

# ABSTRACTS

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

### PROPERTIES

#### The Thermal Conductivity and Electrical Resistivity of Polycrystalline Metals of the Platinum Group and of Single Crystals of Ruthenium

R. W. POWELL, R. P. TYE and M. J. WOODMAN, *J. Less-Common Metals*, 1967, **12**, (1), 1-10

Thermal conductivity and electrical resistivity values for Ru, Os, Pd, Rh and Pt at 300-500°K are reported. Similar studies were made at 80-500°K on polycrystalline samples of Ru, Rh, Ir and Pt and on single-crystal Ru rods with crystallographic axes parallel and perpendicular to the axis of the rod. Minima occurred in the thermal conductivity-temperature curves of three Ru samples measured at temperatures below normal. See *Platinum Metals Rev.*, 1966, **10**, (4), 132.

#### The Thermal Conductivity of Platinum between 300 and 1000°K

M. J. LAUBITZ and M. P. VAN DER MEER, *Canad. J. Phys.*, 1966, **44**, (12), 3173-3184

Thermal conductivity measurements for high-purity Pt at 300-1000°K agree with the work of Bode, and of Martin and Sidles, but disagree with the work of Powell and Tye at higher temperatures. The variation with temperature  $T$  implies that, at high temperatures, the electronic Lorenz number of Pt is an increasing function of  $T$ , exceeding the Sommerfeld value, which can be explained by assuming a low Fermi energy for Pt.

#### Influence of Purity on Some Properties of High Melting Metals

E. RAUB and E. RÖSCHEL, *Metall*, 1967, **21**, (1), 1-9

A discussion on differences in the mechanical properties of Pt, Pd, Ir and Rh and on the influence of purity on their cold-strengthening, recovery and heat resistance is illustrated by results from tests on the effects of metallic impurities on the properties of Pt. As an electron beam volatilises Pd, Au and Ag, less volatile Rh and Ir raise the recovery temperature of Pt.

#### The Colours of Some Metals and Alloys

G. E. GARDAM, *Trans. Inst. Met. Finish.*, 1966, **44**, (5), 186-188

The spectral reflectivity curves of a number of perfectly polished metals and electroplated coatings were measured using a simplified spectrophotometer and were used to calculate the chromaticity coefficients, luminance and position of each in the colour triangle. Rh is very near the white point; Pt and Pd are displaced slightly

towards the yellow; Cu, Au and their alloys have red/yellow colours heavily diluted with white. Rh, Pt, Pd and Au have luminances of 0.815, 0.671, 0.642 and 0.706, respectively.

#### The Structure of Thin Platinum Sheet

J. B. HANLEY and W. I. MITCHELL, *J. Materials Sci.*, 1966, **1**, (4), 412-413

Electron microscopy of 12  $\mu\text{m}$  Pt foils, prepared by cold rolling at room temperature followed by electropolishing in molten NaCl at 801°C, revealed that pure cast Pt had a fully recovered structure with grain size 2-3  $\mu\text{m}$ , that pure sintered Pt had spheroidal defects and a finer grain size, and that sintered Pt containing ThO<sub>2</sub> had a high dislocation density indicating retarded recovery. The difference in mechanical properties appeared to be due to spheroidal defects resulting in dispersion of porosity.

#### The Temperature Dependence of the Surface Energy Anisotropy of Platinum

M. MCLEAN and H. MYKURA, *Surface Sci.*, 1966, **5**, (4), 466-481

Measurements of the variation of the surface free energy  $\gamma$  of Pt with crystallographic orientation at 920-1500°C by the twin boundary groove technique showed that anisotropy decreased with increased temperature. Faceting to {111} and {100} was observed over part of this temperature range. Early roughening of complex surfaces is believed to account for discrepancies between theory and experiment. Surface "melting" may begin at ~1230°C, {100} surfaces "melt" at ~1350°C and {111} surfaces remain atomically smooth to at least 1600°C and probably to the lattice m.p.

#### The Electrical Resistance of Platinum at Repeated Quenching. I. The Reversible Change

A. ČIŽEK, *Czech. J. Phys.*, 1966, **B16**, (10), 842-854

Studies by repeated quenching from high temperature of the reversible change in the electrical resistance of Pt wires of three different radii determined the quench temperature at which the concentration of quenched-in vacancies is independent of quenching rate or of wire diameter as  $1070 \pm 50^\circ\text{K}$ , i.e.  $(0.53 \pm 0.02) T_m$ , indicating an high stacking fault energy.

#### The Low-temperature Specific Heat of Some Dilute Platinum-Iridium and Platinum-Gold Alloys

M. DIXON, F. E. HOARE and T. M. HOLDEN, *Proc. Phys. Soc.*, 1967, **90**, (1), 253-261

Specific heat measurements at 1.2-4.2 °K are

reported for 1.98, 3.89, 5.80, 7.80 and 9.83 at.% Ir-Pt and for 2.00, 3.93, 5.98 and 8.22 at.% Au-Pt. Results were analysed in terms of electronic and lattice specific heat contributions but a constant term of uncertain origin remains.

### Thermodynamic Properties of Copper-Platinum Alloys

J. M. MCCORMACK, J. R. MYERS and R. K. SAXER, *Trans. Met. Soc. A.I.M.E.*, 1966, **236**, (11), 1635-1638

The Knudsen effusion technique was used to study the chemical activity,  $a$ , of Cu-Pt alloys containing 90.0, 74.0, 59.2, 29.9 and 14.7 at.% Cu at 1542-1673°K.  $a_{\text{Cu}}$  and  $a_{\text{Pt}}$  showed negative deviation from Raoult's Law and  $a_{\text{Cu}}$  showed increasing ideality with increasing temperature due to ordered phases. The integral free energy has a minimum value of 4.2 kcal/mole at ~55 at.% Cu, the excess free energy is negative with a minimum at ~55 at.% Cu and the integral enthalpy is negative with a maximum value of 3.4 kcal/mole. At higher temperatures 64-71% Cu-Pt alloys melt to give two phases resulting in straight line plots for free energy, enthalpy and entropy.

### Equiatomic Transition Metal Alloys of Manganese. V. On the Magnetic Properties of the PtMn Phase

A. F. ANDRESEN, A. KJEKSHUS, R. MØLLERUD and W. B. PEARSON, *Acta Chem. Scand.*, 1966, **20**, (9), 2529-2534

X-ray, neutron diffraction and magnetic susceptibility studies of  $\text{Pt}_{45}\text{Mn}_{55}$ ,  $\text{Pt}_{50}\text{Mn}_{50}$  and  $\text{Pt}_{55}\text{Mn}_{45}$  indicate that they are antiferromagnetic with spin quantum numbers  $2S_{\text{Mn}}=4.0\pm 0.2$  and  $2S_{\text{Pt}}<0.2$ .  $\text{Pt}_{55}\text{Mn}_{45}$  is weakly ferromagnetic below ~250°K and has Néel temperature ~710°K.

### Magnetic Properties of Ordered Pt-Co

P. BRISSONNEAU, A. BLANCHARD and H. BARTHOLIN, *I.E.E.E. Trans. Magnetics*, 1966, **2**, (3), 479-482  
50 at.% Co-Pt may be ordered to a tetragonal CuAu-type structure. An ordered single crystal is a system of tetragonal crystallites with  $c$  axes parallel to the  $O_x$ ,  $O_y$ ,  $O_z$  axes of the disordered matrix. Room temperature studies on an ordered macrocrystal with unequal relative volumes of three types of crystallites indicated magnetisation far less than saturation even in an applied field of  $3.10^4$  Oe, i.e. large anisotropy energy.  $J_s=790$  emu/cm<sup>3</sup> and  $K=5.10^7$  ergs/cm<sup>3</sup>. Results probably account for discrepancies in previous data.

