

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Magnetic Susceptibility and Electronic Specific Heat of Transition Metals and Alloys. VI. Pt Metal and Pt-Au and Pt-Ir Alloys

M. SHIMIZU and A. KATSUKI, *J. Phys. Soc. Japan*, 1964, **19**, (7), 1135-1141.

The density of states curve of Pt metal was derived from low temperature specific heat measurements on Pt, Pt-Au and Pt-Ir alloys. Calculation then gave the electronic specific heat C_E and spin paramagnetic susceptibility of Pt and the alloys between 0 and 2000°K. Estimates for Pt gave the molecular field coefficient $\alpha=0.64\sim 0.74\times 10^4$ mole/e.m.u. and the orbital paramagnetic susceptibility $\chi_{orb}=0.13\sim 0.48\times 10^{-4}$ e.m.u./mole. Results confirmed that $C_E<\gamma(0)T$ at higher temperatures, where γ is the temperature coefficient of electronic specific heat.

Equiatomic Transition Metal Alloys of Manganese. I. The Tetragonal PtMn Phase

K. BRUN, A. KJEKSHUS and W. B. PEARSON, *Phil. Mag.*, 1964, **10**, (104), 291-299

CuAu I-type tetragonal PtMn has a and c axes with maximum and minimum size respectively, close to equiatomic composition because of the relative atomic sizes of Pt and Mn.

On the Structure of the Platinum-Silicon System

R. GOHLE and K. SCHUBERT, *Z. Metallkunde*, 1964, **55**, (9), 503-511

X-ray and microscopic studies of the Pt-Si system showed the phase transformations and equilibria of Pt₃Si, Pt₇Si₃, Pt₂Si, Pt₈Si₅ and PtSi. Structures are: Pt₃Si(r), Pt₃Ge-type; Pt₇Si(h₂), U₃Si-type; Pt₂Si(h), Fe₃P-type; Pt₈Si(r), tetragonally distorted CaF₂-type.

The Vapour Pressure of Palladium

P. D. ZAVITSANOV, *J. Phys. Chem.*, 1964, **68**, (10), 2899-2901

The vapour-pressure of Pd from 1537 to 1841°K is represented by $\log P_{atm}=5.99-18,898/T$. Its mean heat of sublimation at 298°K is 89.8 ± 0.9 kcal/mole and its normal boiling point is estimated as 3150 ± 100 °K.

Absorption of Hydrogen by Gold/Palladium Alloys

A. MAELAND and T. B. FLANAGAN, *Abs. Papers, 148th Meeting, Am. Chem. Soc.*, 1964, 12V-30

Absorption of H₂ by Au-Pd alloy wires from

H₂-stirred HCl solutions caused changes in the relative resistance R/R_0 and electrode potential of specimens. R/R_0 is related to the H/metal ratio. Tests at 25°C showed maxima in the relationship which shifted to smaller H/metal and R/R_0 values as Au content increased. The equilibrium amounts of absorbed H₂ at 1 atm., 25°C are: 5.7% Au-Pd, H/metal=0.55; 11.9%, 0.45; 18.8%, 0.33; 26.5%, 0.22; 35.1%, 0.12.

Effect of Temperature on the Lattice Parameters of Some Silver-Palladium Alloys

C. N. RAO and K. K. RAO, *Canad. J. Phys.*, 1964, **42**, (7), 1336-1342

63 and 80 wt.% Ag-Pd alloys showed a straight-line relationship between lattice parameters and temperature from room temperature to 790°C. Deviations from the straight line for 25, 39 and 50 wt.% Ag-Pd may be due to electronic structure changes.

The Influence of Annealing on the Electrical Properties of Cold-worked Ag-Pd Alloys

W. K. CHEN and M. E. NICHOLSON, *Acta Met.*, 1964, **12**, (6), 687-696

Annealing affects the resistivity, Hall constant, magnetic susceptibility and thermo-electric power of Ag-Pd alloys. The anomaly in the electrical resistivity change accompanying cold working in Ag-rich alloys is explained by a short-range order mechanism.

