

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Diffusion of Hydrogen in Palladium

P. A. SILBERG and C. H. BACHMAN, *J. Chem. Physics*, 1958, **29**, (Oct.), 777-781

The diffusion is studied between 200 and 600°C and 10-70 cm Hg using 5, 10 and 20 mil thicknesses of Pd. Commercial grade, dried hydrogen was used. $\log_e Q$ (Q = diffusion rate) is plotted against $10^4/T^\circ K$ and against $P^{1/2}$ (P = hydrogen pressure) for the different Pd thicknesses. The diffusion rate is approximately independent of Pd thickness. The results obtained in the graphs cannot be explained in terms of existing theory.

Rate of Permeation and Diffusion Coefficient of Hydrogen through Palladium

G. TODA, *J. Res. Inst. Catalysis*, 1958, **6**, (1), 13-19

The permeation of hydrogen at different pressures through a 0.3mm diameter Pd wire towards vacuum was investigated. The diffusion coefficient was also determined. The permeation rate is found to be proportional to $P^{1/2}$ and is not perceptibly affected by surface contamination. It thus appears that diffusion controls the rate of permeation.

Results of Low Temperature Studies, XXI—Atomic and Electronic Heat of Ruthenium between 10 and 273°K

K. CLUSIUS and U. PIESBERGEN, *Z. Naturforschung*, 1959, **14a**, (1), 23-27

Below 22°K the atomic heat is the sum of the lattice heat C_g , dependent on T^3 , and the electronic heat, C_e , which is a function of T : C_v (Ru) = $464.5(T/505)^3 + 6.2 \times 10^{-4}T$. Above 100°K the electronic heat is characterised by a fall in the value of the characteristic temperature as observed with Ir and Rh.

The Gold-Silver-Platinum System

O. A. NOVIKOVA and A. A. RUDNITSKII, *Zhur. Neorg. Khim.*, 1958, **3**, 729-749. (*Chem. Abs.*, 1958, **52**, 19832e)

A systematic study of the system was made. A peritectic reaction resulting in the formation of a ternary α -solid solution rich in Au and Ag was observed by thermal analysis. The regions of α - and β -solid solution were determined. Three isothermal cross-sections (20, 600, 900° and annealed samples) were studied by the determination of micro-structure, hardness, tensile strength, expansion, electrical resistance and its tempera-

ture coefficient. The solubility limits of Pt in the ternary α -solid solution are established. The solubility of Au in Ag becomes very limited on introduction of Pt. The addition of 10% Pt results in a second phase, a β -solid solution, in alloys rich in Ag and Au. The addition of Ag to binary Au-Pt alloys reduces the area of α -solid solution and a considerable increase in Au concentration is required to increase the area for the α -phases of the Ag-rich alloys.

Thermodynamics of the Gold-Platinum System

R. J. WEISS and K. J. TAUER, *J. Phys. Chem. Solids*, 1958, **7**, (2/3), 249-251

The electronic, lattice and mixing components of the free-energy of the Au-Pt system are separated. The asymmetric segregation in this system can be ascribed to the filling of the d-band at about 30% Au. The value of the segregation potential is derived as ~ 6090 cal/mole.

Investigation of Platinum-Molybdenum Alloys

H. NISHIMURA, *Nippon Kinzoku Gakkai-Si*, 1958, **22**, (8), 425-428 (*In Japanese*)

The alloys were melted in an argon atmosphere, their melting points were determined and X-ray analyses and microscopic studies were carried out. An equilibrium diagram was constructed from the results. Three solid phases were found: a Pt-rich solid solution, α , an intermediate phase, β , corresponding to a Pt-Mo compound and the Mo-rich solid solution, γ . A peritectic reaction, liquid + $\beta \rightleftharpoons \alpha$, occurs on the Pt-rich side and a eutectic, liquid $\rightleftharpoons \beta + \gamma$, at about 58% Mo and 2100°C. The electric resistivity of the Pt-rich alloys and the thermo e.m.f.s of Mo-Pt alloys against Pt were measured. The resistivity of alloys containing up to 7% Mo increases linearly with addition of Mo. The thermo e.m.f. of alloys containing up to 5% Mo shows a maximum e.m.f. against Pt at the 3.5% Mo alloy.