### Preparation and X-ray Investigation of Platinum Alloys with the Rare-earth Metals ( $\text{Pt}_5\text{Ln}$ and $\text{Pt}_3\text{Ln}$ Phases)

W. BRONGER, *J. Less-Common Metals*, 1967, **12**, (1), 63-68

$\text{Pt}_5\text{Ln}$  phases were prepared by reacting Pt with the La to Tm series in  $\text{H}_2$ . X-ray studies indi-

cated three related structure types. Lighter rare earths formed  $\text{Cu}_3\text{Ga}$ -type structures with Pt; heavier rare earths formed new but similar structures;  $\text{Pt}_3\text{Ln}$  with the Ho to Lu series have  $\text{Cu}_3\text{Au}$ -type structure.

### On the Equilibrium between Monatomic and Diatomic Palladium and the Appearance Potential of $\text{Pd}_2$

K. A. GINGERICH, *Naturwissenschaften*, 1967, **54**, (2), 43

Mass-spectrometric studies showed that the lowest temperature at which diatomic Pd appeared was 1975°K. Appearance potential of  $\text{Pd}^+$  was  $7.7\pm 0.3$  eV. Partial pressure ratios  $p_{\text{Pd}}/p_{\text{Pd}_2}$  at 1975, 2025, 2085°K were  $3.3\times 10^5$ ,  $2.5\times 10^5$ ,  $1.4\times 10^6$  respectively.

### Destruction of Short Range Order in Au-Pd Alloys by Cold Working

T. E. FINE and M. E. NICHOLSON, *Abs. Bull. Inst. Met. Div., Met. Soc. A.I.M.E.*, 1966, **1**, (2), 77

X-ray studies of the influence of plastic deformation on short range order in 45 and 60 at.% Pd-Au alloys showed that  $\alpha_1$ , the local order parameter, which was negative for both alloys, decreased logarithmically as the true strain increased. Annealed values of  $\alpha_1$  were determined for 23.5, 33.0, 45.0, 60.0, 75.5 and 90.5 at.% Pd-Au and exhibit a roughly parabolic relation to composition, with 45 at.% Pd-Au having the most negative value. The curve calculated from heat of mixing data is similar but absolute values do not agree in the low concentration ranges, presumably due to corrections which compensate for systematic errors.

### Magnetic Behaviour of Binary and Ternary Mixed Crystals of Palladium with Rhodium and Silver

E. VOGT, E. OEHLER and W. TREUTMANN, *Ann. Physik*, 1966, **18**, (3-4), 168-177

Results of susceptibility measurements at ~90-~800°K on binary Pd-Rh and Pd-Ag alloys or ternary alloys with Rh:Ag contents 1 at.%-1 at.%, 3 at.%-3 at.%, 5 at.%-5 at.%, 8 at.%-2 at.%, 10 at.%-4 at.%, 12 at.%-6 at.% are discussed within the scope of the rigid-band model. The ternary alloys show weaker paramagnetism than this model leads one to expect. Results can be applied to selecting alloys of required susceptibilities.

### Consequences of the Proton Model for Hydrogen Absorption in the $\beta$ Phase of the Hydrogen-Palladium System

T. B. FLANAGAN and J. W. SIMONS, *J. Phys. Chem.*, 1966, **70**, (11), 3750-3751

The equation  $\ln P_{\text{H}_2}(\text{atm})=A(T)+B(T)n$  for the equilibrium between  $\text{H}_2$  gas and H absorbed in Pd at contents greater than those of the two-phase region, i.e. contents in the  $\beta$ -phase region,

where  $n = \text{H}/\text{Pd}$ , is shown to follow directly from extensions of Lacher's statistical model where a variable energy of electron donation to the electronic band of Pd is included.

### Internal Friction of Palladium Containing Hydrogen

R. R. ARONS, J. BOUMAN, M. WIJZENBEEK, P. T. A. KLAASE, C. TUYN, G. LEFERINK and G. DE VRIES, *Acta Met.*, 1967, **15**, (1), 144-147

After loading electrolytically with  $\text{H}_2$ , 0.3 mm 99.999% Pd wire at 2.7 Hz showed two internal friction peaks: A at 75°K; B at 105°K. The height of A was dependent on concentration of  $\text{H}_2$  and was attributed to stress induced ordering of  $\text{H}_2$  pairs in the  $\beta$  phase. B was observed only if  $\text{H}_2$  and deformations were present and was dependent on purity and annealing conditions, and decreased on addition of C. The activation energies of  $\text{H}_2$  and  $\text{D}_2$  in the system differed by 850 cal/mole. Loading with a mixture of  $\text{H}_2$  and  $\text{D}_2$  gave a single narrow peak between those obtained with the pure gases.

### Thermodynamic Properties of Pd-Cd and of Pd-Sb Alloys

J. B. DARBY, K. M. MYLES and J. N. PRATT, *Abs. Bull. Inst. Met. Div., Met. Soc. A.I.M.E.*, 1966, **1**, (2), 14

Enthalpies of formation of several solid Pd-Cd and Pd-Sb alloys were all exothermic, when determined by liquid-Sn solution calorimetry, and those of the Pd-rich primary solid solutions were larger than those of Pd-rich Pd-Ag alloys. Activities of Pd-Cd alloys were measured by the dew-point method. Pd-Cd alloys were predominantly rich in Pd and were in the  $\alpha$ ,  $\alpha$  prime, and  $\beta$  phase regions. Pd-Sb compositions were in the known single-phase regions.

### The Crystal Structure of $\text{Pd}_{4.8}\text{P}$

B. SELLBERG, *Acta Chem. Scand.*, 1966, **20**, (8), 2179-2186

A single crystal X-ray diffraction study of  $\text{Pd}_{4.8}\text{P}$  revealed a cell content of 18 Pd atoms in 2(a) positions with space group P2 and unit cell dimensions  $a = 5.004 \text{ \AA}$ ,  $b = 7.606 \text{ \AA}$ ,  $c = 8.416 \text{ \AA}$ , maximum error of  $\pm 0.0005 \text{ \AA}$ ;  $\beta = 95.63 \pm 0.0005 \text{ \AA}$  and  $U = 318.8 \text{ \AA}^3$ .

### Rare-earth Intermediate Phases. IV. The High-temperature Lattice of Some R.E. $\text{Pd}_3$ Phases

I. R. HARRIS, G. V. RAYNOR and C. J. WINSTANLEY, *J. Less-Common Metals*, 1967, **12**, (1), 69-74

$\text{CePd}_3$  has much greater lattice expansion with increasing temperature than  $\text{GdPd}_3$ ,  $\text{YbPd}_3$  or  $\text{SmPd}_3$ , probably because variable occupancy of 4 f states in Ce causes conduction band  $\rightarrow$  4 f transitions. Expansion characteristics of  $\text{YbPd}_3$  and  $\text{YbIn}_3$  differ, probably due to the valency states of Yb in them.

