which is embedded a Pt coil connected to a Wheatstone bridge circuit; the other possesses a Pt alloy thermocouple in place of the coil.

### The Catalyst Platinum/Polyvinyl Alcohol

D. V. SOKOL'SKII, O. A. TYURENKOVA, V. A. DASHEVSKII and G. P. YASTREBOVA, *Zh. Fiz. Khim.*, 1966, **40**, (9), 2243-2249

As the polyvinyl alcohol content of colloidal Pt/polyvinyl alcohol increases the rate of hydrogenation at first increases and then begins to fall. The catalyst with 20 mg Pt and 250 mg of polyvinyl alcohol in 10 ml solution has maximum activity. Pt separates out if the polyvinyl alcohol content falls below 2 mg/100 ml solution. Catalyst activity drops off according to the solvent in the order H<sub>2</sub>O > 0.01% NaOH > 50% C<sub>2</sub>H<sub>5</sub>OH. The catalyst is more active at room temperature than at 40°C. Reaction rate increases rectilinearly with catalyst content. Hydrogenation of allyl alcohols is zero order; reduction of C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> is first order. Rate of reduction of C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> in solvents falls in the order: H<sub>2</sub>O > CH<sub>3</sub>OH > dioxane > C<sub>2</sub>H<sub>5</sub>OH > acetone. The catalyst is regenerated by precipitation with alcohol and subsequent dissolution in H<sub>2</sub>O.

### Nonenzymatic Conversion of Penicillins to 6-Aminopenicillanic Acid

D. A. JOHNSON, C. A. PANETTA and R. R. SMITH, *J. Org. Chem.*, 1966, **31**, (8), 2560-2564

Nonenzymatic conversion of several *o*-nitrophenyl-substituted penicillins to 6-aminopenicillanic acid occurred by spontaneous cleavage of the side chain at room temperature after reduction to the substituted amine with H<sub>2</sub> over Pd/C, or, preferably, to the hydroxylamine with alkali borohydride in the presence of Pd/C.

### Homogeneous Catalysis. III. Isomerisation of Deuterio Olefins by Group VIII Metal Complexes

J. F. HARROD and A. J. CHALK, *J. Am. Chem. Soc.*, 1966, **88**, (15), 3491-3497

D<sub>2</sub> movements were studied during isomerisation of vinyl- and allyl-deuterated 1-olefins by homogeneous Rh- and Pd-complex catalysts in the presence and without an unlabelled olefin. With RhCl<sub>3</sub>, D<sub>2</sub> was redistributed to all C atoms in the allylic system, and intermolecular D<sub>2</sub> exchange to all C atoms of the unlabelled olefin occurred. With bis(benzonitrile)dichloropalladium catalyst the double-bond shift occurred by shift of D or H from C<sub>2</sub> to C<sub>1</sub>. Less intermolecular D<sub>2</sub> exchange occurred with less D<sub>2</sub> attached to doubly-bonded C atoms.

### The Mechanism of Isomerisation of Olefins with Transition Metal Catalysts

R. CRAMER and R. V. LINDSEY, *Ibid.*, 3534-3544

The proposed mechanism for olefin isomerisation with Rh, Pd, Pt, Ni or Fe catalysts and various cocatalysts involves rearranging a kinetically stable metal hydride with co-ordinated substrate olefin to a metal alkyl and then to the metal hydride complex of the isomeric olefin. The method of initial hydride formation depends on the cocatalyst and the oxidation state of the metal but isomerisation and hydride regeneration proceed via a reversible reaction involving the reduction of proton to hydride with concurrent two-electron oxidation of the metal.

### The Synthesis of Olefinic Cyanides from Olefins by Means of Palladium(II) Cyanide

Y. ODAIRA, T. OISHI, T. YUKAWA and S. TSUTSUMI, *Ibid.*, (17), 4105-4106

The first reported synthesis of olefinic cyanides from olefins was carried out efficiently using Pd(CN)<sub>2</sub>, probably by  $\pi$ -complex formation. CuCN and Ni(CN)<sub>2</sub> were less effective.

