

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Platinum Expansion Values for Thermal Calibration of High-temperature X-ray Diffraction Cameras and Diffractometers

W. J. CAMPBELL, *U.S. Bur. Mines Inf. Circular 8107*, 1962, 9 pp.

Linear expansion values for Pt are tabulated at 2°C intervals from 26°C to 1700°C from the relation:

$$\text{expansion per cent} = [8.91 + 1.28 \times 10^{-3}(t - 25) + 0.04 \times 10^{-6}(t - 25)^2] \frac{t - 25}{10^4}$$

where t is the temperature in °C. These values are used in the thermal calibration of X-ray cameras and diffractometers. The technique for the use of Pt as an internal standard for measurements with these instruments is described.

Thermal Conductivity and Expansion of Two Platinum Alloys

W. T. ENGELKE and C. D. PEARS, *U.S. At. Energy Com. Rept. UCRL 13061*, 1962, 39 pp.

The thermal conductivity from 500 to 2500°F and the thermal expansion from 1900 to 2500°F were determined for 5% Ru-Pt and 40% Rh-Pt. Apparatus used included novel radial heat flow and graphite dilatometer equipment. The thermal conductivity of 5% Ru-Pt decreased gradually from 450 to 350 Btu/hr/ft²/°F/in. over the range and that of 40% Rh-Pt decreased from 960 to 680 over the same range. The coefficient of thermal expansion at 2000°F of 5% Ru-Pt was 4.75×10^{-6} in./in./°F and of 40% Rh-Pt was 6.3×10^{-6} in./in./°F. The expansions were both about 10% lower than those of pure Pt. The grain size of both alloys increased about three times between 1800 and 2500°F.

On the Magnetism of the Platinum-Manganese Alloys and Their Oxide Phases

T. YOKOYAMA and M. WUTTIG, *Z. Metallkunde*, 1963, 54, (5), 308-311

Studies of the Pt-Mn system showed the existence of a phase containing about 38 at.% Mn. This was less ferromagnetic than Pt₃Mn and had a Curie temperature of about 350°C and a magnetic saturation of about $3000 \cdot 10^{-4}$ Vs/m². The β' and γ' phases were paramagnetic but the β' phase could become ferromagnetic by oxidation. It reached maximum magnetisation when it was Pt₂Mn₃O. Anomalies in susceptibility and thermal expansion existed for the γ' phase between 60 and 280°C which were greatest for PtMn₃.

The Pt-Te System

M. L. GIMPL, C. E. NELSON and N. FUSCHILLO, *Am. Soc. Metals Trans. Q.*, 1963, 56, (2), 209-213

The Pt-Te phase diagram was plotted from results of thermal, microscopic and X-ray diffraction methods. A eutectic occurred at 32.2 at.% Te and 860°C. PtTe formed peritectically at 920°C. Its resistivity was 2.07×10^{-5} ohm-cm and its density was 10.39 g/cm³ at 20°C. PtTe₂ began to decompose at 1020°C in vacuo and melted congruently at 1125°C under a partial pressure of Te. Its resistivity was 3.85×10^{-5} ohm-cm and its density was 6.28 g/cm³ at 20°C. No other compounds were detected.

The Magnetic Susceptibilities of Palladium and Palladium-Rhodium Alloys from 1.85 to 293°K

A. J. MANUEL and J. M. P. ST. QUINTON, *Proc. Roy. Soc.*, 1963, 273, 1354A, 412-426

The high susceptibilities of Pd-rich Rh-Pd alloys at low temperatures were shown by comparison of nominally pure Pd samples to be due to supermagnetism caused by impurities acting as carriers with moments of the order of 9 Bohr magnetons. The alloys contained between 1.04% and 9.97% Rh and 18.42% Rh. Corrections eliminated impurity effects from susceptibility measurements which were then extrapolated to give the values at 0°K. Variations of Stoner's exchange parameter with composition were deduced and showed that the Pd density of states curve has its peak closer to the Fermi level for Pd than thought previously.

