

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Experimental Fusion Curves of Silver, Copper and Platinum to 70 Kilobars

N. R. MITRA, *Diss. Abs.*, 1966, **26**, (9), 5508

The melting curve of Pt at 70 kbar is represented by the Simon equation $(P/430) = (T/2045)^{-1}$ and its melting point is 2378°K, detected by a sharp increase in resistivity. No sign of phase transition was observed in these metals up to the highest pressure and temperature attained.

On the Insolubility of Rhenium in Gold and the Introduction of Rhenium into Gold-Platinum Alloys

K. FLAMMIGER and F. SAUERWALD, *Neue Hütte*, 1966, **11**, (4), 218-221

Tests show that, whereas Re does not alloy with Au, it is possible under certain conditions to alloy Re-Pt with Au-Pt to form a ternary alloy, more especially where the Pt content is high.

Fracture of Au-Pt Alloys with Modulated Structure

R. W. CARPENTER, A. AHMADIEH and E. R. PARKER, *Acta Met.*, 1966, **14**, (4), 543-545

0.02 in. Au-Pt wires were heated, homogenised and quenched. They became subject to brittle fracture with some precipitation at grain boundaries. On ageing, fracture of 20% Au-Pt showed no change but fracture of 60% Au-Pt changed from transgranular shear to brittle intercrystalline.

Some Properties of Co-Pt Alloys

A. G. RABIN'KIN, *Fiz. Met. Metalloved.*, 1966, **21**, (5), 688-692

The Curie point T_c of 51.4 at.% Pt-Co alloy decreases during annealing at all temperatures between 500 and 700°C because of changes in the f.c.c. matrix during the annealing process. An anomaly in the temperature coefficient of electrical resistivity of equiatomic Co-Pt alloy was observed.

Magnetic Properties of Pt Metal Containing Co and Fe Atoms

T. TAKAHASHI and M. SHIMIZU, *J. Phys. Soc. Japan*, 1966, **21**, (4), 681-683

Results from measurements of Curie temperature and magnetisation of Pt metal containing Co and Fe atoms, assuming that 5d electrons of Pt are mobile but that magnetic moments of the dissolved atoms are localised, suggest that values of spin quantum numbers of localised moments and of magnetic field coefficients between localised moments and 5d electrons are similar to those of

Pd metal. Differences are due mainly to the electronic densities of states of the two metals.

A Study of the Effect of Deformation on Ordered Cu₃Pt

J. J. WERT, S. G. CUPSCHALK and F. A. DAHLMAN, *Trans. Met. Soc. A.I.M.E.*, 1966, **236**, (4), 421-425

Data on Cu₃Pt initially ordered to 0.82 and after 1 and 6% deformations showed that deformation greatly reduced the degree of long-range order. Within this range the average particle size hardly changed but the antiphase domain size decreased considerably. Microhardness doubled during the deformation process.

Physical Properties of Several Plutonium Base Intermetallic Compounds

J. M. TAYLOR, *U.S.A.E.C. Rept. BNWL-SA-385*, 1965, 13 pp.

Data were obtained for the melting points, elastic coefficients, moduli of elasticity and structures of intermetallic compounds of Pu with the Pt metals, Co and Si. These have high densities, they are very brittle and handling is difficult. Melting points of Pu-Pt exceed 1000°C.

Electronic Properties for Pd Metal and its Ferromagnetic Alloys. On the Number of Holes in the 4d-Band of Pd Metal

H. KIMURA, A. KATSUKI and M. SHIMIZU, *J. Phys. Soc. Japan*, 1966, **21**, (2), 307-312

Composition dependence of the magnetisation of Pd-Fe and Pd-Co alloys is discussed and residual electrical resistivities of Pd-Ni alloys are calculated using 0.36 as the number of electrons in the 5s band or the number of holes in the 4d band per atom of Pd metal. Temperature dependence of electronic specific heat and paramagnetic susceptibility of Pd are calculated. 0.36 gives better agreement with experiment than the previous value of 0.6 per atom.

Effect of Plastic Deformation on the Resistivity and Hall Constant of Silver-Palladium Alloys

R. W. WESTERLUND and M. E. NICHOLSON, *Acta Met.*, 1966, **14**, (5), 569-574

Measurements on five Ag-Pd alloys containing 10-55 at.% Pd showed that the Hall constant decreased with increasing plastic deformation. In Ag-rich alloys it also decreased as Pd content increased; the decrement was 20% in 40% Pd-Ag. Its rate of change decreased continuously with strain. Hall constant behaviour indicates that the anomalous initial decrease in electrical resistivity is caused by disordering of short-range order by cold work.

The Diffusion Behaviour of Hydrogen in the Alloy Pd:Ag=77:23 in Relation to its Concentration

A. KÜSSNER, *Z. Naturf.*, 1966, **21a**, (5), 515-525

The diffusion coefficient of H₂ in 23% Ag-Pd depends on the H₂ concentration. Studies were made at 30, 50 and 75°C with H:Me concentrations from 0 to 0.4. Pressure hysteresis of potential in compressed Ag-Pd foils is due to mechanically stimulated potentials. Results tend to show that absorbed H₂ is not dissociated into protons and electrons.

The Parahydrogen Conversion on Alloys of the Noble Metals with Palladium

A. COUPER and A. METCALFE, *J. Phys. Chem.*, 1966, **70**, (6), 1850-1853

An electron-activation model is used to interpret data on the activation energies of the parahydrogen conversion for Pd-Ag and Pd-Au systems. Activation energies increase slowly from 2 kcal mole⁻¹ for Pd to ~4 kcal mole⁻¹ for 60 at.% Ag-Pd, and then rise faster to 11.5 kcal mole⁻¹ for Ag.

Electrical Resistance of Dilute Solutions of Hydrogen in Palladium

J. W. SIMONS and T. B. FLANAGAN, *J. Chem. Phys.*, 1966, **44**, (9), 3486-3490

Studies on the temperature coefficient of the relative resistance R/R₀ of the α phase of H/Pd as a function of H₂ content in the range 0-90°C showed a linear increase of R/R₀ with H₂ content at each temperature and indicated a coefficient which can be expressed as d(R/R₀)/dn = 0.542 + 1.042 × 10³/T in this range.