The Palladium-Tantalum System

E. M. SAVITSKII, V. P. POLYAKOVA, M. A. TYLKINA and G. S. BURKHANOV, *Zh. Neorg. Khim.*, 1964, **9**, (7), 1645-1649

Melting-point, microstructural, and X-ray studies of the Pd-Ta system showed the existence of four intermetallic compounds: Pd₃Ta, Pd₂Ta, PdTa and σ -phase. The constitution diagram indicates an eutectic between σ and PdTa at 68 wt.% Pd, 1720 ± 25 °C. PdTa has f.c. tetragonal structure with $a=3.28$, $c=6.00$ Å, $c/a=1.84$. Tetragonal Pd₃Ta has $a=3.87$, $c=7.94$ Å, $c/a=2.05$. σ -phase has $a=9.64$, $c=5.02$ Å, $c/a=0.522$. The system was compared with the Pd-V and Pd-Nb systems. (11 micrographs.)

Magnetic Properties of Dilute Alloys Based on Palladium with Some Transition Metals

J.-P. BURGER, *Ann. Physique*, 1964, **9**, (5-6), 345-372

Magnetic moments and interactions were measured for Pd diluted with small amounts of Fe, Co, Cr, Mn or Ni. For alloys saturated with H₂, paramagnetic Curie points are proportional

to the amount of dilution but magnetic moments are independent of it up to 10%. The polarisation of Pd atoms in non-hydrogenated alloys occurs in two stages. Electron transfer explains results for Pd-Cr and Pd-Mn. A molecular field model was derived to explain the mechanisms.

Magnetic Properties of the Pd₃Mn₂ Alloy

H. YAMAUCHI, *J. Phys. Soc. Japan*, 1964, **19**, (5), 652-657

X-ray, magnetic and thermal studies of Pd₃Mn₂ showed that the ζ-phase has b.c.t. lattice with CsCl-type superstructure and that this is modified in the μ-phase. Both phases are antiferromagnetic. Susceptibility of μ-phase below the 210°C Néel point depends strongly on field strength. Excess heat absorption at this point is 510 cal./mol. and is 890 cal./mol. (Pd_{1.5}Mn) for the ζ-phase. Heat of transformation (μ→ζ) is 180 cal./mol. (Pd_{0.6}Mn_{0.4}).

On the Interaction of Titanium with Iridium

V. N. EREMENKO, T. D. SHTEPA and M. M. CHURAKOV. *Dopovidi Akad. Nauk Ukr. R.S.R.*, 1964, (6), 763-766

1-55 at.% Ir-Ti alloys were studied by metallographic, X-ray and microhardness methods. Three intermediate phases were detected: γ-phase has Cr₃O-type structure with a = 5.00 kX; δ'-phase has CsCl-type structure with a = 3.10 kX; δ-phase has an undetermined structure. The three phases are based on or are modifications of TiIr.

Constitution Diagram and Some Physical Properties of Alloys of the Nickel-Ruthenium System

I. I. KORNILOV and K. P. MYASNIKOVA, *Izv. Akad. Nauk S.S.S.R., Metallurgiya i Gornoe Delo*, 1964, (4), 159-165

The Ru-Ni constitution diagram was built up from microstructural, X-ray and thermal analyses, together with tests of hardness, microhardness and specific resistivity. Crystallisation occurred peritectically at 1823 ± 10°C, when the mutual solubilities of Ru and Ni were 41 and 53 at.% respectively. Mutual solubility decreased at lower temperatures. Ru increased the cell size of Ni but Ni decreased a and c for Ru, although c/a remained constant.

A Constitution Diagram for the Niobium-Ruthenium System above 1100°C

G. F. HURLEY and J. H. BROPHY, *J. Less-Common Metals*, 1964, **7**, (4), 267-277

The Nb-Ru constitution diagram from solidus, metallographic, X-ray, and diffusion couple measurements shows a minimum m.p. at 39 at.% Ru, 1870°C, a maximum m.p. at 50 at.%, 1942°C, an eutectic between the terminal solid solutions at 65 at.% Ru, 1774°C, and an h.c.p. intermediate

phase formed peritectoidally at 75 at.% Ru, 1540°C. Maximum solubilities are 29 at.% Nb in Ru and 58 at.% Ru in Nb but at room temperature the b.c.c. terminal solid solution exists only up to 40 at.% Ru.