On Some Electrical and Mechanical Properties of Binary Alloys of Palladium. I. Palladium Alloys with Elements of the Second Long Period

G. ZWINGMANN, *Z. Metallkunde*, 1963, 54, (5), 286-292

Alloys of Pd with Sr, Y, Zr, Nb, Mo, Ru, Rh, Ag, Cd, In, Sn, Sb and Te were tested for their electrical resistivity, thermoelectric properties, Vickers hardness and tensile strength. Resistivity, hardness and strength all increased with higher amounts of alloyed material but the temperature coefficient of resistivity decreased in all cases. The thermoelectric properties exhibited no uniform behaviour. These properties were all plotted as functions of composition and atomic number. For elements from Ag to Te, the atomic increase in resistivity $\Delta\zeta/a$ and decrease in temperature coefficient $\Delta\alpha/a$ can be expressed by $\Delta\zeta/a = A + B(Z - 1)^2$, where A and B are constants and Z is

the number of valency electrons. The change of thermal e.m.f. can be expressed by $\Delta\varepsilon/a=A \cdot 1/B(Z-1)^3$.

Conductivity and Hall Constant. XXVI. The Crystalline Solid Solutions of Palladium with Platinum, Rhodium, Molybdenum and Vanadium

W. KÖSTER, W. GMÖHLING and D. HAGMANN, *Z. Metallkunde*, 1963, 54, (6), 325-330

Room temperature values of resistivity ρ , Hall constant R , absolute temperature coefficients $d\rho/dT$ and dR/dT and thermoelectric power E are tabulated for Pd solutions with additions of Pt, Rh, Mo or V. Graphs illustrate how these properties and susceptibility vary with the quantity of solute. For each solute the graphs are similar in shape, indicating how the properties depend on an exchange of electrons between the solute atoms and the Pd conductivity bands. All additions to Pd change the sign of dR/dT but comparison with Au-Pd alloys shows that this is not necessarily due to the presence of two conductivity bands in Pd.

An Investigation of the Phase-Diagram Palladium-Arsenic in Connection with Superconductivity

C. J. RAUB and G. W. WEBB, *J. Less-Common Metals*, 1963, 5, (3), 271-277

The Pd-As system was studied by thermal, X-ray diffraction and metallographic methods. Pd_3As and $PdAs_2$ were known previously. This work detected Pd_5As_2 , Pd_7As and Pd_2As with another possible compound at higher As concentration. Eutectics occurred at 20 at.% As (715°C) and 40 at.% As (610°C). Pd_7As formed peritectically at 770°C and Pd_3As at 728°C. Pd_2As was hexagonal, with $a=6.65 \text{ \AA}$, $c=3.37 \text{ \AA}$ above 485°C and $a=9.79 \text{ \AA}$, $c=6.61 \text{ \AA}$ below 485°C. Pd_5As_2 melted congruently at 860°C. Three phases were superconducting; Pd_5As_2 ($T_c=0.46^\circ\text{K}$), Pd_7As high temperature modification ($T_c=1.71^\circ\text{K}$), Pd_2As low temperature modification ($T_c=0.60^\circ\text{K}$).

Investigation of the Wettability of Various Pure Metals and Alloys on Beryllium

R. G. GILLILAND, *U.S.A.E.C. Report ORNL-3438*, 1963, 96 pp.

The wetting of Be by Au, Ag, Cu, Al, 5% Be-Zr, 6% Be-Ti and 2.1% Be-Pd was studied. 2.1% Be-Pd drops wetted a Be block at 1030 and 1080°C in both vacuum and an Ar atmosphere. Metallographic studies of the Be-Pd system showed that Pd alloys very easily with Be.

Effect of Ruthenium on the Structure and Properties of Gold-Palladium Alloys

O. A. NOVIKOVA, *Tr. Inst. Met. im. A. A. Baikova, Akad. Nauk. S.S.S.R.*, 1962, (11), 148-154

Micrographic, mechanical and electrical studies

were carried out on Au-Pd alloys containing up to 60 wt.% Au with additions of up to 15 wt.% Ru. Photomicrographs illustrate the finer structure caused by adding Ru. The hardness of the alloys was increased and the plasticity was reduced, although mechanical working was not prevented. Ru also depressed the resistivity and temperature coefficient of resistivity of the alloys.