Low-temperature Specific Heat of Palladium Containing Interstitial Hydrogen

C. A. MACKLIET and A. I. SCHINDLER, *Phys. Rev.*, 1966, **146**, (2), 463-467

Specific heat measurements at 1.2-4.2°K on specimens with H/Pd atomic ratios of 0.57, 0.70, 0.81 and 0.88 gave electronic specific heat coefficients of 2.52, 1.38, 1.40, and 1.61 mJ/deg² per g. atom Pd and Debye temperatures of 282, 273, 276 and 267°K respectively. Results appear to support the simple band picture of Pd and H-Pd alloys.

Neutron Study of the Diffusion of Hydrogen in Palladium

K. SKÖLD and G. NELIN, *Solid State Commun.*, 1966, **4**, (6), 303-306

Data from inelastic neutron scattering studies of H₂ diffusion in α-phase Pd-H agree with predictions of the jump-diffusion model. Jump length values indicate that H atoms occupy octahedral interstitial sites. Variation of residence time with temperature gives an activation energy value of 3700 ± 500 cal/g.atom.

Electron Diffraction Study on Ordered Alloys of the Copper-Gold-Palladium System.

I. Ordered Alloys of Cu₂AuPd and CuAu₂Pd

A. NAGASAWA, *J. Phys. Soc. Japan*, 1966, **21**, (5), 955-960

Studies on evaporated single crystal films showed that the superlattice structure of Cu₂AuPd is of the modified CuAuI type with space group D_{14h}¹-4/mmm and that the superlattice structure of CuAu₂Pd is identical. Order-disorder transformations occur at about 550°C for Cu₂AuPd and 430°C for CuAu₂Pd. c/a varies from 0.92 at 500°C to 0.87 at 300°C for Cu₂AuPd; 0.98 at 400°C to 0.93 at 200°C for CuAu₂Pd.

Antiferromagnetism in Disordered

Mn₃Pt_{1-x}Rh_x Alloys

E. KRÉN, *Phys. Letters*, 1966, **21**, (4), 383-384

Neutron diffraction measurements showed that these alloys have γ-Mn type anti-ferromagnetic structure. Variation of the Néel temperature with concentration was measured.

Property Changes in the Martensitic β₁ ↔ β₂ Transformation in the Rhodium-Manganese System

A. KUSSMAN, K. MÜLLER and H. WOLLENBERGER, *Z. Angew. Phys.*, 1966, **20**, (5), 461-465

Micrographic, dilatometric and magnetic measurements of the β₁ ↔ β₂ transformation in the Rh-Mn system between -200 and +500°C indicated a spontaneous lattice change, whose hysteresis range could not be constricted by annealings or interruptions, and resembling the α-γ transformation of 25% Ni steels with marked changes of magnetic properties. β₁(f.c.t.) was para- or anti-ferromagnetic. High Mn-content alloys at low temperature were ferromagnetic. β₂(b.c.c.) reached ferromagnetic saturation of ~0.4T at ~60 at.% Mn. Heterogeneous β₁+β₂ had high coercivity. Transformation temperatures and paramagnetic Curie points depended on alloy composition.

Kinetics of the Isomorphous Transformation in Iron-Rhodium Alloys

E. I. ESTRIN, *Izv. Akad. Nauk S.S.S.R., Metall.*, 1966, (3), 150-155

The isomorphous transformation occurring in equiatomic Fe-Rh alloys is similar to martensitic transformation in its athermal character, its range of temperature, and in the temperature hysteresis of transformation during cooling-heating cycles.

The Titanium-Rhodium Alloys

E. RAUB and E. RÖSCHEL, *Z. Metallkunde*, 1966, **57**, (7), 546-551

A proposed constitution diagram of the Ti-Rh system includes a Rh-rich phase with AB₅-type lattice. β-Ti solid solution extends to high concentration and below 0°C. Solubility of Rh in

α -Ti is very small. Solubility of Ti in Rh is ~ 16 at.% at the eutectic temperature and is temperature-dependent.

High-temperature Mechanical Properties and Corrosion Resistance of Iridium and its Alloys

R. D. BERRY and J. HOPE, *Rev. Mét.*, 1966, **63**, (4), 339-345

The properties of Ir are reviewed and the behaviour of 0.3% Zr-Ir is studied. Relaxation times of Ir alloys were measured. 5% W-Ir has only 12% relaxation after 100 h at 600°C. The oxidation of Ir is described and its corrosion resistance to molten metals is tabulated.

Martensitic Transformations in Iron-Iridium Alloys

M. MIYAGI and C. M. WAYMAN, *Trans. Met. Soc. A.I.M.E.*, 1966, **236**, (5), 806-811

Dilatometric, X-ray and metallographic analyses show that Fe-Ir alloys with up to 53 wt.% Ir undergo two different martensitic transformations: f.c.c. to b.c.c. ($\gamma \rightarrow \alpha'$) and f.c.c. to h.c.p. ($\gamma \rightarrow \epsilon$), both of which can be reversed. As Ir content increases the $\gamma \rightarrow \alpha'$ temperature decreases but the $\gamma \rightarrow \epsilon$ temperature increases. Lattice parameters of γ , α' and ϵ have been determined. The $\gamma \rightarrow \alpha' \rightarrow \gamma$ and $\gamma \rightarrow \epsilon \rightarrow \gamma$ transformations of Fe-Ir resemble those of Fe-Ru alloys.

On the Electrical Conductivity and Thermal Conductivity of Ruthenium

L. A. PANTALEIMONOV and O. P. NESTEROVA, *Vest. Moskov. Univ., Ser. II, Khim.*, 1966, (2), 49-50

Sintered and cast Ru test-pieces had densities 11.08 and 12.26 g/cm³ respectively. The electrical conductivity of the sintered Ru decreased by 65% in the 25-700°C range by a non-linear path. That of the cast Ru was 25% less at 700°C. The thermal conductivity of Ru, determined at 35 and 50°C, was 0.220 and 0.234 cal/cm.deg C.sec, respectively.