The Effect of Pressure on the Volume and Lattice Parameters of Ruthenium and Iron

R. L. CLENDENEN and H. G. DRICKAMER, *J. Phys. Chem. Solids*, 1964, **25**, (8), 865-868

Ru and Fe were subjected to 400 kbars pressure at 25°C. Ru has compressibility similar to Rh and Mo. c/a decreases slightly at lower pressures and then rises rapidly to the highest pressure.

Phase Equilibrium Diagram of the Chromium-Osmium System

V. N. SVECHNIKOV, G. P. DMITRIEVA, G. F. KOBZENKO and A. K. SHURIN, *Dokl. Akad. Nauk S.S.S.R.*, 1964, **158**, (3), 668-670.

The composition diagram of the Cr-Os system was built up from X-ray, metallographic and differential thermal analysis tests. Conditions for the formation of the intermetallic compounds Cr₂Os and Cr₃Os were derived. An eutectic reaction occurred at 33 at.% Os, 1840 ± 10°C. Os additions raised the hardness and lattice size of Cr. Hardnesses measures were: Cr₃Os, 600 kg/mm²; σ-phase, 1800-2000 kg/mm²; β-phase, 800 kg/mm².

The Total Emissivity of Rhenium, Rhodium, Palladium and Titanium

W. LANDESPERGER and D. STARK, *Z. Phys.*, 1964, **180**, (2), 178-183

Total emissivities of Re, Rh, Pd and Ti were determined between 1100°K and their m.p. The purity and surface of the wire specimens affected the results, which are compared with those of other workers.

Dispersion-hardening of Laminated Platinum Sheet

W. BETTERIDGE, *Powder Metallurgy*, 1964, **7**, (14), 142-151

Hardness and annealing characteristics were studied for laminated sheet produced from unalloyed Pt by stacking pieces of normal sheet, bonding them by hot forging, cold rolling them and repeating the process to obtain the required lamination thickness. Stress-rupture strength at 1450°C for 100 h life is maximum for ~1000 Å lamination thickness but is not increased by putting ThO₂ between the laminations.

CHEMICAL COMPOUNDS

Sulphospinelns Containing Rhodium

G. BLASSE and D. J. SCHIPPER, *J. Inorg. Nucl. Chem.*, 1964, **26**, (8), 1467-1468

CuRh₂S₄ has cell edge 9.72 Å. Similar com-

pounds containing Fe and Co instead of Cu were obtained in an impure state but X-ray studies detected complicated patterns with Mg, Mn, and Zn. CuRh_2S_4 showed a weak paramagnetism of about 320.10^{-6} e.m.u./g.mol. spinel which was nearly independent of temperature.

Crystal Chemistry and Some Magnetic Properties of Mixed Metal Oxides with Spinel Structure

G. BLASSE, *Philips Res. Rept. Suppl.*, 1964, (3), 139 pp.

The fifth chapter describes oxidic spinels containing Rh. Their formulae are $\text{NiFe}_{2-t}\text{Rh}_t\text{O}_4$, $\text{Li}_{0.6}\text{Fe}_{2.5-t}\text{Rh}_t\text{O}_4$, $\text{CoFe}_{2-t}\text{Rh}_t\text{O}_4$, and $\text{CuFe}_{2-t}\text{Rh}_t\text{O}_4$. Saturation moments, Curie temperatures and lattice parameters were determined for various values of t .

The Preparation of Rhodium (III) Halide Complexes with Tertiary Phosphines and Tertiary Arsines

J. CHATT, N. P. JOHNSON and B. L. SHAW, *J. Chem. Soc.*, 1964, (Aug.), 2508-2513

Mononuclear complexes of the type $[\text{RhX}_3(\text{MR}_3)_3]$, where X=halogen, MR_3 =phosphine or arsine, and binuclear halo-bridged complexes of types $[\text{Rh}_2\text{X}_6(\text{MR}_3)_3]$ and $[\text{Rh}_2\text{X}_6(\text{MR}_3)_2]$ have been prepared. Dipole-moment data are given and some of their reactions are described.

