

# ABSTRACTS

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

### PROPERTIES

#### **The Calorimetric Heats of Adsorption of Hydrogen on Platinum Films**

S. ČERNÝ, M. SMUTEK and F. BUZEK, *J. Catalysis*, 1975, **38**, (1-3), 245-256

Four Pt films were prepared at a pressure of  $10^{-9}$  Torr and heats of adsorption of H were measured calorimetrically up to an equilibrium pressure of  $10^{-4}$  Torr. The initial heats were estimated as 22.0, 22.6, 21.2 and 19.2 kcal/mole; whereas the integral heats were found to have approximately the same value of about 17 kcal/mole on the four films in the investigated range of coverage.

#### **An UV Photoemission Study of NO and CO Adsorption on Pt(100) and Ru (1010) Surfaces**

H. P. BONZEL and T. E. FISHER, *Surface Sci.*, 1975, **51**, (1), 213-227

UV photoemission spectroscopic (UPS) studies of the adsorption of NO, CO and O<sub>2</sub> on Pt(100) and Ru(1010) surfaces at 100°C showed it to be non-dissociative. The UPS spectra exhibited two major emission peaks at initial state energies of -8, 8eV and -11.4eV for Pt(100) and -7, 4eV and -10.6eV for Ru(1010). The NO adsorption behaviour of Pt and Ru with regard to the NO reduction reaction on these catalysts are discussed.

#### **On the Photolysis of [Pt(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>4</sub> Aqueous Solutions**

R. M. ORISHEVA, S. P. GORBUNOVA and G. A. SHAGISULTANOVA, *Zh. Neorg. Khim.*, 1975, **20**, (7), 1934-1937

The mechanism of phototransformation of [Pt(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>4</sub> solutions in relation to the radiation energy and pH of the medium was studied. It is shown that the ultraviolet radiation facilitates the formation of complex amides which are responsible for the observed oxidation-reduction transformations.

#### **Investigation of Sub-solidus Equilibria in the Platinum-Aluminium System Using Diffusion Couples**

D. CHATTERJI, R. C. DEVRIES and J. F. FLEISCHER, *J. Less-common Metals*, 1975, **42**, (2), 187-198

Studies of the Pt-Al system were carried out by X-ray diffraction, microprobe and metallographic examinations of Pt aluminide layers formed on Pt by the diffusion of Al from a pack-aluminiding process. The compositions and stability of most phases are in good agreement with the currently

accepted phase diagram, but a new single phase of nominal composition Pt<sub>2</sub>Al was found and therefore a modification to the existing phase diagram is proposed.

#### **Resistivity Minima in Quench-condensed Films of Palladium**

S. SCHMID-MARČIĆ and J. A. MYDOSH, *Solid State Commun.*, 1975, **17**, (7), 795-797

Studies of the electric resistivity of quench-condensed Pd films 100-700Å thick and at 2-30K showed a shallow low temperature minimum in thin quench-condensed Pd films. The depth and temperature of this minimum depended on the residual resistivity of the film.

#### **Study of Decomposition and Ordering Processes in Copper-Palladium-Silver Alloys**

O. D. SHASHKOV, V. I. SYUTKINA and V. D. SUKHANOV, *Fiz. Metal. Metalloved.*, 1975, **39**, (6), 1275-1283

X-ray and electron microscopy studies of the decomposition and ordering processes in Cu<sub>3</sub>Pd + 8at.%Ag showed that the ordering at concentrations 18-30at.%Pd is accompanied by the formation of periodic antiphase domains. The ordering suppresses the discontinuous decomposition of the alloy, promoting precipitation of highly dispersed Ag which causes an increase in strength. Ag additions to Cu<sub>3</sub>Pd lower the critical temperature of ordering.

#### **Solubility of Hydrogen in Small Particles of Palladium**

M. BOUDART and H. S. HWANG, *J. Catalysis*, 1975, **39**, (1), 44-52

The solubility of H in Pd which is defined as the number of dissolved H atoms divided by the total number of metal atoms was measured at 273-343K from 13.3-53.3kPa. The solubility decreased linearly with increase of the percentage dispersion of metal.

#### **Experimental Study of the Critical-point Behaviour of the Hydrogen in Palladium System. III. Spinodal Curves and Isotherm Relations**

Y. DE RIBAUPIERRE and F. D. MANCHESTER, *J. Phys. C, Solid State Phys.*, 1975, **8**, (9), 1339-1348

Spinodal curve of the PdH system was determined by measuring the anelastic relaxation and the solubility for H in Pd. Comparison of the solubility data with the isotherm equation due to Lacher, which is based on a mean-field approximation, shows that the equation works reasonably well for  $0 < p \leq H/Pd = 0.3$ .

## Electrical Resistivity of Pd-H<sub>x</sub>: I. Residual Resistivity

J. P. BURGER, D. S. MACLACHLAN, R. AMILFERT and B. SOUFFACHÉ, *Solid State Commun.*, 1975, 17, (3), 277-280

Studies of the electrical resistivity of PdH<sub>x</sub> alloys show that the residual resistivity goes through a maximum at 0.73 and then drops sharply as x approaches 1. The results show that the residual resistivity for 0.8 < x < 1 is mainly due to vacancies in H lattice and that H atoms occupy only the octahedral sites of the Pd lattice.

## Tunnelling Experiments on Superconducting Palladium-Deuterium Alloys

A. EICHLER, H. WÜHL and B. STRITZKER, *Solid State Commun.*, 1975, 17, (2), 213-216

Superconducting tunnelling studies made on D/Pd ≈ 0.9 showed that this Pd-D alloy is a weak coupling superconductor ( $2\Delta/kT_c = 3.6$ ). The results show that the high energy localised modes of D in Pd-D share in the electron-photon-interaction which lead to superconductivity.

## Superconductivity in the Palladium-Hydrogen System

D. A. PAPACONSTANTOPOULOS and B. M. KLEIN, *Phys. Rev. Lett.*, 1975, 35, (2), 110-113

Band theory and phonon measurements are used to calculate the electron-phonon coupling constant,  $\lambda$ , for Pd and PdD. The results indicate that superconductivity is absent in Pd metal because of the large value of the Coulomb pseudopotential,  $\mu$ , and that superconductivity occurs in PdD primarily because of coupling with the optic phonons.

