

# ABSTRACTS

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

## PROPERTIES

### Fusion Curves for Graphite, Tungsten and Platinum up to 60 kbar

L. F. VERESHCHAGIN and N. S. FATEEVA, *Zh. eksper. teor. Fiz.*, 1968, **55**, (4), 1145-1152

Optical measurements on Pt agree well with those obtained by thermal analysis. The temperature of fusion of Pt increases linearly with pressure.

### Rheological Properties of Platinum at High Temperatures

V. O. SHESTOPAL, *Fiz. Metal. Metalloved.*, 1968, **26**, (6), 1127-1130

Measurements of the shear modulus, internal friction and creep of annealed and unannealed samples of Pt were carried out between 1300 and 1980°K and results are depicted graphically.

### Coherent and Incoherent Precipitation in the Gold-Platinum System

J. WEISE and V. GEROLD, *Z. Metallkunde*, 1968, **59**, (12), 904-909

Resistivity studies of 15, 20, 60 and 65 wt% Au-Pt wires during isothermal ageing and during re-heating to the homogenisation temperature showed two rates which can be attributed to coherent and to incoherent precipitation. The metastable coherent miscibility gap in the phase diagram was ~100-200 deg C below the stable incoherent gap. The temperature dependence of the rate of resistivity change at the start of annealing 65 wt% Au-Pt agreed with spinodal decomposition theory or a nucleation mechanism.

### Effect of Deformation on the Physico-mechanical Properties of an Alloy of Platinum with Silver

S. N. PAVLOVA, *Fiz.-khim. Mekhan. Mater.*, 1968, **4**, (4), 490-492

Studies of the deformation of 0.1-3 mm Ag-Pt alloy wires after quenching from 1000°C showed that wires of different diameter had different tendencies towards work-hardening. 99% deformation was required to obtain high strength in a 0.1 mm wire but for wires 0.2 mm diameter even 99.8% deformation only produced a UTS of 170 kg/mm<sup>2</sup>.

### Anomalous Low Temperature Susceptibility of Dilute Pt-Co Alloys

J. C. GALLOP and I. A. CAMPBELL, *Solid state Commun.*, 1968, **6**, (11), 831-833

Nuclear orientation measurements of the hyper-

fine field at <sup>60</sup>Co nuclei in Co-Pt as a function of applied field suggest the formation of a spin-compensated state at low temperatures.

### Effect of Chemical Composition and Heat Treatment Conditions on the Magnetic Properties of High Coercivity Cobalt-Platinum Alloys

YU. A. GRATSIANOV and A. G. RABIN'KIN, *Sb. Tr. Tsent. Nauch.-Issled. Inst. Chern. Met.*, 1968, (54), 90-97

Tests on cast and homogenised samples of 24, 25, 26.16, and 29.5 wt% Co-Pt alloys showed that the highest magnetic properties are attained with cast samples, e.g. 24-25% Co-Pt has maximum magnetic energy 40 kJ/m<sup>3</sup>, B<sub>r</sub>=7900 gauss, H<sub>c</sub>=3950 Oe. H<sub>c</sub> decreases for >25% Co-Pt, i.e. highest magnetic properties occur for 23-25% Co-Pt, where concentration disordering is less important. Controlled cooling rates lead to more homogeneous and more dispersed structures due to prolonged keeping of samples at 770-830°C, the temperature favourable to nucleation.

### Platinum-based Permanent-magnet Alloys

H. C. ANGUS, *Proc. Instn Elect. Eng.*, 1968, **115**, (12), 1849-1852

Studies of changes of magnetic properties of PtCo and PtFe when part or all the Pt is replaced by Pd, Rh, Ir, and Ru with various preparations and heat treatments show that the pseudobinary alloys possess no better magnetic properties. Careful heat treatment of sintered and worked or of vacuum-melted PtCo gives energy products of 9.5 and 10.0 × 10<sup>6</sup> Gs-Oe, and coercive forces of 5.0 and 4.5 × 10<sup>3</sup>Oe respectively.

### Study of the Diffusion of Normal Hydrogen and of Hydrogen Enriched with Parahydrogen through a Palladium-Silver Membrane. Determination of the Activation Energies

L. FITOUSSI, *C. r., Sér. C.*, 1968, **267**, (26), 1742-1745

Activation energies measured during diffusion through 23% Ag-Pd were 4.9 kcal/g.atom (±10%) for normal H<sub>2</sub> and 3.54 kcal/g.atom (±10%) for H<sub>2</sub> enriched with parahydrogen.

### Electrical Resistivity Measurements in Palladium-Hydrogen Alloys

C. T. HAYWOOD and L. VERDINI, *Can. J. Phys.*, 1968, **46**, (18), 2065-2071

Studies of Pd and Pd-H at 2-300°K show that at 10°K < T < 60°K the electrical resistivity ρ<sub>i</sub>

$\propto T^n$ , with  $n=3.1$  for pure Pd but  $n$  decreasing to 2.3 when  $H/Pd=0.25$ .  $\rho_i$  depends on time and rate of cooling at high H concentrations and low temperatures. Residual resistivity is lower for faster cooling. The increase in  $\rho_i$  due to 1 at.%  $H_2$  in Pd is of the same order as that of interstitials in other f.c.c. metals but is less than for  $H_2$  in b.c.c. Ta and Nb at room temperature.