Co-ordination Compounds of Iridium (III) with Biguanide

S. P. GHOSH and A. I. P. SINHA, *J. Inorg. Nucl. Chem.*, 1964, 26, (10), 1703-1705

Trisbiguanidinium Ir (III) sulphate, chloride, nitrate, and thiosulphate were prepared. They are almost colourless, are diamagnetic and have octahedral structure with d^2sp^3 bonding. They are slightly more stable than the analogous Co and Rh complexes.

The Formation of Hydrido- and Carbonyl Complexes of Ruthenium by Reaction of Certain of its Complexes with Alcohols

J. CHATT, B. L. SHAW and A. E. FIELD, *J. Chem. Soc.*, 1964, (Sept.), 3466-3475

A mechanism is suggested for the reaction of RuCl_3 -tertiary phosphine complexes with alcohols to give very stable hydrido-carbonyl complexes of Ru, with degradation of the alcohol. CO reacts on the complexes to give new Ru carbonyl tertiary phosphine or arsine complexes. Br and I complexes were also prepared.

Further Investigations of RuC and OsC

C. P. KEMPTER, *J. Chem. Phys.*, 1964, 41, (5), 1515-1516

Syntheses using Ru:10C and Os:10C at 2600°C for 4 h produced WC-type phases of RuC and OsC, which were examined by spectrography, block diffraction and electron probe scanning.

Recent Investigations into the Structure of Noble-Metal Compounds

K. BRODERSEN, *Angew. Chem. Internat. Ed. Engl.*, 1964, 3, (7), 519

The monoclinic form of IrCl_3 forms platelets with $a=5.99$, $b=10.36$, $c=5.98$ Å, $\beta=109^\circ 27'$. PtCl_2 forms needle-like hexagonal prisms with rhombohedral unit cell of $a=8.09$ Å, $\alpha=108^\circ 15'$. The six Pt atoms are arranged octahedrally with twelve Cl atoms in front of the twelve edges of the Pt_6 octahedron. PtCl_2 has a structure with $\text{Pt}_6\text{Cl}_{12}$ complexes and weak metal-metal bonds.

ELECTROCHEMISTRY

X-ray Studies of Hydrogen-Silver-Palladium Electrodes

S. D. AXELROD and A. C. MAKRIDES, *J. Phys. Chem.*, 1964, 68, (8), 2154-2159

Ag-Pd alloys of up to 25 at.% Ag, when charged with H_2 , showed a potential plateau corresponding to the α - β transformation in the H-Pd system but no plateau was observed for 30 at.% Ag and the lattice expanded continuously. Lattice parameter-potential curves of H-Ag-Pd alloys with varying Ag content were coincident in general after β -phase formation despite differences in dissolved H_2 concentration. A model of the system shows dissolved H_2 as protons and the corresponding electrons entering the d-band of the alloy.

Absorption of Hydrogen by Silver-Palladium Alloys

A. C. MAKRIDES, *Ibid.*, 2160-2169

Ag affects absorption isotherms of H_2 on Ag-Pd electrodes by decreasing the pressure p_0 of the α - β transition as Ag content rises to about 25 at.%. No α - β transition occurs above 30 at.% Ag. Solubility of H_2 increases with Ag content for $p \leq p_0$ and heat of solubility at p_0 increases with Ag content. Maximum solubility for $p \gg p_0$ decreases with Ag content.

ELECTRODEPOSITION AND SURFACE COATINGS

Recent Developments Concerning Electrolytic or Chemical Deposits of the Platinum Group Metals

Traitements de Surface, 1964, 5, (42), 25-40

Small quantities of selenic acid added to the sulphate plating solution reduce stress cracking of Rh deposits. A method of stress measurement is described. Electrolytes based on the salts $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$, $\text{Na}_2\text{Pt}(\text{OH})_6$, and H_2PtCl_6 for Pt plating are compared. Pd electrolytes compared are $\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2$ and $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$. Ru and Ir are briefly discussed. Chemical plating of Pd, Pt, Rh, and Ru is described. Applications, particularly in electronics, are illustrated.