## Some Observations on the Heat Capacities of Palladium-Indium and Palladium-Tin Intermediate Phases

A. W. BRYANT, J. M. BIRD and J. N. PRATT, *J. Less-common Metals*, 1975, 42, (2), 249-253

The specific heat capacities of the intermetallic phases Pd<sub>3</sub>In, Pd<sub>2</sub>In, PdIn, Pd<sub>2</sub>In<sub>3</sub>, Pd<sub>3</sub>Sn, Pd<sub>2</sub>Sn and PdSn were measured at 150-298K using differential scanning calorimetry. Significant negative deviations from Neumann-Kopp behaviour were found in the heat capacities of all phases. A possible explanation in terms of changes in electronic and vibrational heats on alloying is suggested.

## Coexistent Phases of the FeSi-type Crystal Structure in Ni-Pd-Ga and Ni-Pt-Ga Alloys

M. K. BHARGAVA, A. A. GADALLA and K. SCHUBERT, *J. Less-common Metals*, 1975, 42, (1), 69-76

The valence electron concentration and the concentration of the outer core electron in the Ni<sub>m</sub>Pd<sub>50-m</sub>Ga<sub>50</sub> and Ni<sub>m</sub>Pt<sub>50-m</sub>Ga<sub>50</sub> phases (m = 0-30) did not change over their linearly extended homogeneity ranges, but the concentration of the inner core electrons changed. At lower Pd and Pt

contents and at 700°C the alloys consisted of phases Ni<sub>3</sub>PdGa<sub>4</sub> and Ni<sub>3</sub>PtGa<sub>4</sub>, respectively. It is assumed that in the coexistent phases the commensurability of the core electron correlation to the crystal structure exhibits a small but characteristic difference.

## The Effect of Hydrogen on the Superconducting Transition Temperature of some Body-centred Cubic Niobium-Palladium, Niobium-Palladium-Molybdenum and Niobium-Palladium-Tungsten Alloys

C. G. ROBBINS and V. MULLER, *J. Less-common Metals*, 1975, 42, (1), 19-27

The superconducting transition temperature of Nb<sub>(1-x)</sub>Pd<sub>x</sub> (0.15 ≤ x ≤ 0.35), Nb<sub>(1-x)</sub>Pd<sub>x</sub>(<sub>(1-y)</sub>Mo<sub>y</sub> (0.15 ≤ x ≤ 0.24; 0.0 ≤ y ≤ 0.1) and Nb<sub>(1-x)</sub>Pd<sub>x</sub>(<sub>(1-y)</sub>W<sub>y</sub> (x = 0.20; y ≤ 0.1) alloys was increased by the introduction of H into these alloys by the electrolysis of H<sub>2</sub>SO<sub>4</sub>. For the Nb-Pd and Nb-Pd-Mo alloys, this effect is accompanied by the loss of body-centred cubic symmetry in the host metal lattice.

## Effect of Palladium Alloying Additions on the Environmental Cracking Resistance of Titanium-7Al-2Nb-1Ta Alloy

G. J. BIEFER and A. J. WILLIAMS, *Corrosion*, 1975, 31, (6), 223-225

Studies of the environmental cracking of a high-strength Ti-7Al-2Nb-1Ta (Ti-721) alloy with 0.26-1.56%Pd additions in 3.5% NaCl solution were made by means of notched specimens to which a rising-load was applied. An increase in the fracture toughness K is observed in alloys with 0.38-1.56% Pd as compared to plain Ti-721. An addition of 0.26% Pd is found sufficient to bring about passivity in the unstressed alloy although the ordinary alloy shows active corrosion. The rapid crack propagation velocity however remains unaltered by Pd additions.

## Gaseous Phosphorus Compounds. XI. Thermodynamic Investigation of the Gaseous Molecule RhP<sub>2</sub>

D. L. COCKE, K. A. GINGERICH and J. KORDIS, *High Temp. Sci.*, 1975, 7, (1), 20-24

The atomisation energies,  $\Delta H^\circ_{\text{atom}298}$ , of the gaseous molecule RhP<sub>2</sub> measured by the Knudsen effusion-mass spectrometry was determined as 199 ± 5.0 kcal/M. The atomisation energy of RhP<sub>2</sub> was derived from the third law enthalpy change. Thermodynamic data favour the asymmetric Rh-P-P structure for RhP<sub>2</sub>.

## Structure and Superconductivity of Metastable Phases in Liquid-quenched Zr-Rh Alloys

K. TOGANO and K. TACHIKAWA, *J. Appl. Phys.*, 1975, 46, (8), 3609-3613

0-36at.% Rh-Zr alloys were rapidly quenched from the liquid state. A b.c.c. solid solution of

Zr is retained up to 17at.% Rh beyond the maximum equilibrium solubility limit of 8at.% Rh. Broad maxima in the X-ray and electron diffraction patterns, indicative of a non-crystalline structure, are obtained for alloys containing 18-27at.% Rh. The non-crystalline phase shows a sharp superconducting transition at 4.1K.

#### Superconductivity in Zr-Ir System

D. P. MOISEEV, E. L. SEMENOVA and S. K. UVAROVA, *Fiz. Metall. Metalloved.*, 1975, 39, (6), 1163-1167  
Studies of superconductivity in the 10-75% Ir-Zr alloys were carried out using an induction method. Superconducting properties were detected in  $Zr_3Ir$  ( $T_c=2.1K$ ) and  $Zr_2Ir$  ( $T_c=7.3K$ ) and also in ZrIr in as cast and as quenched from 1400°C conditions. The alloys  $Zr_2Ir_3$  and  $ZrIr_3$  are not superconducting above 1.85K. Superconducting properties of  $ZrIr_2$  ( $T_c=4.03K$ ) and of alloy with 10at.% Ir ( $T_c=5.5K$ ) were also confirmed.

#### Study of Thermal Dissociation of Ruthenium Dioxide and Rhodium Sesquioxide

V. K. TAGIROV, L. M. CHIZHIKOV, E. K. KAZENAS and L. K. SHUBOCHKIN, *Zh. Neorg. Khim.*, 1975, 20, (8), 2035-2037

High temperature mass spectrometric studies of the dissociation of  $RuO_2$  and  $Rh_2O_3$  were carried out at 985-1190K and at 777-910K, respectively. In both cases the dissociation products were the corresponding metals in a solid state and  $O_2$  gas. The heats of reaction  $\Delta H^\circ_{298}$  were found to be 73.2 kcal/mol and 53.89 kcal/mol for the dissociation of  $RuO_2$  and  $Rh_2O_3$ , respectively. The corresponding dissociation pressures are also given.