Electrode Potentials and Compound Formation in the Palladium-Platinum-Hydrogen System

A. W. CARSON, T. B. FLANAGAN and F. A. LEWIS, *Nature*, 1959, **183**, (Jan. 3), 39-40

The electrode potentials and electrical resistances of Pd wires containing 5, 10, 20 and 25% Pt were measured while absorbing hydrogen from 2N H_2SO_4 solutions. For alloys with up to 20% Pt the plot of relative resistance against electrode

potential is similar to that for the Pd-H system. The results indicate that a two-phase region analogous to β -Pd-H will only occur with alloys containing <25% Pt. Hence alloys with 25-35% Pt, which have an appreciable solubility for H, but which do not form a β -phase, may be preferred to pure Pd for osmosis tubes.

Magnetic Investigations on Solid Solutions of Palladium with Transition Elements

D. GERSTENBERG, *Ann. Physik*, 1958, 2, (5/6), 236-262

Measurements of magnetic susceptibility were carried out on solid solutions of Pd with Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Nb, Mo, Ta, W and Re in the temperature range 90-1100°K. The elements Ti, V, Zr, Nb, Mo, Ta, W, Cr, and Re lower the paramagnetism of Pd by filling its 4d electron band. Mn, Fe, Co and Ni increase the paramagnetism of Pd. For the Pd-Fe, -Co and -Ni systems the measurements were extended to the low temperature ferromagnetic region. In the Pd-Ti system the paramagnetism decreases until at the solubility limit at 25at.%Ti the alloys are diamagnetic. A similar behaviour is observed with the Pd-V system. The results are interpreted on the basis of the collective electron theory of metals.

The Binary System Palladium-Vanadium

W. KÖSTER and W.-D. HAEHL, *Z. Metallkunde*, 1958, 49, (12), 647-649

The system was investigated by thermal analysis, microscopic and X-ray studies and by magnetic and dilatometric measurements. A phase-diagram is constructed from the results. A eutectic is formed at about 60at.%V and at 1340°C. The melting point of Pd is lowered sharply by additions of up to 20% V—further additions have less effect. The miscibility gap between γ -Pd solid solution and α -V solid solution broadens as the temperature decreases. At 840°C the compound PdV₃ is formed by peritectoid reaction. It has a β -W structure and is extremely brittle. In the range of homogeneous Pd solid solution the superstructures Pd₃V and Pd₂V, both with f.c. tetragonal lattices, are formed below 815 and 905°C respectively.

Use of Ruthenium Tetroxide as a Multi-Purpose Oxidant

L. M. BERKOWITZ and P. N. RYLANDER, *J. Amer. Chem. Soc.*, 1958, 80, (Dec. 20), 6682-6684

Ruthenium tetroxide is proposed as an alternative to the more volatile and toxic OsO₄ as an oxidant for organic compounds. It is used in either CCl₄ or alcohol-free CHCl₃ solution. Primary and secondary alcohols are oxidised by RuO₄ to aldehydes or acids and ketones respectively. Aldehydes are oxidised rapidly to acids. Olefinic bonds are cleaved by RuO₄, not hydroxylated as with OsO₄. Ethers are oxidised to esters and

amides to imides. The oxidation of aromatic rings and amines give no identifiable products.

The Bismuth-Rhodium System

G. S. ZHDANOV, N. N. ZHURAVLEV and R. N. KUZ'MIN, *Zhur. Neorg. Khim.*, 1958, 3, 750-755 (*Chem. Abs.*, 1958, 52, 19829d)

The alloys were studied by thermal and microscopic analysis in the region of the compounds Bi₄Rh and Bi₂Rh. Crystals of β -Bi₄Rh and α -Bi₂Rh were prepared and subjected to X-ray analysis. β -Bi₄Rh crystallises in the rhombic system and α -Bi₂Rh in the monoclinic system.

ELECTROCHEMISTRY

Alternating-Current Electrolysis, III—Coarsening of Bright Platinum Electrode by Alternating-Current Electrolysis

S. SHIBATA, *Nippon Kagaku Zasshi*, 1958, 79, 239-243 (*In Japanese*). (*Chem. Abs.*, 1958, 52, 19604d)

The influence of current density on the coarsening of Pt electrodes in the electrolysis of 1N H₂SO₄ by a 50 cycle A.C. was studied. The coarsening predominates for currents above 60 mA/sq. cm when the electrolyte is saturated with oxygen or air, or 85 mA/sq. cm when saturated with hydrogen.