LABORATORY APPARATUS AND TECHNIQUE

An Afterheater for Use with High-temperature Vertical Crystal Pulling

J. D. RIDLEY and B. COCKAYNE, *J. Sci. Instrum.*, 1964, **41**, (10), 647

An afterheater above the melt in the Ir crucible reduces the temperature gradient, and hence the strain level, of laser single crystals. It consists of three concentric Al_2O_3 tubes in a jacket of MgO_2 , the innermost lined with Pt sheet, which is heated by induction coupling to the r.f. field, by infrared radiation from the crucible and by convection of gases from the melt. Melt temperatures up to 2000°C could be allowed if an Ir liner and other heating methods were used.

CATALYSIS

Hydrogenation of Olefins. Part I. Hydrogenation of Ethylene, Propylene and the *n*-Butenes over Alumina-supported Platinum and Iridium

G. C. BOND, J. J. PHILLIPSON, P. B. WELLS and J. M. WINTERBOTTOM, *Trans. Faraday Soc.*, 1964, **60**, (10), 1847-1864

Interactions of C_2H_4 and C_3H_6 with D_2 and of *l*- C_4H_8 , *cis*-2- C_4H_8 and *trans*-2- C_4H_8 with H_2 and D_2 over $\text{Pt}/\text{Al}_2\text{O}_3$ and $\text{Ir}/\text{Al}_2\text{O}_3$ from -20 to 150°C were studied in a static system. Only small amounts of deuterio-olefins and HD were obtained; P(deutero-olefins)/P(paraffins) was generally <0.1. Double-bond migration and *cis*-*trans* isomerisation rates were low compared to the hydrogenation rate. Relative rates of olefin exchange and isomerisation generally increased as $\text{P}_{\text{H}_2, \text{D}_2}/\text{P}_\text{O}$ decreased and as temperature increased. The low relative rate of olefin exchange was due to the virtual inability of an adsorbed C_2H_4 molecule to desorb and not to failure of C_2H_5 radicals to revert to adsorbed C_2H_4 .

Specific Rates and Competitive Rates of Hydrogenation of Cycloalkenes

A. S. HUSSEY, R. H. BAKER and G. W. KEULKS, *Abs. Papers, 148th Meeting, Anx. Chem. Soc.*, 1964, 60S-109

Rates at 25°C in the liquid phase on $\text{Pt}/\text{Al}_2\text{O}_3$ were determined. Catalysts can be prepared with very high activity, which is reproducible from batch to batch. Specific reaction rates (mole. min^{-1} .mole Pt^{-1} . atm^{-1}) ranged from 210 for bicyclo-[2,2,1]-heptene to 10 for cyclooctene.

Isomerisation of *n*-Pentane and *n*-Hexane on Platinum Supported on Borofluorinated Aluminium Oxide

R. I. IZMAILOV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1964, (9), 1713-1715

n-Pentane and *n*-hexane fractions separated from

Romashkin petroleum were isomerised over $\text{Pt}/\text{Al}_2\text{O}_3$, promoted by F and B, at 350°C. *n*-Hexane was 64% converted into *iso*-hexane with 0.91 selectivity. *n*-Pentane was 54% converted to isopentane with 0.94 selectivity. The apparent activation energy for the hexane isomerisation was 19 kcal/mole.

Change of Rate and Direction of Hydrogenolysis of Methylcyclopentane by High Temperature Treatment of Platinum-Alumina Catalyst with Hydrogen

I. I. LEVITSKII, M. G. GONIKBERG, KH. M. MINACHEV and V. I. BOGOMOLOV, *Dokl. Akad. Nauk S.S.S.R.*, 1964, **158**, (5), 1123-1126

High temperature treatment of $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst by H_2 eliminated O_2 and H_2O from it. After treatment at 350°C, the catalyst caused conversion of methylcyclopentane to *iso*-hexane but, after treatment at 550°C, *n*-hexane was the principal product.