## CHEMICAL COMPOUNDS

#### Importance of Chemical Effects in Determining the Free-electron-like Band Structure of $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$

R. P. MESSMER and D. R. SALAHUB, *Phys. Rev. Lett.*, 1975, 35, (8), 533-536

It is shown that a three-band model for the linear Pt chains in  $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$  is inappropriate for a description of the electronic structure. The chemical effects of the ligands force an *s-d* hybridisation which is *k* independent and leads to free-electron-like bands within a basically tight-binding scheme. This results in an explanation of the band structure deduced experimentally. A highly simplified model is also presented to explain the 5/6th occupancy of the band.

#### Mononucleoside Platinum Complexes

P.-C. KONG and F. D. ROCHON, *J. Chem. Soc., Chem. Commun.*, 1975, (15), 599-600

New mononucleoside complexes  $K[Pt(Nuc)Cl_3]$  (Nuc = nucleoside, Guo = guanoside, Ino = ino-

sine and Xao = xanthosine) and the bridge complex  $K_2(PtCl_3)_2(Ado)$  were prepared by reacting  $K_2[PtCl_4]$  and the nucleoside at 60-70°C in  $HCONMe_2$  or  $MeCONMe_2$ . The equimolar ratio of  $K_2[PtCl_4]$  and nucleoside is essential in the preparation of the adenosine complex but not for the synthesis of the Guo, Ino and Xao complexes.  $K[Pt(2,6\text{-lutidine})Cl_3]$  and  $K[Pt(NH_3)Cl_3]$  were also prepared and described.

#### Crystal and Molecular Structures of *cis*- and *trans*-Dichlorobispyridineplatinum(II)

P. COLAMARINO and P. L. ORIOLI, *J. Chem. Soc., Dalton Trans.*, 1975, (16/17), 1656-1659

Crystal structure studies of *cis*- and *trans*-dichlorobispyridineplatinum(II) [(I) and (II)] showed that crystals of (I) are monoclinic, space groups  $C2/c$ , with  $a=9.408$ ,  $b=17.110$ ,  $c=15.270\text{\AA}$ ,  $\beta=98.53^\circ$ ,  $Z=8$ ; crystals of (II) are triclinic, space group  $P\bar{1}$ , with  $a=7.695$ ,  $b=7.091$ ,  $c=5.542\text{\AA}$ ,  $\alpha=87.6$ ,  $\beta=83.7$ ,  $\gamma=79.3^\circ$ ,  $Z=1$ . Shortest Pt-Pt distances are 4.967(I) and 5.542(II) \AA.

#### Isomerisation of *bis*-Thioxane Complexes of Platinum(II)

YU. N. KUKUSHKIN, V. I. VSHIVTSEV and L. V. KONOVALOV, *Zh. Neorg. Khim.*, 1975, 20, (7), 1938-1940

The isomerisation of bis-thioxane Pt(II)chloride with *trans* configuration in the crystalline state produces a corresponding *cis*-isomer. The isomerisation of *trans*- $[Pt(R_2S)_2(H_2O)_2]^{2+}$  into *cis*- $[Pt(R_2S)_2(H_2O)_2]^{2+}$  (where  $R_2S$  = thioxane and diethylsulphide) also takes place in the same solution. The first and second dissociation constants are found to be of the order of  $10^{-2}$ - $10^{-3}$  and  $10^{-5}$ , respectively.

#### The Preparation of Acyl- and Sulphonato-Platinum(II) Complexes from Bis(triphenylphosphine)Platinum Ethylene

S. P. DENT, C. EARBORN and A. PIDCOCK, *J. Organometal. Chem.*, 1975, 97, (2), 307-311

The acyl-Pt complexes *trans*- $[PtCl(COR)L_2]$ , where  $L=PPh_3$  were obtained in high yield from the reaction between  $[PtL_2(C_2H_4)]$  and the acyl chlorides  $RCOCl$ , where R is Ph,  $C_6H_4OMe-p$ ,  $C_6H_4Cl-p$ ,  $CH=CH_2$ ,  $CH=CHMe$ ,  $CMe=CH_2$ , or  $CH=CHPh$ . The sulphonato complexes *trans*- $[PtCl(SO_2R)L_2]$ , where R is Ph or Me were obtained analogously from the sulpholyl chlorides,  $RSO_2Cl$ . The complex *trans*- $[PtCl(COCH=CHPh-trans)L_2]$  undergoes decarbonylation on heating to give *trans*- $[PtCl(CH=CHPh-trans)L_2]$ .

#### Selective Hydrogenation of Dimethylethynylcarbinol on a Complex Palladium Catalyst

T. M. BELOSLYUDOVA and L. A. IL'INA, *Kinet. Kataliz.*, 1975, 16, (3), 788-790.

A modified method of preparation of a complex  $PdCl_2(PPh_3)_2$  catalyst for selective hydrogenation of dimethylethynylcarbinol was developed. The

method uses a 4:1 mixture of benzol and ethanol as a solvent and hydrazine as an activator. The catalyst shows high activity and selectivity.

### Platinum and Palladium Complexes of Thienylpyridine. I. Compounds Containing Metal-Carbon Bonds

T. J. GIORDANO and P. G. RASMUSSEN, *Inorg. Chem.*, 1975, **14**, (7), 1628-1634

The synthesis of Pd(II) and Pt(II) complexes of 2-(2'-thienyl)pyridine (TP) was carried out in order to determine the mode of coordination and the effect of an adjacent thienyl group on the coordination of an *n*-donor ligand. In the complex Pt(C<sub>9</sub>H<sub>7</sub>NS)(C<sub>6</sub>H<sub>4</sub>NS)I the Pt atom is coordinated by two pyridyl nitrogens *trans* to one another, a thienyl C, and an I which lies slightly below the plane formed by the Pt and the other 3 coordinating atoms. The metal to C  $\sigma$ -bond forms due to the thiophene ring activity and the chelate stability.