An X-ray Investigation of Ruthenium-Aluminium Alloys

L.-E. EDHAMMAR, *Acta Chem. Scand.*, 1966, **20**, (2), 427-431

The existence of the phases RuAl, Ru₂Al₃, RuAl₂, RuAl₂₋₅ and Ru₄Al₁₃ was demonstrated. RuAl has CsCl-type structure with $a=2.95$ Å. Ru₂Al₃ is isomorphous with Os₂Al₃ and has a tetragonal cell with $a=2.079$, $c=14.33$ Å. Orthorhombic RuAl₂ has $a=8.012$, $b=4.717$, $c=8.785$ Å and TiSi₂-type structure. The Ru-Al and Os-Al systems are compared.

The High-temperature Oxidation of Ductile Cr-Ru Alloys

C. S. TEDMON, *J. Less-Common Metals*, 1966, **10**, (5), 301-311

High-temperature oxidation kinetics of the ductile

15 and 19 at.% Ru-Cr alloys, which bracket the b.c.c. α -phase solubility limit, were studied by thermogravimetric, metallographic, X-ray and electron probe techniques. Volatile Ru oxide was formed together with an external scale of Cr₂O₃, which volatilised above 1200°C. Weight-gain measurements indicated parabolic kinetics above 1000°C. Kinetics of samples oxidised in air resembled those in O₂. No Cr₂N was formed during oxidation in air. 19 at.% Ru-Cr oxidised more slowly than pure Cr.

The Vanadium-Osmium Alloys

E. RAUB and E. RÖSCHEL, *Z. Metallkunde*, 1966, **57**, (6), 470-472

Thermal, microscopic and X-ray analysis of V-Os alloys indicated the existence of a B₂ phase V₃Os₂, which melts congruently in a flat maximum of the liquidus curve, and of an A15 phase VOs, which is formed by a peritectoid reaction between B₂ and A₃ below 700°C. Solutions of Os in V and of V in Os are relatively high and are temperature dependent.

Emission Properties of the Alloys Pt-Th, Ir-Th, Os-Th and Re-Th

B. CH. DYUBUA, L. A. ERMOLAEV and O. K. KULTASHEV, *Radiotekh. Elektron.*, 1966, **11**, (6), 1149-1150

Results are tabulated for tests on 2% Th alloys of Pt, Ir, Os and Re of electron work function, temperature coefficient of work function, and maximum coefficient of secondary electron emission σ_{MAX} . A monolayer of Th apparently forms on Os and Re but not on Pt or Ir, because Pt₅Th and Ir₅Th are very stable. Surface adsorption of Th probably causes σ_{MAX} to be higher in Th-Ir than in pure Ir. σ_{MAX} is lower for Th-Pt than for pure Pt.

Emission Properties of the Alloys Pt-La, Ir-La, Os-La

E. V. VASIL'VA, B. CH. DYUBUA, L. A. ERMOLAEV and O. K. KULTASHEV, *Ibid.*, 1150-1151

Similar results to the above are tabulated for 0.5% La alloys of Pt, Ir and Os. The La is believed to be present as Pt₅La, Ir₅La and Os₅La. Decrease of work function and increase of the coefficient of secondary electron emission compared to pure metals is probably due to a monolayer of La on the surface. σ_{MAX} is higher for La-Ir and La-Os than in the Th alloys and is lower for La-Pt than for Th-Pt.

CHEMICAL COMPOUNDS

The Chemistry of Platinum Hexafluoride. I. Reactions with Nitric Oxide, Dinitrogen Tetroxide, Nitrosyl Fluoride, and Nitril Fluoride

F. P. GORTSEMA and R. H. TOENISKOETTER, *Inorg. Chem.*, 1966, **5**, (7), 1217-1222

PtF₆ reacted with nitrosyl fluoride, nitril fluoride

and dinitrogen tetroxide to form NOPtF_6 , NO_2PtF_6 and $\text{N}_2\text{O}_3\text{PtF}_6$ respectively. $(\text{NO}_2)_2\text{PtF}_6$ was formed with excess nitrosyl fluoride. The infra-red, X-ray and epr data for these compounds were studied. PtF_6 did not react with nitrous oxide up to 100°C .

On the Homogeneity Range of the PtS Phase

A. KJEKSHUS, *Acta Chem. Scand.*, 1966, **20**, (2), 577-579

X-ray studies of the PtS phase were extended nearly to 1000°C and showed linear increases in the lattice constants, which fit the relations $a = 3.4701[(1 + 3.8 \times 10^{-6}(t - 20))\text{\AA}]$ and $c = 6.1092[1 + 6.0 \times 10^{-6}(t - 20)]\text{\AA}$.

Carbonylation of Platinum and Palladium Organo-complexes

G. BOOTH and J. CHATT, *J. Chem. Soc., A, Inorg. Phys. Theor.*, 1966, (6), 634-638

Acyl derivatives of the *trans*- $[\text{MX}(\text{COR})(\text{PEt}_3)_2]$ type ($\text{M} = \text{Pt}$ or Pd , $\text{X} = \text{Cl}$, Br or I ; $\text{R} = \text{Me}$, Et or Ph) were prepared by action of CO on alkyl and aryl derivatives of the type $[\text{MXR}(\text{PEt}_3)_2]$. CO reacts with *cis*- $[\text{PtMe}_2(\text{PEt}_3)_2]$ to give $[\text{Pt}_3(\text{CO})_n(\text{PEt}_3)_6]$ ($n = 3$ or 4). Other related disubstituted derivatives gave unstable or intractable products. Some alkyl and aryl Pt and Pd derivatives were too unstable for carbonylation or gave products too unstable to isolate.

Hydridopentammine- and Hydridoquo-tetrammine-rhodium(III) Sulphates

J. A. OSBORN, A. R. POWELL and G. WILKINSON, *Ibid.*, (14), 461-462

Preparation of the first two pure hydrido-complex salts is reported. They are $[\text{RhH}(\text{NH}_3)_5]\text{SO}_4$ and $[\text{RhH}(\text{H}_2\text{O})(\text{NH}_3)_4]\text{SO}_4$.