Transport of Hydrogen through Palladium-Clad Electrodes

S. SCHULDINER and J. P. HOARE, *Canad. J. Chem.*, 1959, 37, (1), 228-237

Electrochemical polarisation studies on the transport of hydrogen atoms and protons through Pd, Pt and Pd-clad Pt, Au, Ni and Fe electrodes in 2N H₂SO₄ were conducted. Transport of hydrogen atoms occurred only for Pd and Pd-clad Fe. Protons migrate through Pt when it is sandwiched between Pd, but no transfer of hydrogen atoms occurs. Transport of hydrogen in any form through Au and Ni was not detected.

Advances in Non-Consumable Anodes—Development of Titanium/Platinum

ANON., *Corrosion Technol.*, 1959, 6, (2), 49, 62

Considerable work has been carried out on the possible use of Ti/Pt anodes instead of graphite anodes in the electrolysis of brine to NaOH and Cl₂. The Ti/Pt anodes have the following advantages: maintenance of anode-cathode gap due to absence of erosion or corrosion, high oxygen and low chlorine overvoltage and elimination of contaminants. Favourable results have also been obtained in tests on Ti/Pt anodes in cathodic protection and the purification of water by electro-dialysis. Other possible uses include sodium hypochlorite manufacture, electro-descaling and galvanising, colloid separation (electrophoresis) and in Rh plating equipment.

Electrode Potentials of the Palladium-Hydrogen System

T. B. FLANAGAN and F. A. LEWIS, *J. Chem. Physics*, 1958, **29**, (Dec.), 1417-1418

The Pd specimen was immersed in 2N H₂SO₄ and charged with hydrogen electrolytically and by gas bubbling. Its resistance change and electrode potential against Pt were measured. When gas-charged the potential falls continuously to zero on absorbing hydrogen up to 0.69 H/Pd; when electrolytically-charged the potential rises to a maximum before falling to zero. These differences may be due to the presence of oxidising components. No evidence for a difference in free-energy was found.

The Mechanism of the Joint Electrochemical Formation of Ozone, Persulphuric Acid and Oxygen on the Platinum Electrode

A. A. RAKOV, V. I. VESELOVSKII, K. I. NOSOVA, E. V. KASATKIN and T. I. BORISOVA, *Zhur. Fiz. Khim.*, 1958, **32**, (12), 2702-2710

The anodic process in electrolysis of 10N H₂SO₄ on a Pt electrode consists of three stages. The first stage, 0.1-1.8V, gives oxygen evolution and Pt oxidation, in the second mainly persulphuric acid (H₂S₂O₈) and oxygen are formed, and in the third, 5.5-7.0V, mainly ozone and oxygen. These three stages correspond to different states of the electrode surface and involve surface compounds of Pt.

ELECTRODEPOSITION

The Role of Rhodium in the Battle against Corrosion

R. LEVY, *Corrosion et Anticorrosion*, 1958, **6**, (12), 463-466

Rhodium plating is used both decoratively and in industry. Decorative or "brilliant" Rh plating, used in the jewellery trade to protect Ag, corresponds to layers <0.5μ thick. For industrial uses layers >1μ are required. The method of plating and properties of the deposit are briefly described.

Bright and Thick Rhodium Deposits

R. LEVY, *Werkstoffe u. Korrosion*, 1958, **9**, (11), 686-689

The difficulties experienced in attempting to plate Rh deposits that are both thick and bright are discussed. The effect of various additives was determined. A sulphate bath was used containing 10g/l Rh and operating at a temperature of 35-40°C and a current density of 1A/sq.dm. The addition of metallic ions to the bath gave no significant improvement in the deposits obtained. The addition of non-ionogenic wetting agents seems to be promising. The results obtained were sometimes contradictory but additions of 1:10,000 parts of a 40 molecule polymer of castor oil resulted in bright Rh deposits of up to 2μ thick.