#### The Diffusion of Hydrogen in $Cu_3Pd$ Alloy

V. B. VYKHODETS, V. A. GOL'TSOV and P. V. GEL'D, *Fiz. Metal Metalloved.*, 1968, **26**, (5), 933-935

Results are plotted and tabulated for studies of the activation energy  $Q$  for  $H_2$  diffusion in ordered and disordered  $Cu_3Pd$  by measuring the rate of penetration  $p$ , the diffusion coefficient  $D$  and the solubility  $S$ .

#### Investigation of Alloys of the $Pd_2Al$ -Ag System

L. A. PANTELEIMONOV, D. N. GUBIEVA and L. V. AZIKONDA, *Vest. moskov. Univ., Ser. II, Khim.*, 1968, **23**, (6), 87-90

The phase diagram and microhardness of these alloys are depicted.

#### On the Relation of Spontaneous Magnetisation to Composition of the Ordered Alloys $Fe(Pt_xPd_{1-x})_3$

S. K. SIDOROV, V. V. KELAREV and A. I. KOZLOV, *Fiz. Metal Metalloved.*, 1968, **26**, (5), 776-780

A theory is developed for magnetisation of the ordered  $Fe(Pt_xPd_{1-x})_3$  alloys in which ferromagnetic-antiferromagnetic exchange reactions occur between the atomic components.

#### On the Nature of the Coercive Force and Structure of Equiatomic Iron-Palladium Alloys

L. M. MAGAT, A. S. ERMOLENKO, G. V. IVANOVA, G. M. MAKAROVA and YA. S. SHUR, *Ibid.*, (3), 511-516

The maximum value of the coercive force of equiatomic Fe-Pd occurs in the single phase regulated state. The coercive force of hardened and annealed samples is explained by delay in ordering ferromagnetic domain boundaries at antiphase boundaries. At first the deformed samples after annealing are much more ordered than the hardened and annealed samples but crystallites of the tetragonal phase are so small that they appear to be the main factor determining the size of the coercive force.

#### Thin Films of Iron-Palladium Alloys with High Coercivity

YA. S. SHUR, L. M. MAGAT, A. A. GLAZER, E. V. SHCHERBAKOVA and N. N. SHCHEGOLEVA, *Ibid.*, (5), 938-939

Studies of FePd showed that the coercivity  $H_c$  is greatest when the crystallites of the alloy are smallest. It follows that a film, consisting of the

smallest grain size of all, possesses the highest  $H_c$ . Thermal ordering increases the grain size and thereby decreases  $H_c$ .

#### The Surface Tension and Density of the Liquid Alloys Pd-Fe, Pd-Cr, Pd-Si

V. F. UKHOV, E. L. DUBININ, O. A. ESIN and N. A. VATOLIN, *Zh. fiz. Khim.*, 1968, **42**, (10), 2631-2634.

Liquid Fe-Pd alloys are nearly ideal. Isotherms of surface tension for molten Cr-Pd are smooth. In molten Si-Pd, molecular groupings in the ratio of the PdSi compound are maintained during isotherms of surface tension.

#### Alloys with Extra Specific Electrical Resistance and Low Temperature Coefficient of Resistance in a Wide Range of Temperature

M. P. RAVDEL' and O. I. EVDOKIMOVA, *Sb. Tr. Tsentr. Nauch.-Issled. Inst. Chern. Met.*, 1968, (54), 26-34

Alloying Ni with Mn-Pd does not alter the resistivity  $\rho$  or the temperature coefficient  $\alpha$  of resistance of the alloy but annealing Mn-Pd-Ni at 300°C alters both  $\rho$  and  $\alpha$ . 0.3 mm diameter rods of 65% Mn-15% Pd-15% Ni-5% Cu have:  $\rho=240\text{ohm.m}$ ,  $\alpha=3.10^{-5}$  per deg C at -60 to +120°C,  $\alpha=(7-8).10^{-5}$  per deg C at 120-300°C, e.m.f. versus Cu E=0.7 mV/deg C,  $\sigma=62-68\text{ kg/mm}^2$ ,  $\delta=20-28\%$ . Repeated heating and cooling between -60 and +300°C does not change their electrical properties. Protracted annealing at 300°C does not alter their structure or properties but at 500-600°C reduces  $\rho$  and leads to brittleness and decomposition.

#### Properties of Alloys of Manganese-Palladium, Manganese-Germanium, and Manganese-Gallium Systems

*Ibid.*, 35-42

The search for a high-resistivity alloy showed that when quenching high Mn content alloys from the  $\gamma$  region a f.c. tetragonal lattice appears which upon alloying becomes f.c.c. Resistivity of Mn-Pd quenched from the  $\gamma$  region is higher than that of Mn-Cu or of Mn-Ni. Resistivity  $\rho$  of 20-32.7% Pd-Mn varies slightly with temperature at 0-350°C.  $\rho$  decreases abruptly above 350°C for all Pd-Mn alloys and dilatometric curves indicate a phase transformation at 350°C.