### Equilibrium Energetics of *cis-trans* Isomerisation for a Series of Palladium(II)-Phosphine Complexes. Study of Phosphine Electronic Effects

A. W. VERSTUYFT and J. H. NELSON, *Inorg. Chem.*, 1975, **14**, (7), 1501-1505

The n.m.r. studies of the *cis-trans* isomerisation of the series of para-substituted phosphine complexes, [(p-ZC<sub>6</sub>H<sub>4</sub>)<sub>n</sub>P(CH<sub>3</sub>)<sub>3-n</sub>]<sub>2</sub>PdX<sub>2</sub> (n=1, Z=OCH<sub>3</sub>, CH<sub>3</sub>, H, Cl; n=2, Z=CH<sub>3</sub>, H, Cl; X<sup>-</sup>=Cl<sup>-</sup>, N<sub>3</sub><sup>-</sup>) show that the *cis* isomer is thermodynamically more stable than the *trans* for both the chloride and azide complexes. It is found that the isomerisation process is entropy controlled and probably occurs via a solvent-association mechanism. The enthalpy and entropy of the reaction *cis*-(R<sub>3</sub>P)<sub>2</sub>PdX<sub>2</sub>  $\rightleftharpoons$  *trans*-(R<sub>3</sub>P)<sub>2</sub>PdX<sub>2</sub> both increase as the basicity of the phosphine increases.

### Crystal and Molecular Structure of Dichloronitrosylbis(triphenylphosphine)rhodium, RhCl<sub>2</sub>(NO)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>

S. Z. GOLDBERG, C. KUBIAK, C. D. MEYER and R. EISENBERG, *Inorg. Chem.*, 1975, **14**, (7), 1650-1654  
X-ray studies of RhCl<sub>2</sub>(NO)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub> show that the compound crystallises in the monoclinic space group *I*2/c with 4 molecules in a unit cell of dimensions a=22.019, b=9.604, c=15.854 Å and  $\beta$ =104.57°.

### Dinuclear Bridged d<sup>8</sup> Metal Complexes. Evidence for the Complex [RhCl(CO)(C<sub>2</sub>H<sub>4</sub>)(NH(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>)] of the Mono and Dinuclear Species

J.-J. BONNET, Y. JEANIN, A. MAISONNAT, P. KALCK and R. POILBLANC, *Comptes Rendus Sér. C*, 1975, **281**, (1), 15-17

The complex [RhCl(CO)(C<sub>2</sub>H<sub>4</sub>)(NHEt<sub>2</sub>)]<sub>n</sub> obtained by addition of two equivalents of diethyl-

amine to the complex [RhCl(CO)(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>]<sub>2</sub> is mononuclear in the solid state. It has a square planar structure with the diethylamine ligand in the *trans*-position to the ethylene ligand.

### The O-O Bond Length in Oxygen Adducts of Iridium and Rhodium Complexes

M. LAING, M. J. NOLTE and E. SINGLETON, *J. Chem. Soc., Chem. Commun.*, 1975, (16), 660-661

Studies of the crystal structures of dioxygen salts, [MO<sub>2</sub>(L<sub>2</sub>)<sub>2</sub>]<sup>+</sup>X<sup>-</sup> [M=Ir or Rh, L=PMe<sub>2</sub>Ph, X=BPh<sub>4</sub> (I and II); M=Rh, L=AsMe<sub>2</sub>Ph, X=ClO<sub>4</sub> (III)], as changing L<sub>2</sub> from dppe (where dppe=Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>) to (PMe<sub>2</sub>Ph)<sub>2</sub> or (AsMe<sub>2</sub>Ph)<sub>2</sub> showed that the O-O values were in the range of 1.43-1.49 Å. The long bond of 1.625 Å reported for [IrO<sub>2</sub>(dppe)<sub>2</sub>]<sup>+</sup> is an artefact caused by the disorder in the crystal.

### Crystal Structure and Molecular Geometry of Ir(B<sub>3</sub>H<sub>8</sub>)Br<sub>2</sub>(CO)(PMe<sub>3</sub>)<sub>2</sub>, a Product from the Oxidative Addition of Bromopentaborane to IrCl(CO)(PMe<sub>3</sub>)<sub>2</sub>, and some Comments on the Structural *trans* Influence of $\sigma$ -Bonded Boron

M. R. CHURCHILL and J. J. HACKBARTH, *Inorg. Chem.*, 1975, **14**, (9), 2047-2051

A single crystal X-ray diffraction study of the complex Ir(B<sub>3</sub>H<sub>8</sub>)Br<sub>2</sub>(CO)(PMe<sub>3</sub>)<sub>2</sub> shows that the complex belongs to the centrosymmetric monoclinic space group *P*<sub>2</sub><sub>1</sub>/*c* [C<sub>2h</sub><sup>5</sup>; No. 14] with a=13.824, b=10.661, c=13.611 Å and  $\beta$ =104.90°. The molecular geometry determinations show the complex to be *cis*-dibromo-*trans*-bis-(trimethylphosphine)(2-pentaboranyl)carbonyliridium(III). The *cis* and *trans* angles, and the Ir-P and Ir-Br distances are given.

### Bi-heterometallic Hydrido Transfer between Iridium and Platinum

J. P. C. M. VAN DONGEN, C. MASTERS and J. P. VISSER, *J. Organometal. Chem.*, 1975, **94**, (2), C29-C32

Hydrido transfer from IrH<sub>2</sub>L<sub>2</sub> to Pt<sub>2</sub>Cl<sub>4</sub>L<sub>2</sub> or Pd<sub>2</sub>Cl<sub>4</sub>L<sub>2</sub>, where L=PPr<sub>3</sub>, occurs readily at room temperature, and in the case of the Pt dimer proceeds via a hydrido bridged Pt-Ir complex.

### Preparation, Structure and Properties of Europium Ruthenium Hydride

J. S. THOMPSON, R. O. MOYER and R. LINDSAY, *Inorg. Chem.*, 1975, **14**, (8), 1866-1869

Eu<sub>2</sub>RuH<sub>6</sub> was prepared by reaction of EuH<sub>2</sub> and Ru at 800°C and in 1 atm of H<sub>2</sub>. X-ray powder studies showed that the structure is consistent with the *Fm*3*m* space group. Magnetic susceptibility measurements at 77-296K showed that Eu<sub>2</sub>RuH<sub>6</sub> obeys a Weiss-Curie law with  $\theta$ =-143K indicative of ferromagnetic interactions. Electrical resistivity measurements indicate that Eu<sub>2</sub>RuH<sub>6</sub> behaves as a semiconductor.