Testing Rhodium Baths in the Hull Cell

S. DORNER and M. FROELS, *Metallwareind.*, 1958, **49**, (12), 539-543

The effect on Rh deposits of additions of organic wetting agents such as those found in modern detergents and of certain brightening agents was investigated. A normal Rh plating bath was used, but with the Rh concentration reduced from 2.5g/l to 1.8g/l. The following additions were made: a commercial detergent, two non-ionogenic wetting agents, a cationic wetting agent and a brightening agent used in Ni baths. In all cases these additions either completely inhibited Rh deposition or caused deposition of dull, striated deposits. Because of the unfavourable effect of these additions it is important that Rh baths should be protected from contamination by detergents and by brightening agents from other plating baths.

LABORATORY APPARATUS AND TECHNIQUE

Palladium Film Dosimeter

H. M. CHILDERS, *Rev. Sci. Instruments*, 1958, **29**, (11), 1008-1010

The dosimeter consists of a film of PdO, coated with paraffin, on an insulating base. On irradiation the PdO is reduced to Pd by hydrogen evolved from the paraffin. This effect is measured by the large resistance decrease in the film. The instrument can be adapted for measuring irradiation doses from a few rads to several million rads by varying the quantities of hydrogenous material (paraffin) and PdO.

A High Temperature Recording Dilatometer

R. J. BEALS and J. H. LAUCHNER, *Amer. Ceram. Soc. Bull.*, 1958, **37**, (11), 486-488

Automatic recording equipment for dilatation studies up to 1300°C is discussed. A Pt wound furnace arranged to give a uniform temperature to the sample rod is used. One Pt/10%Rh-Pt thermocouple is connected to a programme controller which regulates the rate of temperature rise and another is connected to the centre of the sample. The dilatation is measured by the e.m.f. difference between two photovoltaic cells one of which has a shield between it and the light source, which is moved by dilatation of the sample. The dilatation curve is plotted automatically as a function of specimen temperature. Data are presented for some ceramic materials.

Effect of a Ceramic Coating on the Creep Behaviour of Some High-Temperature Alloys

J. R. CUTHILL, J. C. RICHMOND and N. J. TIGHE, *Amer. Ceram. Soc. Bull.*, 1959, **38**, (1), 4-12

Creep tests were conducted on uncoated and ceramic coated sheet-metal specimens of type

310 stainless steel and two commercial 80Ni-20Cr type alloys at 1800°, 1900° and 1975°F. Platinum-alloy wound furnaces were used for the creep tests; the windings surrounded the upper, middle and lower portions of the specimen in order to facilitate maintenance of uniform temperature. The creep extensometer attached to the gauge length of the specimen consisted of a Pt wire; temperature control was maintained by Pt/Rh-Pt thermocouples. The ceramic coatings were found to markedly decrease the creep or extension in most cases.

CATALYSIS

Catalysts in Action

G. A. MILLS, *Chem. in Canada*, 1958, **10**, (9), 39-48
A review embodying historical and theoretical sections, descriptions of typical catalytic processes, modes of action of catalysts and their selection and use.

Hyperbolic Law of Deactivation of a Platinum-Alumina Catalyst

J.-E. GERMAIN and R. MAUREL, *Compt. rend.*, 1958, **247**, (Nov. 24), 1854-1856

The activity of Pt-Al₂O₃ catalysts in the dehydrogenation of trimethyl-1,1,3-cyclohexane decreases hyperbolically with temperature. This is interpreted by the occurrence of a second order polymerisation reaction on the catalyst surface.

Fast and Slow Sorptions of Hydrogen on Evaporated Palladium Films

A. MATSUDA and T. NAKATA, *J. Res. Inst. Catalysis*, 1958, **6**, (1), 88-92

The initial rapid chemisorption and subsequent slow sorption of hydrogen on Pd were observed separately. Small amounts of hydrogen were introduced stepwise into the evacuated reaction vessel and the change in pressure with time recorded on an oscillograph. Isotherms of the slow and rapid sorption are plotted. The fast chemisorption tends to a saturation value with increasing pressure.

Action of Certain Heterogeneous Catalysts on the Oxidation of Ammonia in Aqueous Solution by Ozonised Oxygen

S. I. PAPKO, *J. Appl. Chem. U.S.S.R.*, 1957, **30**, (9), 1361-1365. (*English Transl. of Zhur. Priklad. Khim.*)

Ozone oxidises aqueous solutions of ammonia to ammonium nitrate. The effect of various catalysts, prepared by impregnating a Schott filter, on the rate of the reaction was studied. Tungstic anhydride, metallic Pt, Pd (prepared by reduction of PdCl₂ with H₂), Ir and Rh have some catalytic action. Increasing the reaction temperature from 25-75°C with a Pt catalyst increases the amount of NH₃ oxidised from 40.3-52.2%.