Dissociation of Iridium Oxide

W. E. BELL, M. TAGAMI and R. E. INYARD, *J. Phys. Chem.*, 1966, **70**, (6), 2048-2050.

The composition of $\text{IrO}_2(\text{s})$ deviates hardly at all from stoichiometry in the range $800-1050^\circ\text{C}$. The formation reaction for the oxide at high temperature can be represented by $\text{Ir}(\text{s}) + \text{O}_2 = \text{IrO}_2(\text{s})$. Dissociation pressure data are tabulated. ΔH_{298}° is calculated as -57.4 kcal/mole and ΔS_{298}° as -43.8 eu for the formation of $\text{IrO}_2(\text{s})$.

ELECTROCHEMISTRY

Anodic Polarisation of Platinum in Sodium Chloride Solutions

E. L. LITTAUER and L. L. SHREIR, *Electrochim. Acta*, 1966, **11**, (5), 527-536

Below $\sim 1.6\text{V}$, Cl_2 is evolved on a clean Pt surface in NaCl solution but at higher potentials a surface oxide develops on the electrode and causes a rapid jump of potential. The kinetics for oxida-

tion of Cl and subsequent Cl_2 discharge are affected by other ions. Molarity and pH also affect the anodic behaviour of the Pt.

The Influence of Increasing Superimposed 50 c/s a.c. on the Anodic Dissolution of Platinum in 3% Sodium Chloride

R. JUCHNIEWICZ, *Corrosion Sci.*, 1966, **6**, (2), 69-77
A r.m.s. ac $> 70.7\%$ dc causes a change in electrode reactions from monopolar to bipolar operating conditions. Under the latter at 50 Hz, H_2 is evolved which is believed to interfere with the normal passive film present on Pt, so causing increased corrosion. Knowledge of the causes of the monopolar-bipolar transition explains a wide range of electrochemical reactions previously observed.

The Electroreduction of Oxygen on Pt-Ru and Pt-Rh Alloys

T. P. HOAR and E. W. BROOMAN, *Electrochim. Acta*, 1966, **11**, (5), 545-547

1.9, 3.8 and 9.3% Ru-Pt and 1.6, 3.7, 9.1 and 17.4% Rh-Pt alloys are more active electrochemically than bright Pt for O_2 reduction in H_2SO_4 solution (pH 1.28) at 25°C . Enhancement ratios of up to 4.63 at 0.68V(nhe) and up to 8.91 at 0.10V(nhe) were recorded. See also *Platinum Metals Rev.*, 1965, **9**, (4), 122-125

H/D Separation Factors in Electrolysis and Diffusion Using Pd and Pd/Ag Membranes

H. BRODOWSKY, H. GIBMEIER and E. WICKE, *Z. Phys. Chem. (Frankfurt)*, 1966, **49**, (3-5), 222-239

The diffusion factor of an H/D mixture through a Pd tube from 775 to 200 Torr at $0-50^\circ\text{C}$ was $S_D = 1.6 \pm 0.1$. H_2 is concentrated in the diffusion stream because it is more soluble in Pd than D_2 rather than because of its higher mobility. The separation factor for a 1:1 H/D mixture through a 25% Ag-Pd diffusion tube anode was $S_A = 1.7 \pm 0.15$ and was almost independent of temperature at $20-70^\circ\text{C}$ and of current capacity ($20-70$ mA/cm²). Cathodic separation factors at Ag-Pd tubes from KCO_3 solutions with $\text{D}_2\text{O}/\text{H}_2\text{O} \approx 0.85/0.15$ were 8 (at 60°C) to 16 (at -30°C).

Anodic Corrosion of Ruthenium in Hydrochloric Acid Solution

J. LLOPIS, I. M. TORDESILLAS and J. M. ALFAYATE, *Electrochim. Acta*, 1966, **11**, (6), 623-632

Chloro-complexes of Ru(III) and/or Ru(IV), depending on the potential, are formed by the action of dc and ac on Ru in HCl solution. RuO_4 may form by the action of dc on Ru in HClO_4 solution and it subsequently dissolves in the electrolyte to some extent. Square-wave ac of < 4 c/s increases attack on Ru in HCl solution and $[\text{RuCl}_6]^{3-}$ and/or $[\text{RuCl}_6]^{2-}$ are formed. Ru has corrosion resistance in HCl solution higher than Rh or Pt but of the same order as Ir.

Passivation of Ruthenium in Hydrochloric Acid Solution

J. LLOPIS and M. VÁZQUEZ, *Ibid.*, 633-640

Anodic and cathodic charging curves for Ru in HClO₄ and HCl solutions showed that passivation depends on formation of an oxide film several molecules thick; in HClO₄ this is Ru₂O₃ and/or RuO₂, with oxidation to RuO₄ at higher potentials; in HCl this is probably Ru₂O₃.

ELECTRODEPOSITION AND SURFACE COATINGS

Developments and Tendencies in Precious Metal Finishing

H. BENNINGHOFF, *Galvanotechnik*, 1966, 57, (7), 451-463

A comprehensive review of recent work on metal finishing with the Pt metals, Au and Ag. (191 refs., 1965-66 refs. listed separately).

Heavy Platinum Deposits on Nickel and Molybdenum

G. T. BAKHVALOV, V. I. LAINER and A. S. MASLENNIKOVA, *Izv. Vysshikh Uchebn. Zavedenii, Tsvetn. Met.*, 1966, 9, (1), 148-152

A solid Pt film 28 μm thick is produced on Ni by the procedure detailed. Mo can be platinised by first depositing Ni or Cr on the Mo to improve adhesion and then plating with Pt.

Electrodeposition of Iridium and Iridium-Rhodium Alloys from Chloride Electrolytes

B. S. KRASIKOV and V. S. KRIVONOS, *Zh. Prikladnoi Khim.*, 1966, 39, (6), 1332-1338

Partial polarisation curves for the deposition of Ir-Rh alloys from electrolytes containing Ir and Rh salts, 2 mol/l NaCl at pH 0.5, 25°C established that Rh was deposited with superpolarisation, Ir with depolarisation.