#### A Palladium-Magnesium Alloy Phase of $Co_2Al_5$ Type

L. WESTIN, *Acta. Chem. Scand.*, 1968, **22**, (8), 2574-2580

X-ray studies of hexagonal  $PdMg_{\sim 2.5}$  give dimensions  $a=8.646-8.660\text{ \AA}$  and  $c=8.175-8.169\text{ \AA}$ . The phase has a range of homogeneity.

#### The Structure of the PuPd Compound

A. V. BEZNOSIKOVA, E. S. SMOTRITSKAYA and N. T. CHEBOTAREV, *Atomnaya Energ.*, 1968, **25**, (5), 430-431

$Pu_3Pd_4$  has lattice parameters  $a=7.028\pm 0.005$ ,

$b=4.571 \pm 0.001$ ,  $c=5.658 \pm 0.002$  Å. Interatomic distances have been determined and are tabulated and a model is depicted.

### Magnetic Susceptibility of Alloys of Plutonium with Palladium

N. T. CHEBOTAREV, YU. N. SOKURSKII, M. A. ANDRIANOV and A. A. IVANOV, *Ibid.*, 431-433

Magnetic susceptibilities of Pu-Pd alloys are tabulated and shown in graphical form.

### Thermomagnetic Measurements on Alloys of the Platinum Metals with Chromium

A. KUSSMAN, K. MÜLLER and E. RAUB, *Z. Metallkunde*, 1968, 59, (11), 859-863

Alloys of Pt metals with Cr which have similar structures have similar magnetic properties. F.c.c.  $LI_2$  phases of Cr with 25-30 at.% Pt, Pd or Ir have a distinct maximum of magnetisation with typical ferromagnetic behaviour. Saturation magnetisation at  $-193^\circ\text{C}$  is  $\sim 0.39$  Vs/m<sup>2</sup> for Pt,  $\sim 0.15$  Vs/m<sup>2</sup> for Pd,  $\sim 0.06$  Vs/m<sup>2</sup> for Ir and the respective Curie points are 900, 400 and  $170^\circ\text{C}$ . Tetragonal PdCr with  $LI_0$  structure is weakly ferromagnetic. Rh-Cr, Ru-Cr and Os-Cr possess no  $LI_2$  structure and are very weakly ferromagnetic. F.c.c. solid solutions rich in Cr are anti-ferromagnetic with high Néel points.

## CHEMICAL COMPOUNDS

### Mass Spectrometric Determination of the Dissociation Energies of Gaseous RuC, IrC and PtB

N. S. MCINTYRE, A. VANDER AUWERA-MAHIEU and J. DROWART, *Trans. Faraday Soc.*, 1968, 64, (11), 3006-3010

RuC, IrC and PtB molecules have been detected with dissociation energies  $D_0^\circ(\text{RuC})=151.0 \pm 3.0$ ,  $D_0^\circ(\text{IrC})=148.4 \pm 3.0$ ,  $D_0^\circ(\text{PtB})=113.3 \pm 4.0$  kcal/mole.

### Preparation and Properties of Some Ternary Selenides and Tellurides of Rhodium

R. H. PLOVNICK and A. WOLD, *Inorg. Chem.*, 1968, 7, (12), 2596-2598

$\text{MRh}_2\text{X}_4$ , where M is Cr, Co, Ni and X is Se, Te, and  $\text{Rh}_2\text{Te}_4$  have the monoclinic  $\text{Cr}_2\text{S}_4$ -type structure with space group  $I2/m$ , except for  $\text{CoRh}_2\text{Te}_4$  and  $\text{NiRh}_2\text{Te}_4$ , which are trigonal with space group  $P\bar{3}m1$ . The symmetry of these compounds with defect NiAs structure depends on whether metal ion vacancies are ordered or randomly arranged in alternate metal layers.

### Reversible Activation of Covalent Molecules by Transition Metal Complexes. The Role of the Covalent Molecule

L. VASKA, *Accounts chem. Res.*, 1968, 1, (11), 335-344

A review of recent work on the mechanism of

reactions involving Ir and Rh complexes. Data discussed are from determinations of the role of the reacting gas by studies of a series of reactions of one metal complex  $\text{ML}_i$  with a variety of addenda, and by comparison of kinetic, equilibrium and thermochemical data from these reactions and the electronic and geometric properties of the corresponding adducts ( $(\text{XY})\text{ML}_i$ ).

### Thermal Decomposition of Rhodium, Iridium, and Ruthenium Chlorides

A. E. NEWKIRK and D. W. MCKEE, *J. Catalysis*, 1968, 11, (4), 370-377

Decomposition studies of  $\text{RhCl}_3$ ,  $\text{IrCl}_3$  and  $\text{RuCl}_3$  hydrates in air and in  $\text{H}_2$  were studied by thermogravimetric analysis and reduction studies were made for dispersions on low- and high-area substrates. Reduction to the respective metals was complete at 105, 190, and  $\sim 350^\circ\text{C}$ . In air, dechlorination and oxidation was complete at 890, 680 and  $\sim 440^\circ\text{C}$  respectively.  $\text{B}_4\text{C}$ , which has low area, has little effect on the reduction temperature of the Rh salt but  $\text{Al}_2\text{O}_3$ , which has high area, is associated with desorption of decomposition products.