A Chromatographic Technique for Studying the Mechanism of Surface Catalysis

K. TAMARU, *Nature*, 1959, **183**, (Jan. 31), 319-320

The adsorption during a gaseous reaction is measured on a chromatographic column. One reactant is used as carrier gas, a small sample of the other reactant is introduced at the top of the catalyst charged column and its adsorption measured by its retention on the column. Experiments with various gases on a Pd catalyst are described.

Ferrimetric Determination of Phosphite: Catalysis by Palladium Chloride

G. G. RAO and G. SOMIDEVAMMA, *Z. anal. Chem.*, 1958, **164**, (4), 391-394 (*In English*)

Phosphite can be determined volumetrically through oxidation with Fe at 100°C if some PdCl₂ is added to the solution as catalyst.

Selective Oxidation of Hydrogen in Carbon Monoxide over Palladium Catalyst, Part I—Effect of Hydrogen Chloride

T. SATO and K. ISHIZUKA, *J. Res. Inst. Catalysis*, 1958, **6**, (1), 1-12

The activity of Pd-black and an alkali-free Pd catalyst, with and without additions of HCl was investigated in the oxidation of small amounts of H₂ in CO. The catalyst structure was studied by chemical analysis and electron diffraction. The gas stream used contained ~6% H₂, ~4% O₂ and ~90% CO. The addition of HCl to the catalysts increases their activity in H₂ oxidation and their selectivity. The Pd-black has a higher selectivity than the alkali-free Pd catalyst. In the presence of HCl the Pd surface is covered with PdCl₂ or adsorbed chlorine. Thus the oxidation of H₂ occurs effectively on a PdCl₂ or adsorbed chlorine surface.

Review of Recent USA Patents on Catalysts for the Petroleum Industry

H. HEINEMANN and H. SHALIT, *World Petroleum*, 1958, **29**, (Nov.), 90-94

Catalysts used in cracking, reforming and similar processes are reviewed.

Catalytic Reforming

N. J. EMMS, *Canad. J. Chem. Eng.*, 1958, **36**, (Dec.), 267-270

The process of catalytically reforming petroleum to high octane gasoline is described with particular reference to the Powerforming process. The basic chemistry of the process is given. The catalyst used in the Powerforming process is Pt-Al₂O₃. The operating conditions are: 300-600 p.s.i.g. pressure, 900-1000°F reactor inlet temperature, a 4000-6000 SCF/bbl recycle gas rate and 1-4 space velocity. The regeneration process is described. Typical feed stocks are low octane naphthas, boiling point 175-400°F. The reformate

is normally of 100 Research octane number clear. By combining the reformer with an aromatic extraction unit higher octane numbers can be obtained.

Octane Flexibility for D-X Sunray

J. H. MILLER, *Oil Gas J.*, 1959, **57**, (Jan. 5), 93-96
The following units have been installed at the Tulsa refinery of D-X Sunray Oil Co.: a 20,000 bbl/day Unifiner, 12,000 bbl/day Platformer, 1200 bbl/day LPG recovery unit, 2400 bbl/day butane isomerisation unit, 2500 bbl/day HF alkylation unit. The combination of these new installations with existing units will enable a wide range of octane number gasolines to be produced. Details are given of the operation of each unit and its relationship to other units.

The Synthesis of Benzene Derivatives from Petroleum

H. G. MCGRATH, *Chim. et Ind.*, 1958, **80**, (Nov.), 561-567

Describes the catalytic reforming and hydroforming processes. The relative efficiencies of Pt, Mo and Cr catalysts are compared with respect to the nature of the starting materials and the yield of benzene. Pt catalysts are always used when high octane rating is the prime object, but for special cases, e.g. benzene and toluene synthesis, Mo-Al₂O₃ and Cr-Al₂O₃ catalysts are used.

Comparative Evaluation of Catalytic Properties of Platinum under Conditions of Aromatisation of Gasoline at Atmospheric and Elevated Hydrogen Pressure

Kh. M. MINACHEV, N. I. SHUIKIN and V. L. VINOGRADOV, *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, 1958, 866-869 (*Chem. Abs.*, 1958, **52**, 21016d)

Comparison of 0.8% Pt-C and 4% Pt-C catalysts showed the former to be more active and stable for aromatisation of gasoline from Volga-Ural petroleum. The reaction was conducted under a hydrogen pressure of 20 atm at 460°. The atm pressure reaction is much less efficient.