Study of Atomic Platinum Dispersion on a Zeolite Support

J. A. RABO, P. E. PICKERT and V. SCHOMAKER, *Abs. Papers, 148th Meeting, Ann. Chem. Soc.*, 1964, 5U-9

$\frac{1}{2}$ % Pt/calcium Y zeolite prepared by cation exchange, pre-treated by heating to 350°C and reducing with H_2 at 300°C, was not poisoned by 10 p.p.m. thiophene but isomerised *n*- C_6H_{14} to produce > 14% of 2,2-dimethylbutane at 350°C. Zeolite impregnated with $\frac{1}{2}$ % Pt in anionic form from H_2PtCl_6 , and similarly pretreated was deactivated rapidly by 10 p.p.m. thiophene and 2,2-dimethylbutane output dropped to 7% in 24 h. The mechanism by which Pt becomes loaded on the catalyst in each case indicates atomic dispersion of Pt after cation exchange and a reduction in the tendency to poisoning by S compounds.

Reductive Amination of Acetone. III. Study of the Hydrogenation of Acetone-Isopropylamine Mixtures in Ethanol and Water

A. LE BRIS, G. LEFEBVRE and F. COUSSEMANT, *Bull. Soc. Chim. France*, 1964, (7), 1584-1600

Reductive amination of acetone by isopropylamine took place over 5% Pt/C at 29°C in ethanol in two stages; formation of an intermediate imine homogeneously and heterogeneous hydrogenation of this to diisopropylamine.

The Catalytic Oxidation of Methyl Alcohol and Formaldehyde in Aqueous Solutions

T. C. FRANKLIN and Y. C. CHIU, *Abs. Papers, 148th Meeting, Am. Chem. Soc.*, 1964, 40V-101

CH_3OH and HCHO were oxidised by O_2 in aqueous NaOH and H_2SO_4 solutions over platinised Pt. The catalyst area was measured by its H_2 -absorption. The oxidation rate for CH_3OH

was first order with respect both to CH_3OH and to Pt area. The rates per unit area were similar in both solutions indicating identical mechanisms. The rate of oxidation of HCHO was negligible but the application of a potential to the catalyst increased rates of oxidation for both CH_3OH and HCHO. The rate for HCHO was then first order with respect both to HCHO and to Pt area.

Kinetics of the Hydrogen Transfer Reaction of Cyclohexene on Palladium Powder

S. CARRA, P. BELTRAME and V. RAGIANI, *J. Catalysis*, 1964, **3**, (4), 353-362

Pd powder catalysed the disproportionation of cyclohexene to C_6H_{12} and C_6H_8 in tetrahydrofuran solution at 50-60°C. 1,3-Cyclohexadiene was more reactive under similar treatment and may be an intermediate in the cyclohexene disproportionation.

Kinetics and Mechanism of the Catalytic Oxidation of Ethylene in the Presence of Aqueous Solutions of Palladium and Copper Salts

K. I. MATVEEV, I. F. BUKHTOYAROV, N. N. SHUL'TS and O. A. EMEL'YANOVA, *Kinetika i Kataliz*, 1964, **5**, (4), 649-657

There are two mechanisms for oxidation of C_2H_4 to CH_3CHO in the presence of $\text{PdCl}_2/\text{CuCl}_2$ in aqueous solution via a complex of C_2H_4 and PdCl_2 . An equilibrium reaction with Cu(II) ions and subsequent irreversible reaction with OH^- has a higher rate of reaction than direct reaction with OH^- . On this basis, an empirical reaction relationship is derived which agrees well with results of the process.

Kinetics of the Oxidation of Ethylene by Aqueous Palladium (II) Chloride

P. M. HENRY, *J. Am. Chem. Soc.*, 1964, **86**, (16), 3246-3250

C_2H_4 oxidation to CH_3CHO in aqueous HClO_4 - NaClO_4 solution in the presence of PdCl_2 consisted of initial rapid C_2H_4 uptake followed by a slow reaction, first order in Pd (II) but inhibited by Cl^- , for which the rate expression, isotope effect, and reaction parameters were derived. A π -complex \rightarrow σ -complex mechanism is proposed.