### On the Superconductivity of Hf-Rh Alloys

H. WÜHL, *Z. Physik*, 1966, **197**, (3), 276-287

Rh strongly increases transition temperatures  $T_c$  of quenched Hf-Rh alloys in the hexagonal phase, as with homologous systems Ti-Rh and Zr-Rh, but it does not stabilise the cubic high temperature phase. For  $> 6 \text{ at. \%}$  Rh-Hf, Hf $_2$ Rh is formed with  $T_c = 1.98^\circ\text{K}$  and there is a transition at  $1.73^\circ\text{K}$ , probably due to HfRh.

### Electron and Ion Emission from Iridium and Lithium Vapour

R. G. WILSON and E. D. WOLF, *J. Appl. Phys.*, 1966, **37**, (12), 4458-4462

Electron emission S curves for the Li-Ir system in Li vapour at 275-450°C indicate only an uniform heavily Li-covered work function of 2.8 eV which is constant in the Li arrival flux range of  $10^{13}$  to  $10^{18} \text{ at./cm}^2\text{sec}$ . The adsorption/desorption energy, 2.1 eV, of Li on Ir at low coverage is found to be similar to that of Cs.

### Lattice Parameters of Some h.c.p. Binary Alloys of Rhenium and Osmium: Re-W, Re-Ir, Re-Pt, Os-Ir, Os-Pt

P. S. RUDMAN, *J. Less-Common Metals*, 1967, **12**, (1), 79-81

Lattice parameters a, c, c/a are reported for the binary alloys of Re-W, Re-Ir, Re-Pt, Os-Ir, Os-Pt and the lattice parameter-group number relationship is studied. No unique relationship exists for all these alloys.

### Laves Phases of the Scandium Group Elements with Ruthenium, Osmium, Iridium, and Platinum

A. E. DWIGHT, J. W. DOWNEY and R. A. CONNER, *Trans. Met. Soc. A.I.M.E.*, 1966, **236**, (10), 1509-1510

New or revised crystallographic data are tabulated for 31  $\text{AB}_2$  laves phases, where A is a rare earth and B is Ru, Rh, Os, Ir or Pt. The Rh, Ir and Pt phases have cubic  $\text{MgCu}_2$  type structures but the Ru and Os phases have hexagonal  $\text{MgZn}_2$ -type structures.

## CHEMICAL COMPOUNDS

### Oxygen Complexes of Zero-valent Nickel, Palladium and Platinum

G. WILKE, H. SCHOTT and P. HEIMBACH, *Angew. Chem.*, 1967, **79**, (1), 62

Triphenylphosphine complexes  $(\text{Ph}_3\text{P})_4\text{Pt}(\text{O})\text{O}_2$  and  $(\text{Ph}_3\text{P})_4\text{Pd}(\text{O})\text{O}_2$  are more stable than similar Ni complexes at low temperatures but decompose at 20°C after prolonged stirring to produce the metals in the zero-valent state. Complexing reoccurs by addition of excess  $\text{Ph}_3\text{P}$ . Each Pd atom can catalyse the oxidation of 500 molecules of  $\text{Ph}_3\text{P}$ .

### $\pi$ -Complexes of PdCl<sub>2</sub> with Straight-chain Olefins

G. F. PREGAGLIA, M. DONATI and F. CONTI, *Chem. & Ind.*, 1966, (46), 1923-1924

$\pi$ -complexes of the general formula (C<sub>n</sub>H<sub>2n</sub>.PdCl<sub>2</sub>)<sub>2</sub>, where C<sub>n</sub>H<sub>2n</sub> is any straight chain olefin, are synthesised by direct addition of PdCl<sub>2</sub> to the olefin in the liquid state. The product is generally a mixture of the  $\pi$ -complex of isomeric olefins in which the *cis*-form is predominant. The complexes are stable in air for a few hours. They are yellow-brown, crystalline compounds which decompose on melting.

### $\pi$ -Allylic Complexes of Palladium(II) Chloride with Straight Chain Mono-olefins

M. DONATI and F. CONTI, *Inorg. Nucl. Chem. Letters*, 1966, 2, (11), 343-347

Compounds of the type [(C<sub>n</sub>H<sub>2n-1</sub>)<sub>2</sub>Pd<sub>2</sub>Cl<sub>4</sub>] were prepared by reacting  $\pi$ -allyl [PdClC<sub>n</sub>H<sub>2n-1</sub>]<sub>2</sub> with PdCl<sub>2</sub> in *n*-octene or *n*-decene at 100°C for 12 h, followed by addition of excess pet ether and filtration, to give the brown compound. On cooling the reaction mixture to -78°C a yellow compound was obtained, (C<sub>n</sub>H<sub>2n-1</sub>.PdCl)<sub>2</sub>. NMR and IR studies show that the coordinated molecule PdCl<sub>2</sub> can easily be displaced indicating weak bonding, and a cluster structure with weak metal-metal bonds is proposed.

### Synthesis of Metal-Metal Bonds via Iridium and Rhodium Anions

J. P. COLLMAN, F. D. VASTINE and W. R. ROPER, *J. Am. Chem. Soc.*, 1966, 88, (21), 5035-5037

Reduction of Ir(CO)<sub>2</sub>L<sub>2</sub> with Na amalgam in tetrahydrofuran under p<sub>CO</sub> = 60 psi yielded the intermediate Na<sup>+</sup>[Ir(CO)<sub>3</sub>L]<sup>-</sup>, where L = Ph<sub>3</sub>P. The intermediate reacted with (CH<sub>3</sub>)<sub>3</sub>SnCl, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnCl, (CH<sub>3</sub>)<sub>2</sub>SnCl<sub>2</sub>, L-AuCl, and Hg(CN)<sub>2</sub> to form crystalline, air-stable compounds, which apparently contain metal-metal bonds. Reduction of RhL<sub>2</sub>(CO)Cl with Na amalgam yielded Na<sup>+</sup>[RhL<sub>2</sub>(CO)<sub>2</sub>]<sup>-</sup>, which combined with (CH<sub>3</sub>)<sub>3</sub>SnCl to form (CH<sub>3</sub>)<sub>3</sub>Sn-RhL<sub>2</sub>(CO)<sub>2</sub>.

### The Mechanism of the Formation of an Iridium Complex of Molecular Nitrogen via Organic Azides

J. P. COLLMAN, M. KUBOTA, J.-Y. SUN and F. VASTINE, *Ibid.*, 1967, 89, (1), 169-170

Spectral studies enabled the mechanism of formation of an Ir complex with N<sub>2</sub> to be elucidated as one stage in the search for a catalyst to hydrogenate N<sub>2</sub> under mild conditions and thereby fix atmospheric N<sub>2</sub>.

### Reactivity of Dodecacarbonyltriruthenium

J. P. CANDLIN, K. K. JOSHI and D. T. THOMPSON, *Chem. & Ind.*, 1966, (47), 1960-1961

The reactions of Ru<sub>3</sub>(CO)<sub>12</sub> with PPh<sub>3</sub>, P<sub>2</sub>(CH<sub>3</sub>)<sub>4</sub> and moist NO to give, respectively, (PPh<sub>3</sub>)<sub>3</sub>Ru<sub>3</sub>(CO)<sub>9</sub>, [(CH<sub>3</sub>)<sub>2</sub>P]<sub>3</sub>Ru<sub>2</sub>(CO)<sub>6</sub> and poly-

mer Ru(CO)<sub>2</sub>(NO)<sub>2</sub> were studied in order to elucidate the solid state structure of Ru<sub>3</sub>(CO)<sub>12</sub> with respect to Fe<sub>3</sub>(CO)<sub>12</sub> which X-ray analysis suggests is slightly different. Reactions with P<sub>2</sub>(CH<sub>3</sub>)<sub>4</sub> and moist NO yielded compounds analogous to those of Fe, whereas with PPh<sub>3</sub> the resultant product showed no cleavage of metal-metal bonds as found in the analogous Fe compound. Physical data for the Ru products are tabulated.