The Oxidation of Alcohols with Platinum and Oxygen, II—Investigation of the Initial Step with the help of ¹⁸O

M. ROTTENBERG and M. THÜRKAUF, *Helv. Chim. Acta*, 1959, **42**, (1), 226-231

The tracer experiments showed no incorporation of ¹⁸O from the H₂¹⁸O medium into either ethanol or 2-propanol when these are treated with oxygen and a Pt catalyst for extended periods of time. This demonstrates that the Pt catalysed reaction of alcohols with oxygen does not involve reversible dehydrogenation as the initial step and therefore must proceed by some form of autoxidation.

Positional Isomers Formed During the Hydrogenation of Methyl Linoleate under Various Conditions

E. R. COUSINS, W. A. GUICE and R. O. FEUGE, *J. Amer. Oil Chem. Soc.*, 1959, **36**, (1), 24-28

The hydrogenation was carried out using Ni, sulphur-poisoned Ni, 10% Pd-C and PtO₂ catalysts at temperatures of 30-200°C and catalyst concentration 0.1-0.4%. The products were analysed for content of *trans* isomer and positions of residual double bonds. With all the catalysts the greatest double bond concentration occurs in the 10 position except at low temperatures where most occur in the 9 and 12 positions. Pt and Pd catalysts gave higher proportions of *trans* isomer than did the Ni.

Stereochemistry of the Catalytic Hydrogenation of Some Bicyclic- α , β -Unsaturated Ketones

R. L. AUGUSTINE, *J. Org. Chem.*, 1958, **23**, (12), 1853-1856

The hydrogenation of $\Delta^1,^8$ -octalone-2 in ethanol using 10% Pd-C, 30% Pd-C, PtO₂ and 2%Pd-SrCO₃ catalysts resulted in a mixture of *cis* and *trans* isomers. Addition of a little dilute HCl gave a product containing almost exclusively the *cis* isomer (93%). The hydrogenation behaviour of $\Delta^4,^5$ -hexahydroisoquinoline-6 is similar but addition of acid only increases the amount of *cis* isomer to 85%.

Hydrogenation of Fat using a Palladium Catalyst, II—Hydrogenation of Whale Oil

M. ZAJCEW, *Fette-Seifen Anstrichmittel*, 1958, **60**, (11), 1051-1052

The hydrogenations were carried out at 175°C and about 1 atm pressure, in a stainless-steel vessel using a Ni catalyst dispersed in solid fat (25% Ni) and 1, 2 and 5% Pd-active charcoal catalysts. The whale oil used as starting material had an iodine number of 111, free fatty acid 0.08% and a peroxide number of 4. Special treatment was required for the sulphur compounds present to prevent them poisoning the catalyst. For hydrogenations to form 'hard' fat, I.N. 33-35, both catalysts give similar products. In hydrogenations to 'soft' fat, I.N. 73-79 (e.g. winter margarine) however, the product obtained using the Pd catalysts is much superior. It is more oxidation resistant and has a better consistency than the product obtained using a Ni catalyst.

Competitive Reductive o-Debenzylation of Ethers and Esters

W. E. CONRAD and S. M. DEC, *J. Org. Chem.*, 1958, **23**, (11), 1700-1702

Benzyl groups are valuable as protective groups in complex syntheses. It is often useful to be able to remove such groups one at a time and tests were carried out on selective reductive cleavage of

various benzyl groups in ether or ester linkages using Pd-C catalyst. With ethers the selectivity is never complete but more success was obtained with esters.

Hydrogenative Cyclisation of Azido Compounds

K. HOHENLOHE-OEHRINGEN, *Monatsh.*, 1958, **89**, (4/5), 557-569 and 597-602

The catalytic reduction of α -azidodiphenylacetonitrile, α -azidodiphenylacetic acid and some of its derivatives was investigated using a Pd-C catalyst. The acetonitrile gives the cyclic compound, 4-imino-5,5-diphenyldihydro-1,2,3-triazole, on reduction. The azido-acid does not cyclise and forms the amino-acid, but its ester, in alcoholic solution, gives the cyclic compound, 5,5-diphenyl-4-hydroxy-1,2,3-triazole. Cyclisation also occurs in other α -azido-carboxylic acid systems, but the yields are reduced.