Form of the Occurrence of Rhodium in Sulphate Electrolytes

S. I. GINZBURG, N. N. CHALISOVA and B. S. KRASIKOV, *Zh. Neorg. Khim.*, 1966, 11, (6), 1384-1387

Rh sulphate plating electrolytes may be prepared electrolytically. Rh dissolved electrolytically in H₂SO₄ exists in anionic form in the complex trisulphate H_m[Rh_n(SO₄)_{3n}O_x]. During the electrochemical dissolution of Rh metal in H₂SO₄ the same complex Rh sulphate is formed as with Rh(OH)₃ and H₂SO₄.

CATALYSIS

An Investigation of the Surface Diffusion of *n*-Butane on a Platinum-Alumina Catalyst

D. GELBIN, *Chem. Tech.*, 1966, 18, (4), 200-206

A surface diffusion effect contributes to the

diffusion of adsorbed *n*-butane on Pt/Al₂O₃ and an equation for it has been derived, which agrees with measurements. The activation energy and heat of adsorption are of the same magnitude.

Isomerisation, Hydrogenation and Hydroisomerisation of Some Hydrocarbons on Type Y Synthetic Zeolites Containing Group VIII Metals

KH. M. MINACHEV, V. I. GARANIN, L. I. PIGUZOVA and A. S. VITUKHINA, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1966, (6), 1001-1005

Using Pt and Pd on CaY zeolites (SiO₂:Al₂O₃ = 3.4), ~60% isomers of hexane were produced from *n*-hexane at 400°C, 30 atm and ~50% methylcyclopentane from cyclohexane at 370°C. Rh and Ir zeolite catalysts have high activity for hydrogenation and gave 97.8 and 91% yields respectively of cyclohexane from C₆H₆ at 200°C, 30 atm. The activity of Pd for hydroisomerisation of C₆H₆ and isomerisation of cyclohexane depends on the ratio of SiO₂:Al₂O₃ in the zeolite. When this ratio is 4.5, 67.3% methylcyclopentane was produced from C₆H₆ at 320°C and 57.0% from cyclohexane at 330°C.

Precious Metal Distribution on Supported Catalysts

H. KRAL, *Z. Phys. Chem. (Frankfurt)*, 1966, 48, (3-4), 129-144

The effects of the support, the noble metal distribution and the method of impregnation for Pt/Al₂O₃ and Pd/C were studied by X-ray, CO adsorption and heat of wetting methods to determine the distribution of the active phase. This depends on the specific surface area of the support. Despite irregularities it is shown that fine distribution of the noble metal promotes reactivity of the catalysts.

Compact Design Pays off at New Nitric Acid Plant

E. C. BINGHAM, *Chem. Engng.*, 1966, 73, (11), 116-118

The 500 ton/d HNO₃ plant built by D. M. Weatherly Co. for Farmers Chemical Assn. Inc. at Tyner, Tennessee, has a conversion efficiency of at least 95% of the N in NH₃ during oxidation on Pt gauze at ~1650°F, 9 atm. Design details of the plant are explained by reference to a flow diagram. A catalytic burner prevents NO₂ contamination of the air by tail gas.

Application of Infra-red Spectroscopy and Surface Potential Measurements in a Study of the Oxidation of Carbon Monoxide on Platinum

H. HEYNE and F. C. TOMPKINS, *Proc. Roy. Soc.*, 1966, 292A, (1431), 460-478

Kinetics of the heterogeneous oxidation of CO by O₂ over Pt/Aerosil and over evaporated Pt

films were studied at 250–370°K and results show that there is qualitative and quantitative agreement with the expression:

$$\text{rate} = \{k[\text{O}_2(\text{g})]/[\text{CO}(\text{g})]\} \exp(-q_1/RT).$$

Isomerisation of Low-melting Paraffins in the Presence of Commercial Platinum Catalysts

YA. R. KATSOBASHVILI, A. V. MINIBAEV and T. S. GRACHEVA, *Khim. i Tekhnol., Topliv i Masel*, 1966, (7), 12–15

54.8% yield of isoparaffins was achieved at 440°C, rate 1 h^{-1} from the 220°C fraction over commercial Pt catalyst with 76.5 wt.% selectivity. 57.8% yield was achieved at 460°C from the 150–300°C fraction which freezes at –67°C.

Conversion of Hydrocarbons in the Presence of Spent and Reactivated Platinum Reforming Catalysts

V. V. SHIPIKIN, G. N. MASLYANSKII, B. B. ZHARKOV and N. R. BURSIIAN, *Neftekhimiya*, 1966, 6, (3), 401–406

After 15000 h work, Pt/Al₂O₃ reforming catalyst was still active for dehydrogenation of C₆ naphthenes but possessed reduced activity for isomerisation and dehydrocyclisation of paraffins. Reactivation of spent Pt/Al₂O₃ by Cl₂-containing gas, after removal of Fe and Na impurities, gave it activity for dehydrogenation comparable to fresh catalyst, more activity than fresh catalyst for dehydrocyclisation of paraffins, but less activity for their isomerisation. Results indicate increased acidity of the Pt catalyst raises its activity for dehydrocyclisation of paraffins.

Catalytic Conversion of an Organophosphate Vapour over Platinum-Alumina

W. M. GRAVEN, S. W. WELLER and D. L. PETERS, *Ind. Engng. Chem., Process Des. Dev.*, 1966, 5, (2), 183–189

Conversion of dimethyl methylphosphonate vapour in streams of air or N₂ was studied on 0.5 wt.% Pt/Al₂O₃ commercial and laboratory-prepared catalysts at 300–500°C, 0.15–2.7 sec, particle sizes 0.31–2.4 mm. Fresh commercial catalyst had too much activity but deactivated catalyst showed approximately first order kinetics with activation energy of 7–8 kcal/mole vapour. The conversions in air and N₂ were about equally rapid. Initial reaction was mainly hydrolysis to CH₃OH and a P acid. Intraparticle pore diffusion was important. Catalyst deactivation was $k = k_0 e^{-\alpha t}$, where k is the first order rate constant.