## Improved Synthesis of Cyclo-olefin Complexes of Ruthenium via Metallic Zinc Reduction

P. PERTICI, G. VITULLI and L. PORRI, *J. Chem. Soc., Chem. Commun.*, 1975, (20), 846

A new method of preparation of cyclo-olefin complexes of Ru used in homogeneous catalysis is described.  $\eta$ -Cyclo-olefin Ru(O) and -Ru(II) complexes can be prepared in high yields by reaction of cyclo-diolefins and  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  in the presence of Zn dust and  $\text{C}_2\text{H}_5\text{OH}$ . A possible mechanism for the formation of Ru(O) compounds is given.

## Thermal and Light-induced Decomposition of Azido(bis-2,2'-bipyridine) Complexes of Ruthenium(III)

G. M. BROWN, R. W. CALLAHAN and T. J. MEYER, *Inorg. Chem.*, 1975, **14**, (8), 1915-1921

Ru(III) complexes  $\text{Ru}(\text{bipy})_2(\text{N}_3)_2$  (bipy is 2,2'-bipyridine) and  $\text{Ru}(\text{bipy})_2(\text{L})(\text{N}_3)^+$  (L=acetonitrile or pyridine) are oxidised to Ru(III) electrochemically using  $\text{Br}_2$  or Ce(IV). Ru(III) complexes undergo thermal and light-induced decomposition reactions in acetonitrile in which the azide to metal electron transfer occurs. The results of kinetic studies are consistent with either rate-determining intramolecular electron transfer or metal-nitrene formation.

## Ruthenium Carbonyl Complexes of Ruthenium. Part VI. Cyclic Dienyl Complexes

B. A. SOSINSKY, S. A. R. KNOX and F. G. STONE, *J. Chem. Soc., Dalton Trans.*, 1975, (16/17), 1633-1640

Studies of the reaction of cyclopentadiene, cyclohexa-1,3-diene and cyclohepta-1,3-diene with  $[\text{Ru}(\text{MMe}_3)_2(\text{CO})_4]$  (M=Si or Ge) or  $[\{\text{Ru}(\text{SiMe}_3)(\text{CO})_4\}_2]$  showed the yield of dienyl complexes  $[\text{Ru}(\text{MMe}_3)(\text{CO})_3(\text{I-5-}\eta\text{-dienyl})]$ . Cyclohexane-1,3-diene gives  $[\text{Ru}(\text{CO})_3(\text{I-2:3-4-}\eta\text{-C}_6\text{H}_8)]$  as the major product with both Ru complexes, whereas cyclopentadiene and cyclohepta-1,3-diene give the corresponding  $[\text{Ru}(\text{CO})_3(\text{I-2:3-4-}\eta\text{-diene})]$  complex only with  $[\{\text{Ru}(\text{SiMe}_3)(\text{CO})_4\}_2]$ .

## Synthesis and Properties of Osmium(II) and Osmium(III) Ammine Complexes of Aromatic Nitrogen Heterocyclics

R. H. MAGNUSON and H. TAUBE, *J. Am. Chem. Soc.*, 1975, **97**, (18), 5129-5135

The reaction of nitrogen heterocycle with the bis(dinitrogen)tetraammine-osmium(II) ion led to the formation of Os(II) complexes of the type  $[(\text{NH}_3)_4\text{Os}(\text{N}_2)(\text{L})]^{n+1}$  (L=pyrazine, N-methylpyrazinium, isonicotinamide and isonicotinic acid). Os(III) compounds with the general formula,  $[(\text{NH}_3)_4\text{Os}(\text{X})(\text{L})]\text{X}_2$  where L=pyrazine, X<sup>-</sup>=Cl<sup>-</sup>, Br<sup>-</sup>; and L=isonicotinic acid, X<sup>-</sup>=Cl<sup>-</sup> were isolated and reduced to Os(II) ions.

## ELECTROCHEMISTRY

### Comparative Study of Adsorption and Oxidation of Formic Acid and Methanol on Platinised Electrodes in Acidic Solution

A. WIECKOWSKI and J. SOBKOŃSKI, *J. Electroanal. Chem. Interfac. Electrochem.*, 1975, **63**, (3), 365-377

The results of radio- and electrochemical studies of the adsorption of HCOOH and CH<sub>3</sub>OH and the oxidation of their chemisorption products on a platinised electrode in 0.5M H<sub>2</sub>SO<sub>4</sub> are presented and the mechanism of the electrode processes is discussed.

### The Anodic Oxidation of Hydrogen on Platinised Tungsten Oxides. III. Mechanism of H<sub>2</sub> Oxidation on Platinised Lower Tungsten Oxide Electrodes

B. S. HOBBS and A. C. C. TSEUNG, *J. Electrochem. Soc.*, 1975, **122**, (9), 1174-1177

The mechanism of H<sub>2</sub> oxidation on platinised lower tungsten oxide (WO<sub>y</sub>, where 2 < y < 3) electrodes is explained in terms of hydrogen tungsten bronze formation on the surface of WO<sub>3</sub> film. The performance of these electrodes is initially lower than the corresponding WO<sub>3</sub> electrodes, but it improves with time as the surface is converted to WO<sub>3</sub> rich layers. The electrodes have higher long-term stability.

### A Study of Electrochemical Preparation of Chlorates

V. CEZNER, R. MRÁZ, I. ROUŠAR, V. SRB and S. TICHÝ, *Chem. Průmysl*, 1975, **25**, (3), 135-138

The current yield and total power consumption per unit mass of product was measured in a laboratory electrolyser for the preparation of chlorates, using activated Ti anodes. With these anodes whose active layers are formed by a mixture of RuO<sub>2</sub> and TiO<sub>2</sub> the current yield reaches 94% at the current density of 0.4-1.0A/cm<sup>2</sup> at 60-80°C and pH between 6.2-6.3. The effects of additions of Fe, Ca and Na to the electrolyte are discussed.

### Mechanism of the Reduction of Dimeric Ruthenium(IV) in Hydrochloric Acid Solutions

L. W. POTTS and H. S. SWOFFORD, *Anal. Chem.*, 1975, **47**, (1), 131-141

The mechanism by which dimeric Ru(IV),  $[\text{Ru}(\text{IV})_2\text{OCl}_{10}]^{4-}$  is reduced to Ru(III) in HCl solutions has been elucidated using a variety of electrochemical techniques. The results are consistent with an electron transfer-chemical step-electron transfer process involving the irreversible reduction of the dimer to a mixed oxidation state intermediate, which subsequently decomposes to form monomeric Ru(III) and Ru(IV). The rates of the chemical step are discussed.