### The Mechanism of the Reaction of Nucleophiles with Alicyclic Olefin Palladium Complexes

M. GREEN, R. N. HASZELDINE and J. LINDLEY, *J. Organomet. Chem.*, 1966, **6**, (1), 107-108

PdCl<sub>2</sub> catalyses the reaction of cyclohexane with

CH<sub>3</sub>COONa in CH<sub>3</sub>COOH at 20°C in the presence of benzoquinone to yield 76% of cyclohex-2-enyl acetate and 24% of cyclohex-3-enyl acetate rather than cyclohex-1-enyl acetate. CuCl<sub>2</sub> hardly affected this result. The mechanism is discussed.

### Hydride Transfer Reactions Catalysed by Metal Complexes

H. B. CHARMAN, *Nature*, 1966, **212**, (5059), 278-279  
RhCl<sub>3</sub> catalysed the dehydrogenation of *iso*-C<sub>3</sub>H<sub>7</sub>OH to acetone at a decreasing rate as Rh was precipitated during the reaction. This involved the reversible transfer of an hydride ion from the  $\alpha$ C atom of the alcohol to form a Rh hydride intermediate which either reacted with a proton to give H<sub>2</sub> or decomposed to give Rh metal. No Rh precipitation occurred when using a RhCl<sub>3</sub>-SnCl<sub>2</sub> complex.

### Kinetics and Mechanism of the Homogeneous Catalytic Activation of Carbon Monoxide in Solutions. I. Catalytic Activity of Bromide Complexes of Pd(II)

G. G. KUTYUKOV, A. B. FASMAN, A. E. LYUTS, YU. A. KUSHNIKOV, V. F. VOZDVIZHENSII and V. A. GOLODOV, *Zh. Fiz. Khim.*, 1966, **40**, (7), 1468-1474  
CO reacts with bromopalladate(II) in aqueous solution by its introduction into the co-ordination sphere of the complex with subsequent oxidation therein. Bromopalladate(II) was studied by spectrophotometry in aqueous and acetonitrile solutions with [Br<sup>-</sup>]/[Pd<sup>2+</sup>] = 4-6000. Quantity of catalyst, temperature, concentrations of Br<sup>-</sup>, H<sup>+</sup>, and HBr, and p<sub>CO</sub> all affect the activity of [PdBr<sub>n</sub>]<sup>2-n</sup> during CO reduction of  $\alpha$ -naphthoquinone in 3:7 H<sub>2</sub>O-dioxane. [PdBr<sub>3</sub>H<sub>2</sub>O]<sup>-</sup> anions have most activity. The mechanism may be formation of an intermediate Pd(II) carbonyl-bromide complex, which decays to [PdBr<sub>n</sub>]<sup>2-n</sup>.

### II. Effect of the Concentration of Cations and Anions on the Kinetics of the Reduction of N-Benzoquinone

V. D. MARKOV, V. A. GOLODOV, G. G. KUTYUKOV and A. B. FASMAN, *Ibid.*, 1527-1532

The concentrations of H<sup>+</sup>, Cl<sup>-</sup> and Br<sup>-</sup> affect the activity of K<sub>2</sub>PdCl<sub>4</sub> and K<sub>2</sub>PdBr<sub>4</sub> solutions for the CO reduction of N-benzoquinone. The effect of acidity on activity was determined by the change amount of Pd(II) acidocomplex. Bromide complexes were 3-4 times as active as chloride complexes. Maximum activity of the solutions occurs in the range of conversion from [PdL<sub>3</sub>H<sub>2</sub>O]<sup>-</sup> to [PdL<sub>4</sub>]<sup>2-</sup>.