Isomerisation and Hydrogenation of *n*-Paraffins on Palladium Catalysts

M. HARTWIG, *Bremstoff-Chem.*, 1964, **45**, (8), 234-239

70% of *n*-hexane was isomerised over $\text{Pd}/\text{Al}_2\text{O}_3$ - B_2O_3 and only 1% was cracked. 0.1% Pd gave the best yield of isohexane and Al_3O_3 - B_2O_3 was superior to ThO_2 , ZrO_2 , Al_2O_3 , and TiO_2 . Larger amounts of Pd reduced the temperature for isomerisation but increased the amount of cracking. 33.5% of C_{11} - C_{12} *n*-paraffins were isomerised at 300°C, 25 atm., H_2 :hydrocarbon = 4 : 1 without measurable formation of cracking products.

Catalytic Dehydrocyclisation of Diethyl Ether with the Formation of a Five-Membered Heterocyclic System

A. L. LIBERMAN, O. V. BRAGIN and T. V. VASINA, *Izv. Akad. Nauk. S.S.S.R., Ser. Khim.*, 1964, (7), 1352-1354

Tetrahydrofuran and its decomposition products were formed by the dehydrocyclisation of diethyl ether in the presence of 20 wt.% Pt, Pd, Ir, Os, or Rh/C at 250-300°C. Also observed was dehydrocyclisation of C_6 hydrocarbons and cyclisation of secondary amines into pyrrolidine.

Deuteration of Pyridine and the Azines with Heavy Water and Transition Metal Catalysts Prepared by Self-activation, Hydrogen, and Borohydride Reduction

G. E. CALF and J. L. GARNETT, *J. Catalysis*, 1964, **3**, (5), 461-463

Catalytic deuteration and tritiation of pyridine and diazines is recommended rather than radiation methods. Pt was most active of the metals tested: Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt. H_2 reduction or NaBH_4 reduction of oxide catalysts gave better results than with chloride catalysts. Self-activated PtO_2 is better than H_2PtCl_6 for reaction with pyridine.

On the Selectivity of Metallic Catalysts and Stereoselectivity of Platinum and Palladium Catalysts in the Reaction of Butadiene with Deuterium

Z. LESZCZYŃSKI and P. B. WELLS, *Przemysl Chem.*, 1964, **43**, (9), 508-515

Differences in the stereoselectivity of Pt and Pd catalysts for the reaction of butadiene-1,3 with D_2 were expressed by the *cis-trans* ratio of butene-2 isomers and the amount of D_2 in the isomers. Reaction mechanisms on the catalysts are the same. Differences in action depend on the *syn*- and *anti*-configurations of butadiene on the catalysts and on the importance of the reactions $\text{C}_4\text{X}_6 \rightleftharpoons \text{C}_4\text{X}_8 \rightleftharpoons \text{C}_4\text{X}_9$.

CATHODIC PROTECTION

Experimental Use of Platinised Titanium for Ground-Beds

J. R. WALTERS, *Corrosion Prevention & Control*, 1964, **11**, (10), 18-21

Platinised Ti mesh has been used as the anode connecting telecommunications cables to ground beds of coke breeze. Anodes have operated at 2A and at 5A since 1961 without corrosion of the platinised area. The mesh was platinised with 50 μ in. Pt. Tests on platinised Ti driven directly into the earth are in progress. Platinised Ti rods are used as ground electrodes for repeated submarine cables. Their construction and installation are described and they are in use over several routes with satisfactory performance.

TEMPERATURE MEASUREMENT

Thermocouples for Measurement of High Temperatures

B. I. STADNYK and G. V. SAMSONOV, *Teplofiz. Vysokikh Temp.*, 1964, 2, (4), 634-637

Thermocouple materials and sheaths are reviewed. Pt metal combinations are Pt: 10% Rh-Pt, 20% Rh-Pt: 40% Rh-Pt, 5% Rh-Pt: 20% Rh-Pt, 6% Rh-Pt: 30% Rh-Pt, Rh: 20% Rh-Pt, Rh: 30% Rh-Pt, Rh: 8% Re-Pt, Pt: Re, Ir: 40% Rh-Ir, and Ir: 60% Rh-Ir.