### The Metallic Nature of Osmium Dioxide

J. E. GREEDAN, D. B. WILLSON and T. E. HAAS, *Inorg. Chem.*, 1968, 7, (11), 2461-2463

Single crystals of  $\text{OsO}_2$  were prepared and electrical conductivity and Hall effect measurements were made. The data can be rationalised on the basis of a wholly collective electron approach involving the concepts of narrow bands and high density of states which are often encountered in the transition metals and their compounds.

## ELECTROCHEMISTRY

### Hydrogen Adsorption Equilibrium on Platinum Electrodes

I. TELCS and M. JÁKY, *Acta Chim. Acad. Sci. Hung.*, 1968, 58, (3), 275-285

A review of experimental evidence and theory of  $\text{H}_2$  adsorption equilibrium on Pt electrodes shows that most probably the observed effects are due to the several states of  $\text{H}_2$  adsorption on Pt, all of which obey the Langmuir adsorption isotherm to a good approximation. There are probably  $\leq 4$  such states.

### Diffusion Coefficient of Hydrogen in Palladium Alloy Electrodes

J. BERSIER and A. KÜSSNER, *U.S. Rept N68-33984*, 1968, 9pp

Diffusion coefficient of  $\text{H}_2$  in 23% Ag-Pd alloy and in this alloy with 0.5, 0.9, 2.0 and 3.0 at.% B additions was determined as a function of  $\text{H}_2$  concentration and temperature at 30-300°C and varies with  $\text{H}_2$  concentration as  $D(\text{C})=12\text{B}[\text{RT} + \text{C}(\text{r} - \text{C})d/d\text{C}(\Delta_{\mu\text{H}}(\text{C}))]$ .

### On the Behaviour of a Ruthenium Electrode-catalyst in Solutions of Sulphuric and Oxalic Acid at Various Temperatures

R. B. TARAN and G. P. KHOMCHENKO, *Vest. moskov. Univ., Ser. II, Khim.*, 1968, **23**, (6), 83-86

The rate of catalytic hydrogenation of  $\text{CH}_3\text{NO}_2$  on Ru was  $\sim$  twice that of electrochemical reduction but the difference decreased as the temperature rose.

### Catalytic and Electrochemical Reduction of Nitromethane on Ruthenium Electrode-catalyst

L. P. MASHKOVA, A. I. PLETYUSHKINA and G. P. KHOMCHENKO, *Ibid.*, 104-106

Further studies of these reactions in 0.1 N  $\text{H}_2\text{SO}_4$ .

## LABORATORY APPARATUS AND TECHNIQUE

### Correction for Temperature Loading and High Gas Pressure Effects for the Constant-temperature Hot-wire Anemometer

H. HASSAN and J. C. DENT, *Br. J. appl. Phys., J. Phys. D.*, 1969, **2**, (1), 85-92

Tests on Pt and 30% Ir-Pt wires enabled a calibration curve to be plotted for a constant-temperature hot-wire anemometer using the alloy at high temperature in a high-temperature and high-density gas flow. The temperature coefficient of resistance for 30% Ir-Pt was determined and also its thermal conductivity.

### Electrolytic Cell with a Rotating Double Ring Electrode for High Frequencies in the Measurement of Fast Reactions

G. TRIMBORN, A. HEINDRICHS and W. VIELSTICH, *Messtechnik*, 1968, **76**, (9), 224-229

The construction of a double ring Pt electrode system is described together with requirements for its use at high speeds of rotation.

## BRAZING AND WELDING

### Bits for Soldering Irons

H. C. ANGUS, R. D. BERRY and B. JONES, *Engng Mater. Design*, 1968, **11**, (12), 1965-1968

The suitability of Ru for the bits of soldering irons is limited by its cost and so methods have been developed to localise it on bit surfaces and also to protect the non-functional shank surfaces. The most promising tipped bit has an Al shank to which is welded Ru facing.

## HETEROGENEOUS CATALYSIS

### UOP Catalyst Improves Yield of Aromatics

*Eur. chem. News*, 1969, **15**, (361, Jan. 3), 34

Reduced operating pressures are claimed at high

severity conditions without loss of stability for U.O.P.'s new R-16 Platforming catalyst. Improved product distribution selectivity at lower pressures permits dehydrocyclisation of paraffins and dehydrogenation of naphthenes to create aromatics with a minimum of hydrocracking to light hydrocarbons, i.e. yield of motor fuel reformat of a given octane number is higher at lower operating pressures. The aromatics-creating reactions are favoured by lower pressures. Plants which have switched to this catalyst have not yet taken full advantage of R-16 because of their different operating pressures. See also *Chem. W.*, 1969, **104**, (2), 60-61.