## ELECTRODEPOSITION AND SURFACE COATINGS

### The Effect of the Substrate on the Electrical Resistance of Polymer Films

J. E. O. MAYNE and D. J. MILLS, *J. Oil Colour Chem. Assoc.*, 1975, **58**, (5), 155-159

A comparative study has been made of the effect of mild steel and Pt substrates on the electrical resistance of polymer films. Pt and mild steel samples coated with three different varnishes were exposed to 3.5M KCl. It was found that the resistance of films supported on Pt was one or two orders of magnitude higher than those supported on mild steel. It is suggested that this was due to the fact that ionic diffusion occurred from only one side of the Pt substrate.

## HETEROGENEOUS CATALYSIS

### Laboratory Experiments Evaluating the Effects of S and Cu on a Pt-Al<sub>2</sub>O<sub>3</sub> Auto Exhaust Oxidation Catalysts

J. T. KUMMER, *J. Catalysis*, 1975, **38**, (1-3), 166-171

Cu impregnation of Pt/Al<sub>2</sub>O<sub>3</sub> increases its ethylene oxidation activity in a laboratory gas stream but decreases its CO oxidation activity. SO<sub>2</sub> decreases the activity of untreated Pt/Al<sub>2</sub>O<sub>3</sub> catalyst for both CO and C<sub>2</sub>H<sub>4</sub> oxidation. The Cu-treated Pt/Al<sub>2</sub>O<sub>3</sub> catalyst showed decreases in C<sub>2</sub>H<sub>4</sub> and CO oxidation activity due to SO<sub>2</sub> comparing with the untreated one. Reduction of the Cu-treated catalyst greatly increased the CO activity and decreased the C<sub>2</sub>H<sub>4</sub> activity.

### Infra-red Study of the Interactions between Aromatic Hydrocarbons and Alumina Supported Platinum

M. PRIMET and M.-V. MATHIEU, *J. Chim. Phys.*, 1975, **72**, (5), 659-664

I.R. spectroscopy shows that aromatic hydrocarbons are chemisorbed on Pt/Al<sub>2</sub>O<sub>3</sub> with the formation of a  $\pi$ -complex. The electronic transfer between the ring and the metal is dependent on the number of methyl groups in the compound. The hydrogenation of adsorbed species destroys this complex.

### The Influence of Nitrogen Compounds on the Properties of Alumina-Platinum Catalysts with Rare Earth Element Additions

N. S. KOZLOV, V. A. POLIKARPOV, C. V. PAVLOVICH, V. V. SHIPIKIN and P. P. ROMAKHOVICH, *Khim. Tekhnol. Topliv Masel*, 1975, (6), 19-21

The influence of nitrogen compounds on the activity of a 0.5% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst with 0.5, 1.0 and 2.0% additions of Ho<sub>2</sub>O<sub>3</sub> was studied in the reactions of hydrocracking and isomerisation of *n*-hexane. The results show a higher stability of the catalysts with Ho<sub>2</sub>O<sub>3</sub> additions in relation to nitrogen compounds.

### Platinum-Rhenium/Alumina Catalysts. I. Investigation of Reduction by Hydrogen

C. BOLIVAR, H. CHARCOSSET, R. FRETY, M. PRIMET, L. TOURNAYAN, C. BETIZEAU, G. LECLERCQ and R. MAUREL, *J. Catalysis*, 1975, **39**, (2), 249-259

Reduction to metallic Re occurred below 200°C when Re<sub>2</sub>O<sub>7</sub> was mixed with Pt powder. A strong activation by Pt of the reduction of Re<sub>2</sub>O<sub>7</sub> also occurred on Al<sub>2</sub>O<sub>3</sub> samples co-impregnated with H<sub>2</sub>PtCl<sub>6</sub> and Re<sub>2</sub>O<sub>7</sub>. The results showed that the reduction of Re<sub>2</sub>O<sub>7</sub> to metallic Re under 1 atm of H<sub>2</sub> was completed at a low temperature.

### Characterisation of Pt-Sn-Al<sub>2</sub>O<sub>3</sub> Catalysts by Mössbauer Spectrometry

R. BACAUD, P. BUSSIÈRE, F. FIGUERAS and J.-P. MATHIEU, *Comptes Rendus Sér. C*, 1975, **281**, (4), 159-161

A large amount of Sn in PtSn/Al<sub>2</sub>O<sub>3</sub> catalysts is lost during their preparative thermal treatments. The remaining part is present as SnO<sub>2</sub>. For the same number of Pt atoms only 2/3 of this oxide is reduced by H<sub>2</sub>. A quantitative reduction occurs in solids with three times larger Pt content.

### Interaction between Components in Supported Mo-Pt Catalysts Studied by X-ray Electron Spectroscopy

YU. I. ERMAKOV, M. S. IOFFE, YU. A. RYNDIN and B. N. KUZNETSOV, *Kinet. Kataliz*, 1975, **16**, (3), 807-808

The influence of Mo ions on the catalytic activity of 5.5%Pt-4.9%Mo/SiO<sub>2</sub>, 4.4%Pt-1.9%Mo/SiO<sub>2</sub>, 3.9%Pt/SiO<sub>2</sub>, 1.5%Mo/SiO<sub>2</sub> catalysts was studied using electron spectroscopy method. The results indicate a direct interaction between the Pt atoms and Mo ions.

### New Hydrogenation Catalysts with Platinum Deposited on Polyamide 66. II. Activation of Catalysts

J. R. BERNARD, C. HOANG-VAN and S. J. TEICHER, *J. Chim. Phys.*, 1975, **72**, (6), 735-740

Catalytic activity of polyamide 66 supported Pt catalysts in the partial hydrogenation of styrene is observed when the samples are previously activated by H<sub>2</sub> at 80°C. The activity remains constant over the activation temperature range between 120-220°C. Activation of the catalysts can also be produced, in the absence of H<sub>2</sub>, by the support itself. The presence of Pt crystallites is revealed by X-ray diffraction.