Results Obtained from Measurements on Platinum Resistance Thermometers at the Thermometry Section of the Kamerlingh Onnes Laboratorium, Leiden

H. VAN DIJK, *Physica*, 1964, 30, (8), 1498-1512

Tests on 27 Pt resistance thermometers at 1.5-4.3°K, 9-20.3°K and 54-90°K gave the temperature dependence of reduced resistance $\omega = R/R_0^{\circ}C$ for the range 1.5-90°K. Calibration at more than a few temperatures is needed, particularly for 4.2-10°K. $\omega = \omega_0 + AT^2 + BT^5$ for 1.5-4.2°K, where ω_0 , A and B varied accordingly to the origin and purity of the Pt.

NEW PATENTS

METALS AND ALLOYS

Palladium or Palladium Alloy Diffusion Tube for the Separation of Hydrogen from Gaseous Mixtures

JOHNSON, MATTHEY & CO LTD.
British Patent 966,122

A diffusion tube used for the separation of H₂ from gaseous mixtures made of pure Pd or 75 wt.% Pd-25 wt.% Ag alloy, is made more robust and its life is prolonged by the incorporation of stainless steel or Ni coil springs or metal or ceramic rods as stiffening members, which prevent flattening of the tube walls yet permit free passage of gas.

Rhodium-containing Magnetic Alloys

E. I. DU PONT DE NEMOURS & CO.
U.S. Patent 3,144,324

Ferromagnetic materials exhibiting very good saturation magnetisation values and high Curie temperatures comprise in at.% 0.8-1.2 Fe, 0.8-1.2 Rh and 0.01-0.20 of at least one metal of Group IIA atomic no. 4-12 or Group IIIA, IVA, VA or VIA atomic no. 13-83, e.g. Al, Mg, Ge, Si, Sb, S, Ga, etc. See also 3,144,325.

Gold-Platinum Spinneret Alloy

DEUTSCHE GOLD- UND SILBER-SCHNEIDANSTALT
German Patent 1,175,886

The material used for spinnerets, especially for viscose, is unhardened and homogeneous and consists of 68-88% Au and 12-32% Pt. See also 1,177,350.

Easily Worked Ruthenium

INTERNATIONAL NICKEL CO. (MOND) LTD.
German Patent 1,177,349

Ru which is easily formed is obtained by melting Ru in the presence of one or more of the metals Zn, Cd, Bi, Ti, Ge, Ba, Hf, Ce, Er, Gd, Hm, La, Pr, Sm, Yb and Y. Zn is preferred.

Gold Alloy Coatings on Wire

SIEMENS & HALSKE A.G. *German Patent* 1,178,273
Very thin Mo and W wires for electrical discharge devices may be successfully coated with an Au alloy by using an alloy of Au with 3-30 wt.% Pt and at least 3% Ni or Fe.

ELECTROCHEMISTRY

Platinum Group Metal Coated Electrode for Electrochemical Processes

DEUTSCHE GOLD- UND SILBER-SCHNEIDANSTALT
British Patent 965,958

An electrode particularly suitable for alkali-metal chloride electrolysis consists of a large flat area formed by many separate elements, each of which consists of a Cu core surrounded by a layer of Ti coated with a Pt group metal.

Electrolytic Production of Hydrogen

JOHNSON, MATTHEY & CO. LTD.
British Patent 973,810

Extremely pure H₂ is produced efficiently by electrolysis using 1% H₂SO₄ solution as electrolyte and a membrane, diaphragm or tube cathode made of an alloy containing 5-30 wt.% Ag and the balance Pd.

Method of Separating Hydrogen Isotopes

JOHNSON, MATTHEY & CO. LTD.
British Patent 973,820

H isotopes for the manufacture of deuterium as "heavy water" are separated by electrolysis or by electrolytic migration using a membrane, diaphragm or tube diffusion element made of an alloy containing 5-30 wt.% Ag and the balance Pd.

Palladium and its Alloys in the Manufacture of Platinised Noble Metal Electrodes

INSTITUT FRANCAIS DU PETROLE, DES CARBURANTS ET LUBRIFIANTS. *French Patent* 1,354,801
Platinised electrodes of improved activity are