### Results of Testing of Platinum on Alumina Catalysts by Hydrogenating Benzene to Cyclohexane

YU. I. KOZOREZOV and N. M. PIKALO, *Khim. Promyshlennost'*, 1968, (11), 821-822

$\text{C}_6\text{H}_6$  hydrogenation tests using a modified Pt/ $\text{Al}_2\text{O}_3$  catalyst showed that the latter is extremely active, selective and stable, and is suitable for industrial use.

### Investigation of the Conversion of Cyclohexene on Pt-Zeolite Catalyst under Pressure of Hydrogen

V. I. GARANIN, U. M. KURKCHI and KH. M. MINACHEV, *Kinet. Kataliz*, 1968, **9**, (5), 1080-1085

Studies of cyclohexene and cyclohexane isomerisations on decationised zeolite, on CaY and on 0.5% Pt/CaY show that on Pt/CaY the isomerisation of cyclohexane proceeds via formation of cyclohexene on Pt with subsequent isomerisation on the acid centres of the zeolite. The isomerisation of cyclohexene depends on temperature.

### The Effect of Heat Treatment on the Catalytic Activity of Platinum Catalysts

S. A. KHASSAN, S. G. FEDORKINA, G. I. EMELYANOVA and V. P. LEBEDEV, *Zh. fiz. Khim.*, 1968, **42**, (10), 2507-2512

Sintering studies on Pt black in vacuum at 300, 400, 500, 600 and 700°C indicate a second order relation between changes in the activity and surface area. Sintering produces a fixed activity and surface area for each temperature. The relation between activity and roasting temperature is exponential. Given the activity at two temperatures, an equation relating activity to temperature can be derived. Kinetics of decomposition of  $\text{H}_2\text{O}_2$  and of hydrogenation of cyclohexene on sintered black are similar. Specific activity is unrelated to the duration and temperature of sintering but change of surface area and size of crystals are.

### Hydroisomerisation of Normal Pentane over a Zeolite Catalyst

A. VOORHIES and P. A. BRYANT, *A.I.Ch.E. J.*, 1968, **14**, (6), 852-856

A series of screening tests on zeolite hydro-

isomerisation catalysts showed that the most active is Pd/hydrogen mordenite. Typical test conditions were 550°F, 450 lb/in<sup>2</sup>, H<sub>2</sub>:C<sub>5</sub>H<sub>12</sub>=3.4, 8 g *n*-C<sub>5</sub>H<sub>12</sub>/h.g. catalyst. Neither gas to particle mass transfer, nor macropore diffusion nor chemical reactions at Pd sites are rate-limiting.

### Hydrogenation and Hydrogenolysis. X. The Hydrogenation of Methoxy- and Ethoxy-anilines with Rhodium Catalyst

S. NISHIMURA, H. UCHINO and H. YOSHINO, *Bull. Chem. Soc. Japan*, 1968, **41**, (9), 2194-2195

Hydrogenation of alkoxyanilines with alkali-promoted Rh catalysts showed that Rh oxide prepared by fusion of RhCl<sub>3</sub> with LiNO<sub>3</sub> gives high yields of methoxy- and ethoxycyclohexylamines from methoxy- and ethoxyanilines respectively. <6% hydrogenolysis occurred and secondary amine formation was negligible. Studies with LiNO<sub>3</sub> replaced by NaNO<sub>3</sub>, LiOH and NaOH are reported and less satisfactory yields were obtained. Best conditions appear to be 90°C, high p<sub>H<sub>2</sub></sub>, and use of LiNO<sub>3</sub> with RhCl<sub>3</sub> when ~2% catalyst: substrate is required.

### Hydrogenation of Olefins. Part 4. Reaction of *n*-Butenes with Hydrogen Catalysed by Alumina-supported Ruthenium and Osmium

G. C. BOND, G. WEBB and P. B. WELLS, *Trans. Faraday Soc.*, 1968, **64**, (11), 3077-3085

Studies in a static system of product distributions, orders of reaction and activation energies for hydrogenation and isomerisation of but-1-ene, *cis*- and *trans*-but-2-ene at 0-70°C using 1 mol.% Ru/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and at 60-140°C using 1 mol.% Os/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> show that Ru gives more isomerisation than Os. The suggested mechanism is isomerisation by loss of one H atom from adsorbed C<sub>4</sub>H<sub>8</sub> to yield adsorbed C<sub>4</sub>H<sub>7</sub> and H, and hydrogenation where the rate is determined by H addition to adsorbed C<sub>4</sub>H<sub>8</sub> for each C<sub>4</sub>H<sub>8</sub>. Rate-determining steps for *cis-trans* isomerisation and double-bond migration are discussed.