Studies on the Formation and Reactions of 1-Pyrroline

D. W. FUHLHAGE and C. A. VANDERWERF, *J. Amer. Chem. Soc.*, 1958, **80**, (Dec. 5), 6249-6254

The vapour-phase dehydrogenation of pyrrolidine to pyrrole over 5% Pd-C catalyst formed 1-pyrroline as an intermediate. Hydrogenation of pyrrole over Rh-Al₂O₃ catalyst at room temperature gave 1-pyrroline in 31% yield which could be further hydrogenated to pyrrolidine. The behaviour of the pyrrole-pyrrolidine-hydrogen system in the presence of Pt metal catalysts is described by an equilibrium which includes 1-pyrroline as a stable intermediate.

Palladium Dehydrogenation of Methyl Reserpate and Yohimbine in Cymene

H. KANEKO, *J. Org. Chem.*, 1958, **23**, (12), 1970-1973

Dehydrogenation of methyl reserpate with Pd-C in boiling cymene gave 7-methoxyyobyrine and Py-tetradhydroreserpate acid lactone. Under similar conditions yohimbine gave Py-tetrahydroyohimbic acid or Py-tetradhydroyohimbine.

ELECTRONICS AND TELECOMMUNICATIONS

Thermionic Properties of Thorium Deposits on Control Grid Materials

J. A. CHAMPION, *Brit. J. Appl. Physics.*, 1959, **10**, (2), 71-74

Tests were carried out on various grid materials for transmitting valves in an attempt to reduce the grid emission caused by deposition of Th from thoriated W filaments. The materials tested were Pt, Pt₃Mo, Pt₂Mo, Pt₃Mo₂, Mo, Ti and W contaminated with a thin layer of Th. Emission at 1000°C from any of the Pt-Mo

phases is two or more orders of magnitude lower than from Mo. The lowest emission, $<0.7 \times 10^{-7}$ A/sq.cm, is given by the β -phase Pt₃Mo. The emission from Mo is 6.0×10^{-4} A/sq.cm. Grid emission from Pt-Mo is restricted by its lower work-function when covered with Th and in addition at temperatures above 1200-1300°C by the removal of Th from the surface either by solution into the Pt-Mo or by evaporation with the Pt. Emission from Ti grids when thoroughly precleaned is about 100 times less than for W. Titanium and Pt₃Mo could not be used at temperatures above 1000°C and are thus restricted to low-power valves. Other Pt-Mo grids should be applicable at higher temperatures for high-power valves.

TEMPERATURE MEASUREMENT

A Thermometer for High-Speed Aircraft

D. D. CLARK, *J. Sci. Instruments*, 1958, **35**, (12), 433-439

The principles of aircraft thermometer design are reviewed. A flat-plate thermometer with a conical head has many advantages in high-speed flight. The sensitive element is a 50 s.w.g. Pt resistance wire wound on an anodised Al former, enclosed in a resin-bonded paper body. The results of wind-tunnel tests are discussed. The lag and radiation errors are calculated, the latter are reduced by enclosing the temperature element in a highly-reflecting outer-cover. The thermometer is suitable for sub- and super-sonic speeds. It has a high constancy of recovery factor for Mach numbers 0.2-0.9 and a rapid response to temperature changes.

Review of High-Temperature Immersion Thermal Sensing Devices for In-Flight Engine Control

V. D. SANDERS, *Rev. Sci. Instruments*, 1958, **29**, (11), 917-928

Pneumatic probes and high temperature thermocouples are compared for the thermal monitoring and control of modern aircraft propulsion units. The temperature range required is 2000-4000°F and a fast response rate is desirable. The pneumatic probe has a high upper temperature limit and fast response rate but is rendered inaccurate by particles in the gas stream blocking the constrictions. Typical performances and thermoelectric behaviour of 20 metallic thermocouples calibrated above the melting point of Pt are discussed. Special emphasis is given to Pt-Rh combinations and to couples in which one limb is of W, i.e. W-Mo, W-Re and W-Ir. Among other couples discussed are: Rh/8%Re-Pt, Ir/10%Ru-Ir, Ir/40-60%Ir-Rh and Ir/30%Ir-Re. The properties of all the thermocouples mentioned are compared by means of a chart.