Effect of Alkali Metals on the Properties of Platinum Catalysts in the Dehydrocyclisation of N-Hexane

N. R. BURSIIAN, S. B. KOGAN, G. M. OSMOLOVSKII, B. G. LYUDKOVSKAYA and Z. A. DAVYDOVA, *Kinetika i Kataliz*, 1966, 7, (3), 556–559

Studies of the promoting action of Li, Na and Cs

on Pt/Al₂O₃ and Pt/SiO₂ during N-hexane dehydrocyclisation show that the alkali metals inhibit the formation of metal crystals on the catalyst support. Their effectiveness decreases in the order Cs > Na > Li and is explained by differences in their ionic radii.

Some Problems of the Kinetics of Hydrogenolysis of Cyclopentane Hydrocarbons on Platinised Carbon. Part 2. Hydrogenolysis of Stereoisomers of 1,2-Dimethylcyclopentane and Isopropylcyclopentane

B. A. KAZANSKII, O. V. BRAGIN, A. L. LIBERMAN and A. V. PREOBRAZHENSII, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1966, (4), 598–602

Total values of the apparent activation energy of hydrogenolysis of the five studied hydrocarbons on Pt/C are practically the same for any one portion of the catalyst. Screening of bonds of the five-membered ring leads to increased activation energy compared to unscreened bonds of the ring.

Heterogeneous Catalysis in a Continuous Stirred Tank Reactor

D. G. TAJBL, J. B. SIMONS and J. J. CARBERRY, *Ind. Engng. Chem., Fund.*, 1966, 5, (2), 171–175

The reactor was evaluated as a perfect mixer and used to determine the kinetics of CO oxidation by O₂, catalysed by 0.5 wt.% Pd/z-Al₂O₃ pellets. Rate \propto O₂/CO ratio. Apparent activation energy is 28.5 kcal/mole at 205–234°C, 1 atm.

Hydrogenation of Olefins. Part 3. Reaction of Ethylene and Propylene with Deuterium over Alumina-supported Palladium and Rhodium

G. C. BOND, J. J. PHILIPSON, P. B. WELLS and J. M. WINTERBOTTOM, *Trans. Faraday Soc.*, 1966, 62, (2), 443–454

Product distributions and reaction mechanisms are discussed for the reactions C₂H₄+D₂ over Pd/Al₂O₃ at –36 to 67°C, C₃H₆+D₂ over Pd/Al₂O₃ at 19°C, C₃H₄+D₂ over Rh/Al₂O₃ at –18 to 110°C and C₃H₆+D₂ over Rh/Al₂O₃ at 88°C. C₂H₄ desorption and reversion of ethyl radicals to adsorbed C₂H₄ are both easy over Rh and Pd. A ready direct atom transfer between ethyl radicals and C₂H₄ molecules is indicated over Pd.

On the Effect of the pH of the Medium on the Kinetics of Hydrogenation over a Pd Catalyst

S. M. RESHETNIKOV and A. M. SOKOL'SKAYA, *Kinetika i Kataliz*, 1966, 7, (2), 279–283

Charging curves for 5% Pd/BaSO₄ between pH 1.2 and 13.0 indicate an increase in the energy of the Pd-H bond as pH rises. This catalyst contains more adsorbed and less dissolved H₂ than Pd black.

Oxidation of Olefins by Palladium(II). II. Effect of Structure on Rate in Aqueous Solution

P. M. HENRY, *J. Am. Chem. Soc.*, 1966, **88**, (8), 1595-1597

Oxidation kinetics of C_6H_6 to acetone and of *cis*- and *trans*-2- C_4H_8 and 1- C_4H_8 to methyl ethyl ketone are the same as those of C_2H_4 . $-d[\text{olefin}]/dt = k'K_1[\text{PdCl}_4^{2-}][\text{olefin}]/[\text{Cl}^-]^2[\text{H}^+]$, where K_1 is the equilibrium constant for π -complex formation between the olefin and PdCl_2 in H_2O . Change in k' with olefin structure is $C_2H_4 > \text{trans-2-}C_4H_8 \approx C_6H_6 > \text{cis-2-}C_4H_8 \approx 1-C_4H_8$, with total range a factor of 6. This small change denotes little carbonium ion character in the transition state for oxypalladation, the rate-determining step. Oxypalladation, oxymercuration and oxythallation mechanisms are compared. The trend of K_1 with olefin structure is $C_2H_4 > C_3H_6 > 1-C_4H_8 > \text{cis-2-}C_4H_8 > \text{trans-2-}C_4H_8$, which is the same as for π -complex formation with Ag(I) .

Kinetics and Mechanism of Olefin Oxidation with Palladium and Platinum Compounds

R. JIRA, J. SEDLMEIER and J. SMIDT, *Liebigs Ann. Chem.*, 1966, **693**, 99-108

Tests indicated that oxidation of olefins to carbonyl compounds with Pd and Pt salts in aqueous solutions occurred by the formation of a *cis*-monohydroxo-olefin-metal complex. The same mechanism may occur in the formation of vinyl esters, ethers and halides, and in the hydrolysis of vinyl compounds, from olefins in the presence of Pt and Pd salts.

Organic Syntheses by means of Noble Metal Compounds. Part 23. Reactions of π -Allylpalladium Chloride Complexes with Nucleophiles

J. TSUJI, H. TAKAHASHI and M. MORIKAWA, *Kogyo Kagaku Zasshi*, 1966, **69**, (5), 920-924, A49

The π -allylpalladium chloride complex reacts smoothly with ethyl malonate anion and ethyl acetoacetate anion to give allyl- and diallylmalonate and allyl- and diallylacetates respectively. Enamines derived from cyclohexanone reacted with it to give 2-allylcyclohexanone. Alcoholate anions give allyl ether and oxidised product. Co-ordination of the anions on Pd followed by coupling with allyl radical is the probable reaction mechanism.