### The Hydrogenation of Alkadienes. Part II. The Hydrogenation of Buta-1,3-diene Catalysed by Rhodium, Palladium, Iridium, and Platinum Wires

P. B. WELLS and A. J. BATES, *J. Chem. Soc., A, inorg. phys. theor.*, 1968, (12), 3064-3069

Studies of buta-1,3-diene hydrogenation over Rh, Pd, Ir, and Pt wires showed that C<sub>4</sub>H<sub>8</sub> compositions depended on temperature but not on activity, initial p<sub>H<sub>2</sub></sub> or conversion up to 50%. C<sub>4</sub>H<sub>10</sub> yield was zero on Pd and 1-15% on the other wires. But-1-ene was the main product; *trans-cis* ratios for but-2-ene were determined. Chemisorption of buta-1,3-diene by interaction of only one double bond became more important as the temperature rose. Hydrogenation activity of clean Ir was replaced by hydrogenolysis as C residues

accumulated on it. CH<sub>4</sub> was the sole product of hydrogenolysis at 245°C on Ir of C<sub>4</sub>H<sub>8</sub>-1, C<sub>5</sub>H<sub>10</sub>-1, etc. Comparing wires with Al<sub>2</sub>O<sub>3</sub>-supported catalysts, reactions seem characteristic of the metal rather than of the type of catalyst.

## HOMOGENEOUS CATALYSIS

### Homogeneous Catalysis in the Reactions of Olefinic Substances. XI. Homogeneous Catalytic Hydrogenation of Short-chain Olefins with Dichlorobis-(triphenylphosphine)platinum(II)-Tin(II) Chloride Catalyst

R. W. ADAMS, G. E. BATLEY and J. C. BAILAR, *J. Am. Chem. Soc.*, 1968, **90**, (22), 6051-6056

Studies of homogeneous hydrogenation of short-chain olefins with PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and SnCl<sub>2</sub>. 2H<sub>2</sub>O catalyst mixtures showed that mono-olefins hydrogenate rapidly only when the double bond is terminal. Reduction of hexadiene and pentadiene isomers does not stop necessarily at the monoene stage. Dienes react most when both double bonds are terminal. Conjugation is not a necessary step before hydrogenation; short-chain conjugated diene isomers inhibited further reaction. Long-chain conjugated dienes are reduced since their larger size prevents formation of stable catalyst-diene complexes. Unsaturated nitriles are hydrogenated when the double bond is terminal; substituent groups on the  $\beta$ -C atom do not hinder this and the CN<sup>-</sup> group remains intact.

### A Palladium-catalysed Synthesis of Benzyl Esters from Methylbenzenes

D. R. BRYANT, J. E. MCKEON and B. C. REAM, *J. org. Chem.*, 1968, **33**, (11), 4123-4127

Liquid phase production of benzyl esters from methylbenzenes takes place at moderate temperatures using Pd(OAc)<sub>2</sub>-Sn(OAc)<sub>2</sub> catalyst and 1 atm air, e.g. toluene in CH<sub>3</sub>COOH gives benzyl acetate. The secondary oxidation product benzylidene diacetate is formed at high conversions. Other methylbenzenes behave similarly. Xylenes undergo selective diacetoxylation in CH<sub>3</sub>COOH to give  $\alpha,\alpha'$ -diacetates rather than  $\alpha,\alpha$ -diacetates.

### Palladium-catalysed Reactions of Unsaturated Compounds in Non-aqueous Solvents. Synthesis of Vinyl Acetate via Palladium Salt/Ethylene Complexes

R. VAN HELDEN, C. F. KOHLL, D. MEDEMA, G. VERBERG and T. JONKHOF, *Rec. Trav. chim. Pays-bas*, 1968, **87**, (10), 961-991

The rate of the reaction of C<sub>2</sub>H<sub>4</sub> with Pd(OAc)<sub>2</sub> in CH<sub>3</sub>COOH to produce vinyl acetate increases considerably on addition of small amounts of NaOAc, LiCl or LiCl, Fe(OAc)<sub>3</sub> to the system. The reaction is first order with respect to both Pd(OAc)<sub>2</sub> and the additions. When using PdCl<sub>2</sub> and NaOAc the rate is proportional to them.

### Catalytic Asymmetric Hydrogenation Employing a Soluble, Optically Active, Rhodium Complex

W. S. KNOWLES and M. J. SABACKY, *Chem. Commun.*, 1968, (22), 1445-1446

A catalyst precursor which contains optically active tertiary phosphine ligands is prepared by dissolving  $\text{RhL}_3\text{Cl}_3$  complexes with L=tertiary phosphine in 1 : 1 v/v  $\text{C}_6\text{H}_6$  :  $\text{C}_2\text{H}_5\text{OH}$  containing triethylamine and pressurising with  $\text{H}_2$ . Examples of its use are described.

### Catalysis of Hydrogen Transfer by a Method Hypothetically Similar to Fermentation. VI. High-activity Hydrogenation Catalysts on the Basis of $\pi$ -Complexes of Rhodium(I) with Amino Acids

O. N. EFIMOV, M. L. KHIDEKEL', V. A. AVILOV, P. S. CHEKRIL, O. N. EREMENKO and A. G. OVCHARENKO, *Zh. obshch. Khim.*, 1969, 38, (12), 2668-2677

Studies of Rh complex catalysts with N-phenylanthranilic acid and L-tyrosine showed that low-valent compounds are stabilised at the expense of reactions with aromatic rings and carboxyl groups. Both in solid and solution states the complex is supposedly the dimer  $\text{H}[\text{Rh}_2(\text{phen})_2\text{Cl}]$  but H decomposes it to the monomer. The Rh complexes catalyse D exchange with  $\text{H}_2\text{O}$ . A hydrogenation mechanism for *trans*-stilbene is suggested.  $\text{H}_2$  is derived during hydrogenations of fumaric acid and acetylene derivatives by the *cis*-scheme.