### III. Investigation of the Catalytic Activity of Compounds of the Transition Metals

V. D. MARKOV and A. B. FASMAN, *Ibid.*, 1564-1570

Oxidation of CO in aqueous solutions at low temperatures was studied using metallic ions as catalysts. Pd(II) acido complexes showed the maximum activity.

### The Reaction of Vinyl Halide-Palladium(II) Chloride Complexes with Nucleophiles: Catalytic Vinylation

E. W. STERN, N. L. SPECTOR and H. P. LEFTIN, *J. Catalysis*, 1966, **6**, (1), 152-153

$\text{PdCl}_2$  catalysed the reactions of vinyl chloride and  $\text{CH}_3\text{COOH}$  in iso-octane at room temperature, 2 atm pressure and of vinyl chloride and isopropyl alcohol under similar conditions, to form vinyl acetate and isopropyl acetal respectively. In these and similar reactions the reduction of  $\text{PdCl}_2$  to Pd did not occur. The mechanism of these reactions is believed to involve complex formation.

### Hydrogenation of Phosphatides on Palladium Catalysts in Solvents

G. A. POTLOVA and D. V. SOKOL'SKII, *Izv. Akad. Nauk Kaz. S.S.R., Ser. Khim.*, 1966, **16**, (1), 48-54

Cephalin fractions of soya phosphatides were hydrogenated at normal pressure and low temperature on Pd/ $\text{CaCO}_3$ , Pd/ $\text{BaSO}_4$ , Pd/ $\text{SiO}_2$  and Pd/C. Degreased soya phosphatides were hydrogenated similarly on 5% Pd/ $\text{CaCO}_3$ . Kinetic studies on mixed solvents in the latter reaction showed that the rate of hydrogenation is greatest when one solvent is  $\text{C}_6\text{H}_6$ .

### Hydrogenation of Rosin on a Palladium Catalyst

I. I. BARDYSHEV and E. B. SMIRNOVA, *Gidrolizn. i Lesokhim. Prom.*, 1966, **19**, (4), 4-6

Disproportionation to tar acids was the main reaction during the hydrogenation of rosin in  $\text{C}_6\text{H}_6$  solution in the presence of Pd catalysts at 150°C,  $p_{\text{H}_2} < 40$  atm and  $< 0.1\%$  Pd per unit wt. of rosin. Hydrogenation of rosin occurred at 150°C,  $p_{\text{H}_2} \approx 50-60$  atm in the presence of 0.2-0.4% Pd with  $> 1$  mol.  $\text{H}_2$  per mol. tar acid. Further increases of  $p_{\text{H}_2}$  and catalyst concentration gave no further significant rosin hydrogenation. Lower rate of hydrogenation occurred at lower temperatures and above 150°C the rate of disproportionation increased. Catalyst deactivation was prevented by adding one part of catalyst to remove poisons in the rosin and a further part to catalyse hydrogenation of pure rosin.

### The Hydrogenation of Acetylene. III. The Reaction of Acetylene with Hydrogen Catalysed by Alumina-supported Rhodium and Iridium

G. C. BOND and P. B. WELLS, *J. Catalysis*, 1966, **5**, (3), 419-427

Hydrogenations of  $\text{C}_2\text{H}_2$  over Rh/ $\text{Al}_2\text{O}_3$  at 18-150°C and over Ir/ $\text{Al}_2\text{O}_3$  at 45-185°C were ~ first order in  $\text{H}_2$ ; zero (Rh) or negative (Ir) order in  $\text{C}_2\text{H}_2$ . Under comparable conditions Rh was always more selective for  $\text{C}_2\text{H}_4$  production. Selectivity depended on all experimental variables.  $\text{C}_2\text{H}_4$  formation over both metals decreased

with increasing initial  $p_{\text{H}_2}$  and decreasing  $p_{\text{C}_2\text{H}_2}$  and temperature. Olefin hydrogenation was slow in the presence of  $\text{C}_2\text{H}_2$ , rapid in its absence. Rh, Ir, Pd, Pt catalysts for  $\text{C}_2\text{H}_2$  hydrogenation are compared.