### Reactions of Ruthenium Compounds with Sulphuric Acid

S. I. GINZBURG, M. I. YUZ'KO and T. V. FOMINA, *Zh. Neorg. Khim.*, 1966, 11, (11), 2551-2553

Studies on Ru(III) and Ru(IV) compounds with H<sub>2</sub>SO<sub>4</sub> at 100-300°C showed that, whatever the original compounds, the reaction products have the same absorption spectra. The anionic form occurs in solution even at 150°C. Together with coordinated sulphato groups are seen oxidation-reduction processes; Ru(III) is oxidised and Ru(IV) is reduced to the formal state of oxidation 3.5. Green complex Ru sulphate is formed during reduction of Ru(IV) in H<sub>2</sub>SO<sub>4</sub> at 150-200°C and it has an absorption band at 630-640 nm. It contains the peroxy groups -O-O- and -O<sub>2</sub><sup>-</sup>. Green compounds are formed also in aqueous H<sub>2</sub>SO<sub>4</sub> by the reaction of Ru<sup>III,IV</sup> sulphates with H<sub>2</sub>O<sub>2</sub>.

### On Green Ruthenium Sulphate

*Ibid.*, 2554-2559

Green Ru sulphate complexes containing K and Cs were synthesised similarly to those of Ir and Rh. Studies of Ru sulphate indicated the existence of a polynuclear complex anion in which Ru:SO<sub>4</sub> ≈ 2:3 or 3:5, and with sulphate groups with bidentate coordination to the central atoms. The Ru exists in oxidation states Ru<sup>III</sup> and Ru<sup>IV</sup>; formal oxidation state 3.5. O<sub>2</sub><sup>-</sup> or O<sub>2</sub><sup>2-</sup> groups are probably present.

## ELECTROCHEMISTRY

### Interaction of Carbon Dioxide with Hydrogen Chemisorbed on a Platinum Electrode

B. J. PIERSMA, T. B. WARNER and S. SCHULDINER, *U.S. Rept. AD 633,686, N.R.L.6388*, 1966, (April), 12 pp

The interaction of CO<sub>2</sub> with chemisorbed H<sub>2</sub> on a Pt electrode was studied using transient galvanostatic and potentiostatic techniques. The presence of CO<sub>2</sub> or HCO<sub>3</sub><sup>-</sup> in solution was found to inhibit the H<sub>2</sub>-evolution reaction as in the dissociation of HCOOH to H<sub>ads</sub> and CO<sub>2</sub> in which the CO<sub>2</sub> interacts on the Pt to retard further oxidation. Results indicate that the reduction of CO<sub>2</sub> by H<sub>ads</sub> is unlikely and that the rate of oxidation of H<sub>2</sub> is affected by the rate of diffusion of irreversibly chemisorbed H atoms on the Pt electrode.

### Measurement of the Potential of Powder Catalysts in Dielectric Media. II. Reduction of Unsaturated Compounds.

G. V. TANEEVA, A. B. FASMAN and D. V. SOKOL'SKII, *Elektrokhimiya*, 1966, 2, (12), 1457-1463

Comparison of the results of potentiometric and kinetic measurements of changes of potentials of Pt, Pd and Ni catalysts during hydrogenations of phenylacetylene and crotonaldehyde in polar and non-polar solvents indicated saturation of  $-\text{C}\equiv\text{C}-$ ,  $=\text{C}=\text{C}=\text{O}$  and  $=\text{C}=\text{O}$  bonds as the catalyst, solvent and temperature were varied. The value of  $\Delta\phi$  varied across the phase boundaries of the system.

### Radiochemical Study of the Anodic Corrosion of Ruthenium

J. LLOPIS, J. M. GAMBOA and J. M. ALFAYATE, *Electrochim. Acta*, 1967, 12, (1), 57-65

The corrosion and passivation of irradiated Ru in 2 N and 4 N HCl at 50°C, studied electrolytically at up to 1150 mV, show that Ru is passivated at potentials  $>950$  mV. Pt is passivated more completely than Ru, and Ru and Os form well defined oxides.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Production of Foils of the Platinum Group Metals and of Gold and the Measurement of their Thickness

V. N. KAREV, A. P. KLYUCHAREV, L. G. LISHENKO and V. N. MEDYANIK, *Zh. Prikladnoi Khim.*, 1966, 39, (11), 2525-2529

Electrolytes were prepared from which Pd, Pt, Rh and Au were deposited on Cu, which was subsequently dissolved. Deposition conditions are tabulated. Deposit thicknesses were measured with a modified spectrometer.

## LABORATORY APPARATUS AND TECHNIQUE

### Single-crystal Growth of Sapphire

B. COCKAYNE, M. CHESSWAS and D. B. GASSON, *J. Materials Sci.*, 1967, 2, (1), 7-11

Single sapphire crystals are prepared from  $\text{Al}_2\text{O}_3$  using either the vertical pulling technique or the floating zone recrystallisation technique in which the apparatus has been modified by the inclusion of an Ir-lined  $\text{Al}_2\text{O}_3$  jacket to the afterheater, and an additional heating shield of MgO lined with Ir, respectively. Formation of Ir platelets in the crystal due to the decomposition of volatile  $\text{IrO}_2$  in the afterheater is eliminated below 1020° by suitable adjustment of the  $\text{Ar}-\text{O}_2$  or  $\text{N}_2-\text{O}_2$  gas flow; contamination is more severe with the floating zone method. Reduction of pulling rate

to  $\leq 12$  mm/h reduced the formation of voids; use of the afterheater reduced the number of dislocations and low angle boundaries.

### Catalytic Hydrogenation. II. A New, Convenient Technique for Laboratory Hydrogenations. A Simple Automatic Device for Atmospheric Pressure Hydrogenations

C. A. BROWN and H. C. BROWN, *J. Org. Chem.*, 1966, 31, (12), 3989-3995

A wide range of laboratory hydrogenations may be carried out with highly active Pt/C hydrogenation catalyst prepared *in situ* by reduction of Pt metal salts with  $\text{H}_2$  from a generator, which incorporates  $\text{NaBH}_4$  as the source of  $\text{H}_2$ . Advantages of this apparatus include simple assembly, pure  $\text{H}_2$  from the  $\text{NaBH}_4$  source, operation at atm. pressure, accurate measurement of  $\text{H}_2$  uptake, ready hydrogenation of labile materials at low pressure, and no serious limitation on capacity.

## BRAZING

### The Selection of Brazing Alloys

M. L. SLOBODA, *Welding Met. Fabric.*, 1966, 34, (10), 386-393

A review of the suitability of thirty industrial brazing alloys for various applications. Pallabraz 810 and 880 are used principally in vacuum tubes, Pallabraz 1237 is used principally for high strength and oxidation resistance at elevated temperature, and Pt is used for brazing Mo and W for ultra-high temperature service.

## HETEROGENEOUS CATALYSIS

### On the Catalytic Oxidation of Ammonia in the Industrial Production of Nitric Acid

H. HOLZMANN, *Chem.-Ing.-Tech.*, 1967, 39, (2), 89-95

A review of the current state of catalytic oxidation of  $\text{NH}_3$  for production of  $\text{HNO}_3$  and the effects on it of oxidation temperature, gas pressure, rate of flow and of the various possible types of catalyst gauzes. (33 references).