### Selective Homogeneous Hydrogenation of Alk-1-enes Using Hydridocarbonyltris-(triphenylphosphine)rhodium(I) as Catalyst

C. O'CONNOR and G. WILKINSON, *J. Chem. Soc., A, inorg. phys. theor.*, 1968, (11), 2665-2671

$\text{RhH}(\text{CO})(\text{PPh}_3)_3$  efficiently catalyses homogeneous hydrogenation of unsaturated  $\text{RCH}=\text{CH}_2$  compounds. For hex-1-ene and dec-1-ene in  $\text{C}_6\text{H}_6$  solution the rate law is  $\text{rate} = k_1 K_1 c [\text{S}][\text{A}] / (1 + K_1[\text{S}])$ , where [S] and [A] are respective concentrations of alk-1-ene and catalyst, C is  $\text{H}_2$  concentration in solution,  $K_1$  is the formation constant for an alkene intermediate complex, and  $k_1$  is the rate constant for the rate-determining  $\text{H}_2$  activation step. High selectivity for reduction of alk-1-ene is due to steric factors caused by the bulky triphenylphosphine groups.

### Hydroformylation of Alkenes by Use of Rhodium Complex Catalysts

D. EVANS, J. A. OSBORN and G. WILKINSON, *Ibid.*, (12), 3133-3142

The inhibition period of *trans*- $\text{RhX}(\text{CO})(\text{PR}_3)_2$  catalysts, where X=halogen and R=aryl, is removed by addition of hydrogen halide acceptors and the halide complex forms a hydrido-species by hydrogenolysis. The principal catalytic species seems to be  $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$  formed by CO

addition to  $\text{RhH}(\text{CO})(\text{PPh}_3)_2$ , which is also formed by dissociation when  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  is dissolved in  $\text{C}_6\text{H}_6$  or other solvents. Rapid hydroformylation of alkenes occurs at 250°C, 1 atm with  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  catalyst, giving a ratio of ~20 for the formation of straight- and branched-chain aldehydes from alk-1-enes. H exchange and isomerisation of alkenes with  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  are described.

### The Preparation and Reactions of Hydrido-chlorotris(triphenylphosphine)ruthenium(II) Including Homogeneous Catalytic Hydrogenation of Alk-1-enes

P. S. HALLMAN, B. R. MCGARVEY and G. WILKINSON, *Ibid.*, 3143-3150

$\text{RuClH}(\text{PPh}_3)_3 \cdot \text{C}_6\text{H}_6$  was prepared from  $\text{RuCl}_2(\text{PPh}_3)_3$  and  $\text{H}_2$  in ambient conditions in the presence of a base such as triethylamine.  $\text{RuBrH}(\text{PPh}_3)_3 \cdot \text{C}_6\text{H}_6$ ,  $\text{RuClH}(\text{C}_7\text{H}_7)(\text{PPh}_3)_2$ ,  $[\text{RuClH}(\text{bipy})(\text{PPh}_3)_2]_2$ , and  $\text{RuH}_3(\text{CO})(\text{PPh}_3)_3$  were also prepared.  $\text{RuClH}(\text{PPh}_3)_3$  is the most active catalyst yet discovered for homogeneous hydrogenation of alk-1-enes in  $\text{C}_6\text{H}_6$  or  $\text{C}_6\text{H}_5\text{CH}_3$ . It is highly specific but kinetic study is difficult and slow poisoning occurs.

### Carbonylation of Acetylene with $[\text{Ru}(\text{CO})_4]_3$ as Catalyst

P. PINO, G. BRACA, G. SBRANA and A. CUCCURU, *Chem. & Ind.*, 1968, (49, Dec. 7), 1732-1733

Hydroquinone was prepared by carbonylation of  $\text{C}_2\text{H}_2$  under anhydrous conditions, in either tetrahydrofuran or dioxan as solvent, in the presence of  $[\text{Ru}(\text{CO})_4]_3$ . Highest yields occurred at  $p_{\text{H}_2} = 5-10$  atm. Yields up to 65% hydroquinone were obtained by reacting  $\text{C}_2\text{H}_2$  with CO and  $\text{H}_2\text{O}$  or alcohols in the presence of  $[\text{Ru}(\text{CO})_4]_3$  at 150-250°C and relatively low  $p_{\text{CO}}$ .

## FUEL CELLS

### Electrocatalysts for the Direct Electrochemical Oxidation of *n*-Octane in Fuel Cells

E. J. CAIRNS and J. PAYNTER, *J. Electrochem. Soc.*, 1968, 115, (12), 1218-1224

Activity of supported and unsupported Pt prepared in various ways was compared with that of commercial Pt black. An increase in the specific area of a C substrate gave a corresponding increase in electrocatalytic activity up to at least 200 m<sup>2</sup>/g. Some types of Pt/C had 6-18 times the activity of Pt black. No current or voltage cycling occurred with 36 mol.% HF electrolyte at 105°C in contrast to other acid electrolytes.