On the Mechanism of Polymerisation of Butadiene-1,3 in Aqueous Medium under the Influence of Rhodium Compounds

B. D. BABITSKII, V. A. KORMER, I. YA. PODDUBNYI, V. N. SOKOLOV and N. N. CHESNOKOVA, *Dokl. Akad. Nauk S.S.S.R.*, 1966, **167**, (6), 1295-1298

Radioactive labelling, both by C and D_2 and T_2 , was used to study polymerisation of butadiene in

the presence of RhCl_3 and of Rh complexes. Reaction mechanisms are suggested.

Olefin Co-ordination Compounds of Rhodium. III. The Mechanism of Olefin Isomerisation

R. CRAMER, *J. Am. Chem. Soc.*, 1966, **88**, (10), 2272-2282

Soluble Rh olefin complexes catalyse isomerisation of linear butenes by a form of addition and elimination of Rh hydride at the olefin bond, and an intermediate of Rh(III) hydride with co-ordinated olefin which exchanges faster with free olefin than with solvent proton. The mechanism is based mainly on D_2 transfer accompanying isomerisation of deuterated olefin or in deuterated solvent.

Crotonic Condensation of Butyraldehyde in the Presence of Rhodium Catalysts

YA. T. EIDUS, B. K. NEFEDOV, M. A. BECPROZVANNYI and YU. V. PAVLOV, *Neftekhimiya*, 1966, **6**, (2), 282-285

Butyraldehyde undergoes crotonic condensation at 150°C , 10-50 atm in N_2 , H_2 and $\text{CO} + H_2$ in the presence of $\text{Rh}/\text{Al}_2\text{O}_3$ to 2-ethylhexen-2-al-1, which is reduced to 2-ethylhexanal-1, as well as decomposition to H_2 , CO and gaseous hydrocarbons and hydrogenation to butanol-1. Maximum condensation occurs at 30 atm in $\text{CO} + H_2$.

Hydrogenating Activity of an Iridium Catalyst

K. TAYA, *Chem. Commun.*, 1966, (14), 464-465

Ir catalyst prepared by Adams' method is useful for reducing aromatic nitro-compounds to hydroxylamines. Results for 11 nitro-compounds are tabulated. 70 wt.% Ir-Pt, prepared similarly, hydrogenated nitrobenzene to N-phenyl-hydroxylamine at 2-3 times the rate of the Ir catalyst but the yield was 40% instead of 58%.

The Oxidation of Carbohydrate Derivatives with Ruthenium Tetroxide

P. J. BEYNON, P. M. COLLINS, P. T. DOGANGES and W. G. OVEREND, *J. Chem., Soc., C, Org.*, 1966, (12), 1131-1136

RuO_4 converts partially benzoylated, benzylidenated or isopropylidenated methyl glycosides to protected methyl glycopyranosiduloses and also oxidises furanoid derivatives. These conversions facilitate the synthesis of further derivatives.

On the Study of Furan Compounds. XXXI. Hydrogenation of Furan Compounds with Oxygen-containing Functional Groups in the Presence of Ruthenium Catalysts

A. A. PONOMAREV, A. S. CHEGOLYA, N. S. SMIRNOVA and V. N. DYUKAREVA, *Khim. Geterotsikl. Soedinenii*, 1966, (2), 163-168

5% Ru/C and RuO_2 catalysts were tested in liquid phase hydrogenations of alcohols, aldehydes, ketones and carboxylic acids. They

possess high activity for hydrogenation of furan rings, ethylenic bonds and CO groups but are not selective. At room temperature the furan ring is usually hydrogenated to the tetrahydrofuran ring. 1,6-Dioxaspiro-[4,4]-nonane compounds are formed by the hydrogenation of furfurylidene aldehydes, ketones and γ -furyl-alcohols.

Liquid-phase Hydrogenation of Some Nitrogen-containing Heterocyclic Compounds on Ruthenium Catalysts

A. A. PONOMAREV, A. S. CHEGOLYA and V. N. DYUKAREVA, *Ibid.*, 239-242

RuO₂, 5% Ru/C and 5% Ru/SiO₂ catalysed hydrogenations of the N-containing heterocyclic compounds pyrrole, pyridine, indole, quinoline and acridine and their derivatives, and indicated that their high efficiency leads to high yields of saturated compounds. Quinoline and acridine may be selectively hydrogenated at the double bonds of the polycyclic system.

CATHODIC PROTECTION

Anodic Protection of Carbon Steel in Oxalic Acid

L. D. FERRIGO, *Materials Protection*, 1966, 5, (3), 73-76

A Pt cathode was used in tests on the anodic protection of carbon steel in reagent and technical grades of 0.1-0.7M oxalic acid at 22 and 50°C. Greater protection was achieved in reagent grade acid.

Anodic Protection of Austenitic Stainless Steel

R. JUCHNIEWICZ, T. POMPOWSKI and J. WALASZKOWSKI, *Corrosion Sci.*, 1966, 6, (1), 25-31

Anodic protection using a Pt cathode is effective with 0.2% C austenitic stainless steel for prevention of preferential corrosion of ferrite and intercrystalline corrosion, when immersed in 30% H₂SO₄+1% NaCl. Steels most susceptible to corrosion require the highest current densities for passivation.

Platinised Titanium as Anode Material

R. A. LOWE, *Materials Protection*, 1966, 5, (4), 23-24

The advantages of platinised Ti are reviewed with respect to the effects of voltage, current, life, dc ripple, strength, conductivity and shape in use.

Impressed Current Anodes in Brackish Water

A. C. TONCRE and L. V. RICE, *Ibid.*, 61-63

Anodes used include graphite, two types of high silicon Fe, scrap iron, Pb-Ag, and platinised Ti. The latter's cost is offset by long life and ease of installation. 55 Cu-cored platinised Ti anodes

with 0.0001-0.0002in Pt have been installed in various positions and have given good service at up to 120 A/ft² for up to 33 months. Most failures occur because of faulty installation or bad fabrication.