### Chemisorption of Carbon Monoxide on Finely Divided Platinum Held in Aqueous Suspension

J. W. HIGHTOWER and P. H. EMMETT, *J. Colloid Interface Sci.*, 1966, 22, (2), 158-160

Approximately a monolayer of CO is chemisorbed on a stirred suspension of Pt in  $\text{H}_2\text{O}$ , giving a method of determining the surface area of colloidal Pt metals. A Pt suspension was obtained by reduction of  $\text{PtO}_2$  with  $\text{H}_2$  *in situ* and the volume of CO adsorbed was determined by equilibrating the solution with CO at 200 mm for 5h. The CO adsorbed by  $\text{H}_2\text{O}$ , which is linearly dependent on the pressure, was determined in a

blank run. The volume of the monolayer was found by adsorption of  $N_2$  on the dried Pt. The ratio  $CO:N_2$  adsorbed was  $\geq 0.96$ .

### Adsorption and Interaction of Hydrogen and Oxygen on Platinum

V. PONEC, *J. Catalysis*, 1966, 6, (3), 362-370

Conditions under which gases react on Pt were established by studies of the chemisorption and mutual interaction of  $H_2$  and  $O_2$  on Pt films, and of simultaneous resistance changes. A model for the  $H_2$  chemisorption bond for transition metals is suggested.

### Activation of Platinum-on-Alumina Catalyst in the Isomerisation and Hydrogenolysis of Hydrocarbons by Means of High Temperature Treatment by Hydrogen

I. I. LEVITSKII, M. G. GONIKBERG, KH. M. MINACHEV and V. I. BOGOMOLOV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1966, (10), 1695-1701

Treatment of 0.3% Pt/ $Al_2O_3$  by  $H_2$  at 500-550°C sharply increased its activity for isomerisation of cyclohexane and of  $n-C_6H_{14}$  and also for hydrogenolysis of methylcyclopentane. Treatment by  $N_2$ , containing 0.5%  $O_2$ , at 420°C deactivated the catalyst for isomerisation and hydrogenolysis of hydrocarbons but activated it for hydrogenation of  $C_6H_6$ . Treatment by  $H_2$  to remove  $O_2$  and  $H_2O$  from the catalyst at 350-420°C caused methylcyclopentane to be converted to isohexane but after treatment of the catalyst by  $H_2$  at 550°C the main product of hydrogenolysis of methylcyclopentane was  $n$ -hexane.

### The Hydrogenation of Acetylene. IV. The Reaction of Acetylene with Deuterium Catalysed by Alumina-supported Rhodium, Palladium, Iridium, and Platinum

G. C. BOND and P. B. WELLS, *J. Catalysis*, 1966, 6, (3), 397-410

During studies of the  $C_2H_2$ - $D_2$  reaction over Rh/ $Al_2O_3$ , Pd/ $Al_2O_3$ , Ir/ $Al_2O_3$  and Pt/ $Al_2O_3$  no  $C_2H_2$  exchange was observed; H exchange was fairly rapid over Rh and Ir, slow over Pt, negligible over Pd; ethylene- $d_2$  was the most abundant form of ethylene. Major component of ethylene- $d_2$  was the *cis* isomer in high yields over Pd, Pt; higher yields of ethylene- $d_3$  and - $d_4$  were observed over Rh.

### Conversions of Spiro-(4,4)-nonane on Platinum- and Palladium-Alumina Catalysts in Catalytic Reforming Conditions

N. I. SHUIKIN and I. I. VOZNESENSKAYA, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1966, (11), 2052-2053  
o-Methylethylbenzene formed 41% of the catalysate from conversion of spiro-(4,4)-nonane over 0.5% Pt/ $Al_2O_3$  at 450°C,  $p_{H_2}=30$  atm, rate 0.3  $h^{-1}$ , H : hydrocarbon = 5:1. Indane formed

68% of the catalysate by isomerisation of spiro-(4,4)-nonane over 0.5% Pd/ $Al_2O_3$  in similar conditions.

### Catalytic Conversions of Spiro-(4,5)-decane on Platinum-, Palladium- and Cobalt-Alumina Catalysts in Catalytic Reforming Conditions

*Ibid.*, 2054-2055

The main reaction during conversion of spiro-(4,5)-decane over 0.5% Pt/ $Al_2O_3$ , 0.5% Pd/ $Al_2O_3$  and 10% Co/ $Al_2O_3$  at 450°C,  $p_{H_2}=30$  atm is isomerisation to naphthalene, which occurs most easily on the Pt catalyst. Spirodecane breaks at the  $C_5$  ring to form smaller amounts of *gem*-substituted cyclohexanes and alkylbenzenes.

### Study of Supported Catalysts by the Method of Exoelectronic Emission. IV. Platinum on Aluminium Oxide and Zirconium Oxide

YU. P. SIMONITE, V. M. MOZZHUKHINA, A. S. SHASHKOV and I. V. KRYLOVA, *Zh. Fiz. Khim.*, 1966, 40, (11), 2860-2864

Variations of catalytic activity and exoelectronic emission from Pt/ $Al_2O_3$  and from Pt/ $ZrO_2$  as the Pt content changes are similar. Small amounts of Pt sharply reduce exoemission from  $Al_2O_3$  and  $ZrO_2$  but at medium Pt concentrations ( $\alpha \approx 0.01-0.04$ ) there are formed active centres both for emission and for catalysis.

### V. Platinum on Aluminium Oxide; Measurement by Secondary Electronic Multiplication

A. P. FILONENKO and I. V. KRYLOVA, *Ibid.*, (12), 3060-3064

Exoelectronic emission from Pt/ $Al_2O_3$  *in vacuo* was measured by secondary electronic multiplication and was accompanied by strong desorption. Emission from  $Al_2O_3$  and from Pt/ $Al_2O_3$  depends on the nature of the film adsorbed on the surface.

### VII. Platinum on Magnesium Oxide. Investigation by Secondary Electronic Multiplication

I. V. KRYLOVA and O. G. KUPENKO, *Ibid.*, (11), 2918-2920

Exoelectronic emission from Pt/MgO was measured using a Geiger counter and using secondary electronic multiplication *in vacuo*. Samples with high Pt contents show greatly reduced emission after a period in an high vacuum.

### Conversions of Dihydropyran and Propyldioxene on Various Catalysts

N. I. SHUIKIN, R. A. KARAKHANOV and S. N. KHAR'KOV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1966, (11), 2044-2045

2,3-Dihydropyran decomposes at 300-400°C over Pt/C, active C and quartz to form acrolein with up to 30% yield. In analogous conditions 2-propyl-1,4-dioxene undergoes cracking to form gaseous products.

### Dehydrocyclisation of Methyl Propyl Ketone on Metal

D. CORNET and F. G. GAULT, *Bull. Soc. Chim. Fr.*, 1966, (10), 3264-3268

The dehydrocyclisation of methyl propyl ketone to 2-methylfuran was studied gas-chromatographically on supported Pt, and on Pt and Pd metal films. Results indicate maximum conversion between 300° and 360°C. Thermodynamics and mechanism of the reaction are discussed.

### Metal-catalysed Hydrogenation and Exchange of Cyclohexene

G. V. SMITH and J. R. SWOAP, *J. Org. Chem.*, 1966, 31, (12), 3904-3906

To explain how cyclohexene desorbs with D in either its allylic or olefinic position during deuteration over 5% Pd/C, 5% Pt/C, and reduced PtO<sub>2</sub>, a new surface involving an intramolecular H shift is suggested.