### Reactions of Alkanes on Supported Pt-Au Alloys

J. R. H. VAN SCHAİK, R. P. DESSING and V. PONEC, *J. Catalysis*, 1975, **38**, (1-3), 273-282

Studies of isomerisation, dehydrocyclisation and hydrogenolysis of *n*-pentane and *n*-hexane over supported Pt and 1-12.5% Pt-Au alloys at 250-400°C showed that 1-4% Pt-Au catalysed isomerisation, 10% Pt-Au alloys favoured dehydro-

cyclisation and pure Pt catalysed mainly isomerisation. Self-consistent picture of the mechanisms involved is explained by comparison of the *n*-pentane and *n*-hexane reactions.

### On the Mechanism of the Catalytic Effect of Palladium during the Reduction of Molybdenum Oxide with Hydrogen

V. A. LAVRENKO, V. S. ZENKOV, V. I. TIKUSH and I. V. UVAROVA, *Izv. Akad. Nauk SSSR, Metall.*, 1975, (4), 7-9

The effect of 0.1% Pd addition on the reduction process of MoO<sub>3</sub> with molecular and atomic H was studied. It is shown that the highest reaction rates are obtained when atomic H and catalytic additions of Pd are used simultaneously at 450°C. Both Pd and atomic H lower the starting temperature of the reduction.

### Changes in the Catalytic Activity of Cold-worked Platinum during the Oxidation of Carbon Monoxide

S. KISHIMOTO, *Bull. Chem. Soc. Japan*, 1975, 48, (6), 1937-1938

The rate of oxidation of CO was measured on cold-worked Pt to study the influence of annealing on the catalytic behaviour. The presence of lattice defects (dislocations) in the crystal plays a role in initiating the reaction and serves to create new active sites during an acceleration period of the reaction.

### Catalytic Hydrogenation of Nitroethane on Skeleton Platinum-Rhodium Catalysts in the Solutions of Sulphuric and Hydrochloric Acids

L. I. LOGACHEVA, T. M. GRISHINA, V. V. ZHUCHKOVA and G. D. VOVCHEENKO, *Zh. Fiz. Khim.*, 1975, 49, (8), 2099-2100

Studies of nitroethane hydrogenation on skeleton Pt, Rh and 10-90at.% Rh-Pt catalysts in 1N HCl and 1N H<sub>2</sub>SO<sub>4</sub> show a decrease of catalytic activity with an increase of Rh content. The rate of reaction in 1N H<sub>2</sub>SO<sub>4</sub> is found to be higher than in 1N HCl. This is explained in terms of specific adsorption of Cl<sup>-</sup> anions in preference to H. The reaction rate constants at 10-50°C and activation energies are given.

### Supported Metal Complex Catalysts

P. R. RONY and J. F. ROTH, *J. Molec. Catalysis*, 1975, 1, (1), 13-25

Isomerisation catalyst RhCl<sub>3</sub> and hydroformylation catalysts (PØ)<sub>2</sub>RhCOCl, (AsØ)<sub>2</sub>RhCOCl and Co<sub>2</sub>(CO)<sub>8</sub>(PBU<sub>3</sub>)<sub>2</sub> on support were found to be more active when dissolved in a liquid phase. The hydrogenation catalyst (PØ)<sub>3</sub>RhCl was more active as the supported solid catalyst than its supported liquid-phase counterpart. The results showed that the shape of the conversion versus liquid-loading curve is diagnostic of the intrinsic activity of the dispersed catalyst solution.

### Differential Determination of Composite Catalyst Surface Areas by Chromatography. VI. Supported Rhodium

N. E. BUYANOVA, A. P. KARNAUKHOV, N. G. KOROLEVA, N. T. KULISHKIN, V. T. RYBAK and V. B. FENELONOV, *Kinet. Kataliz.*, 1975, 16, (3), 741-748

The chemisorption of O<sub>2</sub> and CO on Rh blacks, Rh/Al<sub>2</sub>O<sub>3</sub>, Rh/SiO<sub>2</sub>, Rh/Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub>, Rh/C and also on pure supports was studied using chromatography and static methods to obtain adsorption isotherms at room temperature. From these, the degree of dispersion and specific surface of Rh were calculated. It is shown that the dispersion changes in the following order: Rh/C > Rh/Al<sub>2</sub>O<sub>3</sub> > Rh/Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub> > Rh/SiO<sub>2</sub> and depends on the nature of the support and the method of preparation of the catalysts.

### On the State of Rhodium in Alumina-Rhodium Catalysts

A. L. SVERDLOVA, G. L. RABINOVICH, G. I. TYSOVSKII, T. A. SLOVOKHOTOVA and V. M. EVGRASHIN, *Zh. Fiz. Khim.*, 1975, 49, (8), 2013-2015

The state of Rh in Rh/γ-Al<sub>2</sub>O<sub>3</sub> catalysts containing 0.15, 0.3 and 0.6% Rh was investigated using magnetic susceptibility and chemisorption measurements. The results show that a proportion of Rh in catalysts containing 0.15 and 0.3% Rh remains in an ionic form even after reducing treatment in H at 500°C.

### Reduction of Nitric Oxide with Carbon Monoxide and Hydrogen over Ruthenium Catalysts

R. J. H. VOORHOEVE and L. E. TRIMBLE, *J. Catalysis*, 1975, 38, (1-3), 80-91

Studies of the reduction of NO with a mixture of CO and H<sub>2</sub> in the presence of H<sub>2</sub>O and CO<sub>2</sub> over Ru/Al<sub>2</sub>O<sub>3</sub> showed two peaks in the NH<sub>3</sub> yield; a CO-assisted NH<sub>3</sub> maximum at ~270°C and a H<sub>2</sub>-assisted NH<sub>3</sub> maximum at ~350°C. The low temperature NH<sub>3</sub> maximum increased with decreasing the particle size of Ru.

### Electron Spin Resonance Study of Supported Ruthenium Catalysts Promoted by Alkali Metal Salts in Dehydrogenation of Cyclohexane

M. KOBAYASHI and T. SHIRASAKI, *J. Catalysis*, 1975, 38, (1-3), 394-401

Studies of the dehydrogenation of cyclohexane over Ru/SiO<sub>2</sub> and Ru/graphite catalysts promoted by alkali metal salts showed that additions of KCN, LiCN and KCl increased the activity of the Ru/SiO<sub>2</sub> catalyst but NaCN, RbCN and CsCN had no effect. The ESR spectra of the Ru/SiO<sub>2</sub> catalysts which absorbed cyclohexane and benzene at 500°C, were observed. There were three signals in these spectra of the catalysts promoted by KCN; a main singlet spectrum (g=2.009) and two spectra of small intensity (splitting 58,63 gauss).