### The Use of Supported Solutions of Rhodium Trichloride for Homogeneous Catalysis

G. J. K. ACRES, G. C. BOND, B. J. COOPER and J. A. DAWSON, *Ibid.*, **6**, (1), 139-141

Advantages of combining heterogeneous and homogeneous catalytic techniques were studied by dissolving  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  in ethylene glycol, adding this solution to Silocel suspended in  $\text{CH}_3\text{OH}$ , evaporating the latter to form a powdered catalyst, and using it to catalyse isomerisation of 1- $\text{C}_6\text{H}_{10}$  to *cis*- and *trans*-2- $\text{C}_6\text{H}_{10}$ .

### Hydrogenation of Phenylacetylene on Rhodium

A. M. SOKOL'SKAYA and K. K. KUZEMBAEV, *Izv. Akad. Nauk Kaz. S.S.R., Ser. Khim.*, 1966, **16**, (1), 78-84

Studies of the hydrogenation of phenylacetylene on 5% Rh/ $\text{BaSO}_4$  and on Rh black at 5, 15 and 30°C in  $\text{CH}_3\text{OH}$  and in 0.1 N HCl and KOH methanolic solutions showed that the first mol.  $\text{H}_2$  was added much more slowly than the second. The hydrogenation was not strictly selective; before 0.5 mol.  $\text{H}_2$  was added, ethylbenzene was detected. During the hydrogenation the catalyst surface was almost fully covered by  $\text{H}_2$ . The catalyst retained its activity after 5 or 6 successive hydrogenations of phenylacetylene.

### Organic Syntheses by Means of Noble Metal Compounds. XXV. Palladium-catalysed Carbonylation of Ethyl Acetylenemono- and -dicarboxylates

J. TSUJI and T. NOGI, *J. Org. Chem.*, 1966, **31**, (8), 2641-2643

$\text{PdCl}_2$  and 10% Pd/C catalysed the room temperature carbonylation in  $\text{C}_2\text{H}_5\text{OH}$  of ethyl acetylenemonocarboxylate to ethyl fumarate, ethyl-ethenetricarboxylate, ethyl-1,1,2-ethanetricarboxylate and ethyl-1,3-butadiene-1,1,4,4-tetracarboxylate, and of the dicarboxylate to ethyl-ethenetricarboxylate, ethyl-1,1,2-ethanetricarboxylate and ethyl-1,1,2,2-ethanetetracarboxylate. HCl in the medium affected the yields.

### XXVII. Decarbonylation of Acyl Halides Catalysed by a Rhodium Complex and Preparation of Acylrhodium Complexes by a Novel Addition Reaction of Acyl Halides

J. TSUJI and K. OHNO, *J. Am. Chem. Soc.*, 1966, **88**, (14), 3452-3453

Decarbonylation of acyl halides with  $\text{RhCl}(\text{Ph}_3\text{P})_3$  proceeds smoothly and efficiently to yield olefins, HCl and  $\text{RhClCO}(\text{Ph}_3\text{P})_2$  under mild conditions. The new acylrhodium complex  $\text{RCORhCl}_2$



(Ph<sub>3</sub>P)<sub>2</sub> can be isolated by carefully controlling the reaction conditions. Electrophilic attack on the Rh by the carbonyl C is thus possible.

### XXIX. Decarbonylation of Acid Halides and Carbonylation of Alkyl Halides Catalysed by Rhodium Complex

*Ibid.*, *Tetrahedron Letters*, 1966, (39), 4713-4716  
(PPh<sub>3</sub>)<sub>2</sub>RhCOCl efficiently catalyses the homogeneous decarbonylation of acyl and aroyl halides to olefins and aryl halides respectively, and the carbonylation of some alkyl halides, e.g. benzyl chloride to phenylacetyl chloride in C<sub>6</sub>H<sub>6</sub> at 150°C, 100 atm p<sub>CO</sub>.