### Hydrogenation of Allyl Alcohols on Platinum and Palladium Catalysts Supported on Polyacrylonitrile

D. V. SOKOL'SKII, O. A. TYURENKOVA, V. A. DASHEVSKII and E. I. SELIVERSTOVA, *Kinetika i Kataliz*, 1966, 7, (6), 1032-1038

Potentiometric studies of the catalytic activities of Pt and Pd on polyacrylonitrile for hydrogenation of allyl alcohols at room temperature and atm. pressure in relation to the medium and the nature of the solvent showed reproducible and stable catalytic properties. The Pd catalyst has more activity than the Pt catalyst. The apparent activation energies were calculated. The reaction is zero order with respect to the hydrogenated substances.

### The Microcatalytic Hydrogenation of Benzene over Groups VIII and Ib Metals and Alloys

D. A. CADENHEAD and N. G. MASSE, *J. Phys. Chem.*, 1966, 70, (11), 3558-3566

Microcatalytic studies of the hydrogenation of C<sub>6</sub>H<sub>6</sub> over Cu-Ni, Cu-Pd and Au-Pd alloys determined specific activities at 84-144°C for the Pd alloys and apparent activation energies. The behaviour of Cu-Pd and Au-Pd indicated the formation of transition metal - Group Ib metal - H<sub>2</sub> ternary systems.

### Poison-resistant Zeolite Catalysts

J. G. FIRTH and H. B. HOLLAND, *Nature*, 1966, 212, (5066), 1036-1037

The reaction between O<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> on Pd adsorbed on zeolite, and on Pd incorporated into the zeolite structure, was studied to determine the resistance to poisoning of the latter. The zeolites were poisoned by preferential adsorption of either hexamethyldisiloxane or CCl<sub>4</sub>. The zeolites incorporating Pd in their structure were not poisoned except where the pore size was large

enough to admit CCl<sub>4</sub> molecules. The experiment also indicated that C<sub>2</sub>H<sub>6</sub> and CCl<sub>4</sub> could react on single atoms of Pd.

### Hydrogenation of Benzene in the Presence of a Palladium Catalyst

A. V. LOZOVoi, T. I. MARKINA, D. P. PCHELINA and S. A. SENYAVIN, *Neftekhimiya*, 1966, 6, 683-689

Studies of hydrogenation of C<sub>6</sub>H<sub>6</sub> at 150-350°C, 50-100 atm over 0.5 and 4.5 wt.% Pd/γ-Al<sub>2</sub>O<sub>3</sub> treated with H<sub>2</sub>S and HF showed 93-100% conversion at 250-270°C and indicated that 99.7-99.9% pure C<sub>6</sub>H<sub>12</sub> can be produced under optimum conditions. Isomerisation of C<sub>6</sub>H<sub>12</sub> to methylcyclopentane was very small at 200-250°C, was 0.13-0.27% at 250-270°C, and was appreciable at 300°C. Treatment of Al<sub>2</sub>O<sub>3</sub> by 0.5% HF left the catalyst activity for C<sub>6</sub>H<sub>6</sub> hydrogenation unaltered but enhanced the isomerisation process. C<sub>6</sub>H<sub>6</sub> hydrogenation at 235-265°C was zero order in H<sub>2</sub>; first order in C<sub>6</sub>H<sub>6</sub>. C<sub>6</sub>H<sub>12</sub> tended to retard the hydrogenation. Apparent activation energy for C<sub>6</sub>H<sub>6</sub> hydrogenation was 8190 cal/mole; temperature coefficient of the reaction rate was 1.157. Raising the pressure from 50 to 100 atm increased the hydrogenation rate by 4% but increasing H<sub>2</sub>:C<sub>6</sub>H<sub>6</sub> from 7.6:1 to 18:1 had little effect.

### USDA-ADM Produce Mazda from Soybean Oil

*Chem. Engng. News*, 1966, 44, (53), 38-39

A process developed by the U.S. Department of Agriculture has been modified by Archer Daniels Midland and a continuous pilot plant is now making a versatile intermediate, known as mazda - methyl azelaaldehyde dimethyl acetal - from soybean oil by ozonolysis of methyl soyate and catalytic hydrogenation of the ozonolysis products over Pd/C. Tests on solvent-to-ester ratio, catalyst type, pressure and temperature of the hydrogenation indicated an H<sub>2</sub>O:methyl soyate optimum of 1.3:1 over Pd/C at 300 p.s.i.g., 75°C. The pilot plant gives almost 90% yield and a \$3.0-\$3.5 million, 10 million lb/yr plant is under design.

### Free and Active Surface of Pd/C catalysts

H. KRAL, *Chem. - Z.*, 1967, 91, (2), 41-47

Kinetics of the hydrogenation of C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>, acetophenone and sorbic acid at 20°C on 5% Pd/C of 560-1060 m<sup>2</sup>/g surface were studied by poisoning the catalyst to determine its selectivity and active sites to find a characteristic quantity more specific than hydrogenation activity alone.

### Hydrogenation and Hydrogenolysis. IX. The Hydrogenation of Benzyl Alcohol with Platinum Metal Catalysts

S. NISHIMURA and M. HAMA, *Bull. Chem. Soc. Japan*, 1966, 39, (11), 2467-2470

The rate of hydrogenation of benzyl alcohol at

25°C,  $p_{H_2} = 1$  atm, shows a more marked decrease for Rh catalysts than for Pt due to the formation of cyclohexanecarboxaldehyde, by isomerisation of the intermediate 1-cyclohexanecarbinol, which inhibits the hydrogenation more on Rh than on Pt.

### Low-pressure Hydrogenation of Some Benzenepolycarboxylic Acids with Rhodium Catalyst

M. FREIFELDER, D. A. DUNNIGAN and E. J. BAKER, *J. Org. Chem.*, 1966, **31**, (10), 3438-3439

Hydrogenation of an aqueous solution of pyromellitic acid using 5% Rh/C catalyst at up to 60°C and <3 atm gave a high yield of cyclohexane-1,2,4,5-tetracarboxylic acid. At 60-70°C, phthalic, isophthalic and tetraphthalic acids similarly gave high yields of dicarboxylic acids. The resulting 1,2- and 1,4-dicarboxylic acids had *cis* configuration whereas the 1,3-dicarboxylic acid was a 60:40 *cis-trans* mixture. Results indicate that H<sub>2</sub>O solubility of the product is more important than that of the starting material.

### On the Conversion of Acetophenone during Hydrogenation on Ruthenium Catalyst

N. S. BARINOV, D. V. MUSHENKO and E. G. LEBEDEVA, *Zh. Prikladnoi Khim.*, 1966, **39**, (11), 2599-2601

Methylcyclohexylcarbinol may be produced from acetophenone on Ru/C. Conversion of acetophenone to the naphthenyl alcohol occurs in two ways; via methylcyclohexylketone and methylphenylcarbinol. Increasing the temperature causes the former to predominate. Content of methylcyclohexylcarbinol in the catalysate decreases during this treatment.

### On the Reduction of Chloronitrobenzenes into Chloroaniline. Part 2. The Use of Ruthenium in the Reduction of para-Chloronitrobenzene

N. P. SOKOLOVA, A. A. BALANDIN, M. P. MAKSIMOVA and Z. M. SKUL'SKAYA, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1966, (11), 1891-1895

5% Ru/BaSO<sub>4</sub> catalyses the reduction of *p*-chloronitrobenzene to *p*-chloroaniline, yielding 99.5-99.7% at optimum conditions with only 0.3-0.5% separation of HCl. The yield is less with 1, 0.5 or 0.05% Ru/BaSO<sub>4</sub>. The use of Al<sub>2</sub>O<sub>3</sub> as the support leads to greater dehalogenation.