A review of refractory oxides suitable for the protection of thermocouples under the conditions of this application is given.

Temperature Error Associated with Imbedded Thermocouples

A. R. THOMAS, B. SCHURIN and J. C. MORRIS, *Rev. Sci. Instruments*, 1958, **29**, (11), 1045-1046

The error in surface temperature of a thin plate in a vacuum as measured by an embedded Pt/10%Rh-Pt thermocouple is investigated experimentally and theoretically.

Immersion Thermocouple Practice

H. V. SCHUBERT, *Iron Steel Eng.*, 1959, **36**, (1), 91-97

A detailed description is given of the basic design, construction, application and maintenance of an immersion thermocouple assembly. The subjects are dealt with from a purely practical viewpoint. Full details are given for taking a temperature reading and analysing whether or not the result obtained is acceptable. Great importance is attached to thermocouple maintenance and details are given for checking the couple together with probable causes of any defects.

NEW PATENTS

Manufacture of Sulphanilamide

F. HOFFMANN-LA ROCHE & CO. A.G. *British Patent* 804,036

A noble metal hydrogenation catalyst is used in a process for the manufacture of 5-sulphanilamido-3,4-dimethyl-isoxazole by reduction of P, P¹ [bis [3,4-dimethyl-isoxazolyl-(5)]-amino-sulphonyl]-azobenzene in a highly acidic liquid medium. The catalyst may be Pd-C or PtO₂.

Uranium Compounds

UNITED KINGDOM ATOMIC ENERGY AUTHORITY
British Patent 804,062

Uranium salts of deuterated higher aliphatic acids are made by treating a uranium salt of a higher aliphatic acid with deuterium in the presence of a hydrogenation catalyst, e.g. Pt.

Alloy

ENGELHARD INDUSTRIES INC. *British Patent* 804,404

A high resistivity high strength alloy suitable for electric resistance wires consists of 20-62% Pd (preferably 30-50%), 28-70% Au and more than 5% up to 18% Fe (preferably 7-12%). The resistivity of the heat-aged alloy is 450-1200 ohms/mil foot. Pt or Rh (up to 10%) may be included.

New Indole Derivatives

SOC. DES USINES CHIMIQUES RHONE-POULENC
British Patent 804,786

Adam's PtO₂ is used as catalyst in a process involving catalytic hydrogenation for the manufacture of specified indole derivatives.

Catalysts

F. HOFFMANN-LA ROCHE & CO. A.G. *British Patent* 804,788

A catalyst is composed of Pd sponge deposited on a substrate of a mixture of Zn(OH)₂ and Fe(OH)₃ and/or ZnCO₃ and FeCO₃ in the ratio

2-9 gram atoms of Pd to 1 of Zn and 1 of Fe. The catalyst is made by treating an aqueous solution of the component ions with an alkaline material and a reducing agent.

Production of Motor Gasoline

THE BRITISH PETROLEUM CO. LTD. *British Patent* 805,045

A high octane gasoline is made by thermally reforming a mixture of a light straight-run gasoline and a "platinum reformat".

Purification of Benzene

THE BRITISH PETROLEUM CO. LTD. *British Patent* 805,050

Benzene is separated from mixtures of benzene and non-aromatic hydrocarbons which form azeotropes with the benzene by catalytically reforming the mixture in the presence of hydrogen at 850-1050°F and pressure of 50 to 1000 p.s.i.g. followed by fractional distillation of the product to obtain a benzene fraction. A Pt-Al₂O₃ catalyst is used.

Preparation of Hydrogen Peroxide

COLUMBIA-SOUTHERN CHEMICAL CORP. *British Patent* 805,101

Hydrogen peroxide is prepared by successively hydrogenating a quinone in a solvent medium and in the presence of a catalyst, e.g. Pd-Al₂O₃, oxidising the product to regenerate the quinone and generate H₂O₂, extracting the peroxide at a temperature below the hydrogenation temperature and heating the solvent from the extraction to the hydrogenation temperature.

Hydroforming of Naphthas

ESSO RESEARCH & ENGINEERING CO. *British Patent* 805,111

A gasoline fraction is produced by hydroforming a naphtha fraction in the presence of hydrogen