### On the Catalytic and Asymmetrising Activity of Ruthenium Catalysts. V. On the Mechanism of Asymmetric Hydrogenation

E. I. KLABUNOVSKII, A. A. VEDENYAPIN, YU. M. TALANOV and N. P. SOKOLOVA, *Kinet. Kataliz*, 1975, **16**, (3), 692-696

Hydrogenation of acetoacetate ester on a Ru/SiO<sub>2</sub> catalyst modified by D-(-) tartaric acid was studied at different temperatures and H<sub>2</sub> pressures. The results show that increasing the pressure of H<sub>2</sub> increases the reaction output from 0% at atmospheric pressure to 5.4% at 80 atm. Increasing the temperature has a similar effect.

## HOMOGENEOUS CATALYSIS

### Carboxymethylation of Organic Halides by Palladium Complexes under Mild Conditions

M. HIDAI, T. HIKITA, Y. WADA, Y. FUJIKURA and Y. UCHIDA, *Bull. Chem. Soc. Japan*, 1975, **48**, (7), 2075-2077

The complexes Pd(CO)(PPh<sub>3</sub>)<sub>3</sub>, Pd<sub>3</sub>(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>4</sub>, Pd<sub>3</sub>(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub> and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> are excellent catalysts for the carboxymethylation of various organic halides under very mild conditions. The reaction is believed to proceed via acyl complexes as the intermediates.

### Kinetic Studies of *n*-Butene Isomerisation Catalysed by Methanolic Rhodium Trichloride

K. TANAKA, *Sci. Papers Inst. Phys. Chem. Res.*, 1975, **69**, (2), 50-60

The isomerisation of *n*-butene catalysed by methanolic RhCl<sub>3</sub>·3H<sub>2</sub>O on its own and in the presence of SnCl<sub>2</sub>, HCl, NH<sub>4</sub>Cl or an alkali chloride as co-catalysts was studied. An induction period was observed only in the presence of SnCl<sub>2</sub> or in the absence of any co-catalyst. Carbon-14 tracer studies suggest the existence of a common intermediate for all three paths which interconnect the three *n*-butene isomers. A structure of the common intermediate and a model for the isomerisation path are proposed.

### Reactions of Amines and Active Methylene Compounds with Buta-1,3-diene and Isoprene: Catalysis by Nickel, Cobalt, Rhodium, and Iridium Complexes

R. BAKER, A. ONIONS, R. J. POPPLESTONE and T. N. SMITH, *J. Chem. Soc., Perkin Trans. II*, 1975, (11), 1133-1138

Studies of the reaction of buta-1,3-diene with morpholine and di-*ni*-propylamine in the presence of NiCl<sub>2</sub>-Ph<sub>3</sub>P-NaBN<sub>4</sub>, CoCl<sub>2</sub>-Ph<sub>3</sub>P-NaBH<sub>4</sub>-Al(OPr)<sub>3</sub> and IrCl<sub>3</sub> showed the yield of two isomeric 2:1 and 1:1 adducts. In the presence of RhCl<sub>3</sub> and CoCl<sub>2</sub>-Ph<sub>3</sub>P-NaBN<sub>4</sub> mainly 1:1 adducts were obtained. When the Ph<sub>3</sub>P and arsine were added to the RhCl<sub>3</sub> catalyst the 2:1 adduct was formed.

### Catalytic Asymmetric Hydrogenation Using Ruthenium(II) Chiral Phosphine Complexes

B. R. JAMES, D. K. W. WANG and R. F. VOIGT, *J. Chem. Soc., Chem. Commun.*, 1975, (14), 574-575

The hydrogenation of unsaturated carboxylic acids was catalysed, under mild conditions, by Ru(II) complexes [Ru<sub>2</sub>X<sub>4</sub>{(±)-diop}]<sub>3</sub> [X = Cl, Br; diop = 2,2-dimethyl-1,3-dioxolan-4,5-bis(methylene)bis(diphenylphosphine)] containing a bridging bidentate phosphine ligand, and gave products of high optical yields (ca.60%).

### Kinetics and Mechanism of the Osmium Tetroxide Catalysed Oxidation of 2-Propanol and 1-Propanol by the Hexacyanoferrate(III) Ion in Aqueous Alkaline Medium

H. S. SINGH, S. P. SINGH, S. M. SINGH, R. K. SINGH, and A. K. SISODIA, *J. Phys. Chem.*, 1975, **79**, (18), 1920-1924

Kinetic studies of OsO<sub>4</sub> catalysed oxidation of 2-propanol and 1-propanol by [K<sub>3</sub>Fe(CN)<sub>6</sub>] showed that the oxidation goes through the formation of an activated complex between the alcohol molecule and OsO<sub>4</sub> which decomposes to an intermediate product and Os(VI) species. Os(IV) are then rapidly oxidised to Os(VIII) with [K<sub>3</sub>Fe(CN)<sub>6</sub>].

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Reaction of Sputtered Pt Films on GaAs

V. KUMAR, *J. Phys. Chem. Solids*, 1975, **36**, (6), 532-541

X-ray diffraction, spectroscopic and backscattering studies of Pt/GaAs interface reaction at 250-500°C showed a rapid diffusion and dissolution of Ga in Pt at the beginning of the reaction; it was then slowed down by the formation of PtAs<sub>2</sub> at the interface. Five different Pt-Ga phases were identified; PtAs<sub>2</sub> and GaPt were the final reaction products. The reaction was self-limited (up to 500°C) for Pt films thicker than 2000Å, probably due to a slow diffusion of Ga through the interfacial PtAs<sub>2</sub>.

### Reactions between the Ta-Pt-Ta-Au Metallisation and PtSi Ohmic Contacts

H. M. DAY, A. CHRISTOU, W. H. WEISENBERGER and J. K. HIRVONEN, *J. Electrochem. Soc.*, 1975, **122**, (6), 769-772

Reactions between Si substrates and a stabilised (Ta-Au metallisation with and without an intervening PtSi layer) were studied as a function of annealing temperatures up to 785°C. The contact resistance of small area PtSi ohmic contacts, with geometrics representative of microwave power transistors overlaid with the Ta-Pt-Ta-Au system, remained constant during anneals up to 400°C for 24h. Thermochemical reactions and diffusion at higher temperatures are discussed.