## HOMOGENEOUS CATALYSIS

### Coordination Chemistry and Homogeneous Catalysis

J. HALPERN, *Chem. Engng. News*, 1966, **44**, (45) 68-75

A review of the use of transition metal complexes, including those of the Pt metals, as coordination

compounds for the homogeneous catalysis of many reactions: activation of H<sub>2</sub>, hydrogenation of olefins and their isomerisation, dimerisation, polymerisation, hydroformylation, and oxidation. Other uses and likely future trends are indicated (8 references).

### Investigation of the Mechanism of Hydrogenation of Ethylene on an Homogeneous Pt-Sn Chloride Catalyst

A. P. KHRUSHCH, L. A. TOKINA and A. E. SHILOV, *Kinetika i Kataliz*, 1966, **7**, (5), 901-904

The hydrogenation of C<sub>2</sub>H<sub>4</sub> in the presence of Pt-SnCl<sub>2</sub> in CH<sub>3</sub>OH solution produced C<sub>2</sub>H<sub>5</sub>D from the systems C<sub>2</sub>H<sub>4</sub>+D<sub>2</sub>+CH<sub>3</sub>OH and C<sub>2</sub>H<sub>4</sub>+H<sub>2</sub>+CH<sub>3</sub>OD. This suggests a reaction mechanism in which C<sub>2</sub>H<sub>4</sub> molecules are combined with Pt-H followed by hydrolysis of the ethyl-platinum derivative.

### Isomerisation of Butenes Initiated by Palladium Chloride

I. I. MOISEEV and S. V. PESTRIKOV, *Dokl. Akad. Nauk S.S.S.R.*, 1966, **171**, (1), 151-154

Studies of the kinetics of isomerisation of butenes in the presence of PdCl<sub>2</sub> lead to proposals for the mechanism of reaction which involves the initial formation of  $\pi$ -complexes of PdCl<sub>2</sub> with subsequent regeneration of the PdCl<sub>2</sub> as the isomers are formed.

### Organic Syntheses by Means of Noble-metal Compounds. XXX. The Mechanism of Simultaneous Formation of Isocyanate and $\pi$ -Allylpalladium Chloride from Sodium Chloropalladate, Allyl Chloride, Primary Amine and Carbon Monoxide

T. TSUJI and N. IWAMOTO, *Chem. Commun.*, 1966, (22), 828-829

Oxidation of a primary amine with PdCl<sub>2</sub> by abstraction of 2 H atoms in the presence of allyl chloride to give  $\pi$ -allyl palladium chloride is believed to be the mechanism of the reaction which occurs between *n*-butylamine, allyl chloride, NaCl and PdCl<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> through which CO was passed for 2 h at 60°C. Dibutylurea was isolated on addition of excess butylamine and evaporation of solvent under pressure yielded  $\pi$ -allylpalladium chloride. A similar reaction is observed in CH<sub>3</sub>OH.

### Aspects of Catalytic Hydrogenation with a Soluble Catalyst

A. J. BIRCH and K. A. M. WALKER, *J. Chem. Soc., C, Org.*, 1966, (21), 1894-1896

RhCl(PPh<sub>3</sub>)<sub>3</sub> catalyses the specific addition of D<sub>2</sub> to systems containing more than one double bond, e.g. cyclohexene, oleic and linoleic acids, and ergosterol, without additional labelling; and catalyses selective hydrogenation in the presence of groups sensitive to hydrogenolysis, e.g.  $\omega$ -

nitrostyrene to phenylnitroethane, and cinnamyl chloride in part to phenyl propyl chloride. 10-20 wt.% catalyst to 100 wt.% compound to be hydrogenated is used and results indicate the reagent is nucleophilic or the mechanism is governed by steric factors.

### Formation and Properties of Some Chloro-carbonyl Complexes of Ruthenium(II) and Ruthenium(III)

J. HALPERN, B. R. JAMES and A. L. W. KEMP, *J. Am. Chem. Soc.*, 1966, **88**, (22), 5142-5147

Kinetics of the reactions of CO with chlororuthenate(II) and (III) complexes in HCl to form  $\text{Ru}(\text{CO})\text{Cl}_5^{2-}$ ,  $\text{Ru}(\text{CO})(\text{H}_2\text{O})\text{Cl}_4^{2-}$  and  $\text{Ru}(\text{CO})_2\text{Cl}_4^{2-}$  were studied and the  $\text{NH}_4$  salts were isolated. Neutral  $\text{Ru}(\text{CO})\text{Cl}_2(\text{PPh}_3)_3$  and  $\text{Ru}(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2$  were obtained by addition of  $\text{PPh}_3$  to the appropriate anions. Homogeneous reduction of  $\text{Ru}(\text{CO})\text{Cl}_5^{2-}$  with  $\text{H}_2$  produced  $\text{Ru}(\text{CO})(\text{H}_2\text{O})\text{Cl}_4^{2-}$ , which catalysed the reaction and also catalysed  $\text{D}_2$ - $\text{H}_2\text{O}$  exchange and hydration of  $\text{C}_2\text{H}_2$ . Ru carbonyl chloride complexes are formed during Ru(III)-catalysed hydration of acetylenes and a reduction of catalytic activity results.

### The Decarbonylation of Formic Acid by Ruthenium(II) Chloride

J. HALPERN and A. L. W. KEMP, *Ibid.*, 5147-5150

$\text{RuCl}_4^{2-} + \text{HCOOH} \rightarrow \text{Ru}(\text{CO})(\text{H}_2\text{O})\text{Cl}_4^{2-}$  in aqueous HCl. The rate of this reaction depends on the concentrations of Ru(II), HCOOH,  $\text{H}^+$ ,  $\text{Cl}^-$  and temperature. Results suggest a stepwise reaction mechanism in which a chlororuthenate (II) complex initially is dissociated.

### Homogeneous Catalysis of the Hydrogenation of Olefinic Compounds by Ruthenium(II) Chloride

J. HALPERN, J. F. HARROD and B. R. JAMES, *Ibid.*, 5150-5155

$\text{RuCl}_2$  catalyses the homogeneous hydrogenation of maleic and fumaric acids in aqueous solution to succinic acid via the apparent formation of a Ru(II)-olefin complex. The rate law for each reaction is  $k[\text{H}_2][\text{Ru}^{\text{II}}(\text{olefin})]$ , where, at 80°C in 3M HCl, for maleic acid:  $k = 2.3 \pm 0.1 \text{ M}^{-1}\text{sec}^{-1}$ ,  $\Delta H^* = 14 \text{ kcal/mole}$ ,  $\Delta S^* = 17 \text{ eu}$ ; for fumaric acid:  $k = 3.6 \pm 0.6 \text{ M}^{-1}\text{sec}^{-1}$ ,  $\Delta H^* = 17 \text{ kcal/mole}$ ,  $\Delta S^* = 8 \text{ eu}$ . Hydrogenation of fumaric acid in  $\text{D}_2\text{O}$  yields mainly DL-2,3-dideuterio-succinic acid, indicating stereospecific *cis* addition.