## CATHODIC PROTECTION

### Corrosion Protection of Drying Cylinders in Paper-making Machines by Cathodic Polarisation

A. ALMAR-NAESS, *Corrosion Sci.*, 1966, 6, (5), 205-225

Electrochemical theory and practical details of the method of protecting cast iron drying cylinders using a Pt anode. (See *Platinum Metals Rev.*, 1966, 10, (2), 48-51).

## CHEMICAL TECHNOLOGY

### Selective Reductions with Electrolytically Produced Hydrogen

J. B. LEE and P. CASHMORE, *Chem. & Ind.*, 1966, (42), 1758-1759

An electrolytic cell containing 5% H<sub>2</sub>SO<sub>4</sub>, an anode of Pt gauze and a cathode of Ag-Pd alloy tube produced H<sub>2</sub> which reduced acetylenes to the corresponding olefins, and acetylenic alcohols and acids to the olefinic compounds. No *trans* olefins were produced. Neither were other types of compounds reduced.

## NEW PATENTS

### METALS AND ALLOYS

#### Palladium Alloy Tubes

J. BISHOP & CO. *U.S. Patent* 3,254,956

An improved process for the production of ultra-pure H<sub>2</sub> utilises a reaction tube made of porous ceramic impregnated with Fe, Ni or Pt and lined with a thin-walled Pd-alloy tube, preferably made of Pd-Ag alloy.

#### Nuclear Fuel Element

ATOMIC ENERGY COMMISSION

*U.S. Patent* 3,261,757

A nuclear fuel element for use in a chemonuclear

## TEMPERATURE MEASUREMENT

### Fifty Years of Temperature Measurement

J. A. HALL, *J. Sci. Instrum.*, 1966, 43, (8), 541-547

A survey of developments in thermometry since 1916 discusses the accuracy and reproducibility of the temperature scale itself and then the accuracy with which practical measurements may be made in terms of that scale. Pt metal thermocouples and the Pt resistance thermometer have become increasingly important and more accurate.

### Silver-Palladium as an Indicator of Thermal Gradients in Pellet Induration

H. W. HITZROT, L. V. FEGAN and R. A. LIMONS, *Trans. Soc. Mining Eng. A.I.M.E.*, 1965, 232, (2), 95-99

Ag-Pd wires with specific melting points from 2000 to 2500°F indicate pellet-bed temperatures in travelling-gate or shaft furnaces. Wires are encased in ceramic capsules which accompany a sample of green pellets in a Nichrome wire basket during firing. After exposure, each capsule is recovered from the basket and examined to find the maximum temperature attained. Disadvantage of the method is that it is not continuous but it is cheaper than thermocouples.

### The Total Hemispherical Emittance of Coated Wires

D. BRADLEY and A. G. ENTWISTLE, *Br. J. Appl. Phys.*, 1966, 17, (9), 1155-1164

A theory for the derivation of hemispherical spectral emittance and hence total hemispherical emittance, for a uniformly coated cylinder is applied to fine 10% Rh-Pt wires coated in fused SiO<sub>2</sub> at 340-1350°C and agrees with experiment. Effect of coating thickness is discussed.

reactor comprises an inner core composed of an alloy of 50-98 wt.% Pd, 1-30 wt.% U and 1-20 wt.% Pt and a 0.2-6μ external coating of Pt.

## ELECTROCHEMISTRY

### Electrolytic Technique for Hydrogen Recovery

AMERICAN CYANAMID CO. *British Patent* 1,039,411

An electrolytic process for separating and recovering H<sub>2</sub> from a gaseous mixture, where the gas-permeable anode is made of, or contains a Pt group metal, preferably Pt, Pd or Rh. See also 1,039,412.