CHEMICAL TECHNOLOGY

Mechanism of the Corrosion Behaviour of Titanium-Palladium Alloys

J. B. COTTON and M. L. GREEN, *Chem. Process.*, 1966, 12, (7), 42-46

Tests on dilute Ti-Pd alloys showed that Pd is present as Ti₂Pd. This dissolves in hot non-oxidising acids that corrode unalloyed Ti and a local concentration of soluble Pd forms on the metal surface and is deposited to protect the alloy by anodic passivation. Plants operating under dynamic flow conditions may require an increase in Pd content from 0.15% to 0.5% to ensure that sufficient soluble Pd is present on the metal surface. Under such conditions with a recirculated liquor, the corrosion resistance of unalloyed Ti may rise significantly by adding as little as 10 p.p.m. soluble Pd to the liquor.

GLASS TECHNOLOGY

The Use of Platinum in the Glass Industry

H. MORITZ, *Silikattechnik*, 1966, 17, (5), 140-144
A review of the use of Pt and its alloys in glass manufacture, glass fibre production, etc. (33 references).

ELECTRICAL AND ELECTRONIC ENGINEERING

Semiconductors Produced by Diffusing Iridium into Oxide Glasses

C. C. SARTAIN and W. D. RYDEN, *Bull. Am. Phys. Soc.*, 1966, 11, (3), 403, abs. JH17

Conductivity studies were carried out on aluminosilicate, barium-silicate, borosilicate, calcium-borate, lead-borate, lead-silicate, lead-borosilicate and zinc-borate glasses made semiconducting by heavily doping with Ir.

Thermopower and Electrical Resistance of Contact Materials on Noble Metal Base

E. VINARICKY, *Metall*, 1966, 20, (7), 727-729

The thermo-e.m.f. against Pt, the thermopower at 20 and 100°C and the electrical resistance of a series of noble metal alloys based on Ag, Au, Pt, Pd were measured. Cu only slightly affected the thermopower of the base elements but Ni affected it strongly. Pd-Ag alloys clearly showed the effect of alloying on thermopower. Electrical resistance depends on the alloying element and its concentration.

TEMPERATURE MEASUREMENT

Temperature Control in the Production Part of a Vertical Drawing Machine Furnace

V. M. OBUKHOV, *Steklo i Keramika*, 1966, 23, (5), 11-12

6% Rh-Pt : 30% Rh-Pt thermocouples are used as temperature sensors in apparatus which stabilises a vertical glass drawing furnace to reduce its temperature oscillation to not more than $\pm 1-1.5^{\circ}\text{C}$.

Platinum Resistance Thermometry in the Range 630 to 900°C

R. J. BERRY, *Metrologia*, 1966, 2, (2), 80-90

Procedures for stabilisation of Pt resistance thermometers at 630-900°C, annealing-out quenching effects and reducing insulation leakage

are based on studies of the performance of commercially-produced, standard instruments. The mica insulation places the 900°C upper limit on them. Insulation leakage at high temperatures, and at low temperatures due to H₂O released from the mica during high-temperature use, is the worst problem.

Measurement of Bath Temperature in the Basic Oxygen Furnace

A. E. SCHRAEDER, *Iron Steel Eng.*, 1966, 43, (5), 137-140

A sinker thermocouple assembly for standard S-type thermocouples has been developed for molten steel temperature measurement in the basic O₂ furnace either during or following the O₂ blow. It is made of cast iron or steel and is as simple and reliable as lance-type thermocouples. No costly additions or modifications to the furnace structure are required.

NEW PATENTS

METALS AND ALLOYS

Ruthenium Alloys

INTERNATIONAL NICKEL LTD.

British Patent 1,032,005

Ductility of Ru is improved by alloying it with 0.25-25 wt.% Re by a powder metallurgy technique.

Manufacture of High Density Alloys

THE GENERAL ELECTRIC CO. LTD.

British Patent 1,032,118

A sintered high density alloy is produced by forming a homogeneous powdered mixture of W and/or Mo and 0.01-10 wt.% one or more Pt group metal, forming a self-supporting compact, heating it at 900-2000°C in a non-oxidising atmosphere so that alloying of the constituents takes place and maintaining the high temperature until the desired degree of densification has been attained.

Metallic Appliances and Components Subjected to Contact with Molten Materials at High Temperature

COMPTOIR LYON-ALEMAND, LOUYOT ET CIE.

British Patent 1,033,317

Metallic appliances which come into contact at high temperatures with glasses, oxides, etc., comprise a composite metallic material consisting of three layers joined by cladding so that there is an inner layer of pure Pt contacting the molten material, an outer layer of Pt-Rh alloy and a central layer of Pt alloy with Ir, Ru, Rh or Os.

Inter-Metallic Compounds and their Preparation

INTERNATIONAL BUSINESS MACHINES CORP.

British Patent 1,035,875

The intermetallic compounds A₂M₂, where A is Gd, Tb, Dy or Ho and M is Pd or Pt, which have good ferromagnetic and mechanical properties, are produced by supporting a finely-divided mixture of the metal powders on a cold Cu hearth in an inert atmosphere, melting a portion out of contact with the hearth, allowing it to solidify, inverting it and repeating several times.

Processing of a Vitreous Composition in a Reducing Atmosphere

BAUSCH & LOMB INC.

U.S. Patent 3,233,993

A container for processing of a vitreous composition in a reducing atmosphere has its cavity lined with Ir or an alloy of 50-100% Ir, 0-50% Rh and max. 20% Pt.

Alloys of Gold with Group VIII Metals

W. C. HERAEUS G.m.b.H.

U.S. Patent 3,238,040

A tension strip for measuring instruments is made of an alloy of 30-80 wt.% Au and the balance Pt, Pd, Ir, Rh, Fe, Co, Ni or their mixtures.

Platinum Group Metal Alloy Tensioning Strips

W. C. HERAEUS G.m.b.H.

U.S. Patent 3,245,781

Tensioning strips which may be used in measuring instruments are made of alloys of 1-50 wt.%, preferably 5-40 wt.%, Fe, Co, Ni, W, Mo, Cu or Ag or their mixtures and balance Pt, Pd and/or Rh.