## FUEL CELLS

### Hydrocarbon Fuel Cells with Fluoride Electrolytes

E. J. CAIRNS, *J. Electrochem. Soc.*, 1966, **113**, (11), 1200-1204

The ternary acid electrolyte system  $\text{CsF-HF-H}_2\text{O}$

is suitable for high-performance fuel cells with Teflon-bonded Pt electrodes operating near 150°C on paraffins.  $\text{C}_2$ - $\text{C}_4$  *n*-paraffins give maximum performance when electrolyte composition is  $\text{F/Cs} = 2.0$ ,  $\text{H}_2\text{O} = 10 \text{ mole}/\%$ .  $\text{C}_1$  and  $\text{C}_4$ - $\text{C}_{16}$  *n*-paraffins give somewhat lower performance. Good performance is obtained with  $\text{C}_2$ - $\text{C}_4$  *n*-paraffins and HF- $\text{H}_2\text{O}$  electrolyte at 105°C also.  $\text{C}_3\text{H}_8$  is converted completely to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  at 105-166°C in both sets of electrolytes at a wide range of current densities. There is no current or voltage cycling.

### Electrochemical Cells with Halogen Fluoride Electrolytes

M. S. TOY and W. A. CANNON, *Electrochem. Technol.*, 1966, **4**, (11-12), 520-523

The anodic and cathodic polarisation curves of the pure electrolytes  $\text{BF}_3$ ,  $\text{BrF}_3$  and  $\text{ClF}_3$  were determined using electrodes of Pt, which was found to be the only material with sufficient inertness and low polarisability. The polarisation behaviour, measured galvanostatically and potentiometrically, showed, respectively, an anodic and cathodic limiting current of 20  $\text{mA}/\text{cm}^2$  and a rapidly attained high current density. Investigations of potential/current density show Pb-Pt couple to have the highest cell voltage but show Cd-Pt couple to have a constant current density up to dissolution of the anodes.

### Use of Raney Platinum for Anodic Oxidation of Hydrocarbons, Alcohols, and Carboxylic Acids into Carbon Dioxide

H. BINDER, A. KÖHLING and G. SANDSTEDE, *Advanced Energy Conversion*, 1966, **6**, (3), 135-148

Studies of current-voltage curves and of potentiostatic-coulometric determinations of conversions over Raney Pt at 25-100°C of hydrocarbons, alcohols, aldehydes, ketones and carboxylic acids in acid and alkaline electrolytes permit its evaluation as a catalyst for anodic oxidation in fuel cells.

## CHEMICAL TECHNOLOGY

### On the Measurement of the Hydrogen Permeability of Palladium and Iron Cathodes by the $\text{H}_2$ -Pressure Formed in the Closed Diffusion Chamber

F. LANGE, E. KAHRIG and D. KIRSTEIN, *Chem. Tech.*, 1966, **18**, (11), 672-674

$\text{H}_2$  diffusing through Pd causes a rise in the pressure in a closed diffusion chamber and no back-diffusion is observed up to 170 atm. The permeability P of Pd and Fe for  $\text{H}_2$  can be calculated from the pressure-time curve by the equation  $P = V_r[p - p_1 + M_1 p_0 / V_r] / F p_0 t$ , where  $V_r$  = residual gas volume, F = area of diffusion surface, p = pressure,  $p_0 = 1 \text{ atm}$ ,  $p_1$  = initial pressure in chamber, t = time, and  $M_1 = \beta V_0$ , where  $\beta$  is the solubility coefficient and  $V_0$  is the volume.

## GLASS TECHNOLOGY

### An Electrochemical Theory for Oxygen Reboil

J. H. COWAN, W. M. BUEHL and J. R. HUTCHINS,  
*J. Am. Ceram. Soc.*, 1966, **49**, (10), 559-562

O<sub>2</sub> reboil with the development of O<sub>2</sub> blisters may occur during glass melting in air in Pt vessels but can be reduced by elimination of electron conductors from the system, removal of O<sub>2</sub> from the atmosphere above the melt, application of an external bucking potential, reversal of concentration gradients, and removal of temperature gradients. A mechanism for the phenomenon is proposed.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Influence of Platinum Group Metal Films on Oxide Cathode Emission

YU. A. VOLODIN, A. V. DRUZHININ and V. A. SMIRNOV, *Radiotekh. Elektron.*, 1966, **11**, (12), 2262-2265

Thermionic emission from an heated cathode can be controlled by coating with Pt, Ir, or Os, which suppress emission from the coated areas. 0.3-0.5 $\mu$  coatings of Ir reduce emission from an

oxide cathode by 300 times, 0.3-0.5 $\mu$  Pt by 10 times, 0.01 $\mu$  Os by 100 times.

## TEMPERATURE MEASUREMENT

### Survey of Thermocouples

C. P. SMITH, *Engng. Materials Design*, 1966, **9**, (12), 1966-1970

A survey of base and Pt metal thermocouples, with the instrumentation required and factors to be considered in selection and installation. A guide to fifty-one British thermocouple manufacturers is included.

### Use of Noble Metals and Noble Metal Alloys for Temperature Measurement

S. LANDOR, *Mérés Automat.*, 1966, **14**, (3), 85-88

Values of thermal e.m.f.  $E_x$  are tabulated against temperature  $t$  for Pt:10-100% Rh-Pt thermocouples and for Pt:0-100% Au-Pd thermocouples. Data for combinations of Pt with Pt-Mo, Pt-W, Pt-Re, Pt-Os, Pt-Co, Pt-Cu, Pt-Ir and Pt-Pd-Au are presented graphically. Advantages of various thermocouple alloys are discussed in relation to  $E_x$  and to physical properties. Some discrepancies exist between these experimental results and accepted British figures.

## NEW PATENTS

### METALS AND ALLOYS

#### Composite Metal

DEUTSCHE GOLD- & SILBER- SCHEIDANSTALT  
*British Patent* 1,051,994

Better adherence of Pt to Ti is achieved when the Ti is pickled in a solution which is at least 10 N in H<sup>+</sup> and 10 N in Cl<sup>-</sup> until a dark grey covering layer is formed and a metal of the Pt group is firmly bonded to the treated substrate by cold welding with a reduction in thickness of at least 25%.

#### Ruthenium Alloys for Powder Metallurgy

THE INTERNATIONAL NICKEL CO. INC.  
*U.S. Patent* 3,278,280

A liquid-phase sintered alloy which has powder metallurgy applications comprises 5-35 wt.% Au, 5-35 wt.% Pd and the balance Ru.

#### Magnetic Platinum Metal Alloys

E. I. DU PONT DE NEMOURS & CO.  
*U.S. Patent* 3,279,914

A new alloy consists of 20-75% Mg, 20-62% Ge and 1-35% Pd and/or Rh.

#### Ruthenium Alloys

INTERNATIONAL NICKEL LTD.  
*French Patent* 1,438,650

Alloys which are extremely useful in powder metallurgy comprise 0.25-2.5 wt.% Re and the balance Ru.

#### Iridium Alloy for Springs

INTERNATIONAL NICKEL LTD.  
*German Patent* 1,224,936

A suitable alloy for springs exposed to temperatures of 500°C and more consists of Ir with 0.5-7%, especially 2-7% W.

## CHEMICAL COMPOUNDS

### Production of Trimeric Ruthenium Tetracarbonyl

LONZA LTD. *British Patent* 1,047,794

Trimeric Ru(CO)<sub>3</sub> is produced by reacting an enolisable Ru compound or basic Ru carboxylate with CO and H<sub>2</sub> in the presence of an organic solvent, at 100-250°C and 50-350 atm.