### Structure and Performance of Hydrophobic Gas Electrodes

A. D. D. TANTRAM and A. C. C. TSEUNG, *Nature*, 1969, 221, (5176, Jan. 11), 167-168

Electron microscopy showed that a catalyst pre-

pared by mixing Pt black with a dispersion of PTFE and applying it to a metal screen before drying and curing at 300°C consists of porous aggregates of Pt intermingled with PTFE. Performance is very dependent on microstructure. Whereas hydrophilic electrodes become flooded with electrolyte hydrophobic electrodes become full of gas and the whole thickness of the electrode is effective. The effect of catalyst surface area was studied using graphite powder as the catalyst.

## CHEMICAL TECHNOLOGY

### The Separation of Hydrogen from Ammonia Synthesis Exhaust Gases by the Method of Diffusion through Palladium

YU. K. BAICHTOK, M. B. AIZENBUD, V. A. KURKOVSKII, A. S. FURMANOV, I. YA. AZBEL' and Z. V. KORBUTOVA, *Khim. Promyshlennost'*, 1968, (10), 744-746

NH<sub>3</sub> synthesis is more economic when H<sub>2</sub> in the exhaust gas is purified and when Ar is recovered. Tests on such gas and on pure N<sub>2</sub>-H<sub>2</sub> mixtures compared pure Pd and 5% Ni-10% Ag-Pd foils for H<sub>2</sub> purification by diffusion at 400 and 500°C. Both gas mixtures gave similar results. Ag dusted on Pd foil activated the latter for H<sub>2</sub> diffusion.

## TEMPERATURE MEASUREMENT

### The Effect of Stress on the Thermal EMF of Platinum-Platinum/13% Rhodium Thermocouples

E. S. MORGAN, *Br. J. appl. Phys., J. Phys. D*, 1968, 1, (11), 1421-1429

Variations in thermal e.m.f. with stress of Pt and 13% Rh-Pt wires with junctions at 20 and 550°C are -47 and -12 pV deg C<sup>-1</sup>kg<sup>-1</sup>cm<sup>-2</sup> respec-

tively. The thermal e.m.f. hysteresis loop of some metal-sheathed mineral-insulated thermocouples is explained; the maximum discrepancy from this loop is 23μV at 550°C by calculation, 14μV by experiment on a single thermocouple. Mechanical hysteresis of the loop may cause fracture. A reliable thermocouple of this type needs matching expansion coefficients of sheath and thermocouple.

### Comparison of Platinum Resistance Thermometers between 63K and 373.15K. Part I. Part II

M. R. M. MOUSSA, H. VAN DIJK and M. DURIEUX, *Physica*, 1968, 40, (1), 33-48, 49-60

Twelve Pt resistance thermometers were compared with a reference one at 63-273.15°K and at 373.15°K using a constant temperature bath with the thermometers inserted in a Cu block immersed in liquid iso-C<sub>5</sub>H<sub>12</sub>, C<sub>3</sub>H<sub>8</sub>, O<sub>2</sub>, or N<sub>2</sub> and the differences of the reduced resistances W = R(t)/R(0°C) of them were determined. The number of calibration points to determine the W-T relation was studied and discussed.

### A Direct-reading Bridge for a Platinum Resistance Thermometer

C. W. VAN DER WAL and L. C. E. STRUIK, *J. sci. Instrum., J. Phys. E*, 1969, 2, (2), 143-145

A Wheatstone bridge for a Pt resistance thermometer was modified so that the angle of rotation of a linear potentiometer is proportional to the temperature with bridge sensitivity fairly independent of temperature. Although not intended for high precision thermometry, irrespective of the inaccuracy of the thermometer itself the reading accuracy is to better than ±0.1 deg C at 0-500°C and the bridge can be used for both temperature control and temperature measurement.

## NEW PATENTS

### METALS AND ALLOYS

#### Methods of Improving the Mechanical Properties of Metals and their Alloys

JOHNSON MATTHEY & CO. LTD  
*British Patent* 1,134,492

Pt metal alloy articles are given greater strength by cold working and annealing to give oriented recrystallisation.

#### Improvements in and Relating to the Treatment of Platinum Group Metals and Alloys

JOHNSON MATTHEY & CO. LTD  
*British Patent* 1,139,897

An alloy having properties of oxidation resistance and high mechanical strength is made by alloying

Pd with a minor amount of Cr capable of forming a stable refractory compound or alloying Rh or Pt (or Rh, Pt with another Pt-metal) with a minor amount of an element capable of forming a stable refractory compound (the element may be Be, Mg, Al, Si, Th, U or a transition metal) and heating (1000°C) the alloy in a gas (e.g. air or O<sub>2</sub>) to form the refractory compound (e.g. oxide) in the alloy.

## CHEMICAL COMPOUNDS

### New Chemical Compounds

IMPERIAL CHEMICAL INDUSTRIES LTD  
*British Patent* 1,138,867

These new chemical compounds are Pt group