Study of Palladium-Ruthenium Alloys

O. A. NOVIKOVA, *Tr. Inst. Met. im. A. A. Baikova, Akad. Nauk S.S.S.R.*, 1962, (11), 155-163

The phase diagram of Ru-Pd alloys was determined for alloys with up to 30 wt.% Ru. A eutectic occurred with 12% Ru at 1520°C and below this temperature the alloys existed as a mixture of two solid solutions, depending on the temperature. The limit of solubility of Ru in Pd was less than 1%. Hardness increased and plasticity decreased as the Ru content rose to 15%. Ru raised the resistance of the alloys but the temperature coefficient of resistivity depended on the condition of the solid solutions. The thermal e.m.f. rose to a fairly steady value for Ru amounts in excess of 0.5%.

Influence of Hydrogen on Electric and Magnetic Properties of a Nickel-Palladium Alloy

J. J. VAN LOEF, *Philips Res. Repts.*, 1963, 18, (1), 71-74

46% Ni-Pd foils 0.1 mm thick were vacuum-annealed at 1000°C for several hours and then were charged electrolytically with H_2 at room temperature in 0.1 N H_2SO_4 + 50 mg/l As_2O_3 by 0.02 A/cm² for 2½ hours. Their resistance at 77°K rose by about 20% when H/Pd=0.6. The magnetisation decreased about 50% when H/Pd=0.45. The Curic temperature T_c was derived as $435 \pm 10^\circ\text{K}$ when H/Pd=0.45 with one Ni-Pd-H phase over the range 0°K- T_c °K. The magnetic properties were caused by one electron per H atom being added to the d shell of the Ni atom. Metallographic tests on the foils showed grain boundary cracking in the hydrogenated alloys.

Structural Data on Metallic Phases. VIII

K. SCHUBERT, K. FRANK, R. GOHLE, A. MALDONADO, H. G. MEISSNER, A. RAMAN and W. ROSSTEUSSCHER, *Naturwiss.*, 1963, 50, (2), 41

Crystalline structure types and lattice parameters are given for 28 metallic phases. Pt metals phases listed are VPt, MoPt, VPt_{23} , $Nb_{40}Pd_{80}$, $Pt_{75}Al_{15}Si_{10}$, $Pd_{84}Ge_{16}$, and Pd_2As .

The Niobium-Ruthenium Alloys

E. RAUB and W. FRITZSCHE, *Z. Metallkunde*, 1963, 54, (5), 317-319

Tabulated results of X-ray diffraction and microscopic studies of Nb-Ru alloys showed that the body-centred tetragonal phase for alloys containing between 41 and 46.5 at.% Ru is homogeneous

and that a face-centred rhombic structure exists between 47 and 58 at. % Ru. The mutual solubilities extend to 17 at. % Nb and 40 at. % Ru. A B2 superlattice similar to that in the V-Ru system exists for part of the Nb-Ru system.

Marcasite-Type Semiconductors

F. HULLIGER, *Nature*, 1963, **198**, (4885), 1081-1082
Lattice parameters of RuPAs, RuAs₂, RuAsSb, OsPAs and OsAs₂ were measured and tabulated. They, together with FeP₂, FeAs₂, FeSb₂, RuP₂, OsP₂, RuSb₂ and OsSb₂, all exhibit semi-conducting properties. Preliminary electrical and magnetic data of some of these Ru and Os marcasite-type compounds are listed. Ru⁴⁺ and Os⁴⁺ have an even number of *d* electrons and their compounds are diamagnetic. CrFeAs₄ is also semi-conducting, with $\theta_p = -30^\circ\text{K}$ and $C_m = 0.9^\circ\text{K cm}^3/\text{mol}$. Here it is assumed that Fe⁴⁺ is diamagnetic with two spins in the Cr⁴⁺ ion.

Absence of Antiferromagnetism in Palladium

S. C. ABRAHAMS, *J. Phys. Chem. Solids.*, 1963, **24**, (4), 589-590

Neutron diffraction techniques demonstrated the absence of antiferromagnetism in pure Pd and no magnetic scattering was detected in ferromagnetically contaminated Pd at 4.2°K. The preparation of the Pd crystals is described.

Third Spectrum of Palladium (Pd III)

A. G. SHENSTONE, *J. Res. Nat. Bur. Stds.*, 1963, **67A**, (2), 87-112

1,110 lines in the Pd (III) spectrum between 688 and 2991 Å are tabulated and identified.

CHEMICAL COMPOUNDS

Some Properties of Platinum Iodides

G. R. ARGUE and J. J. BANEWICZ, *J. Inorg. Nucl. Chem.*, 1963, **25**, (8) 923-925

PtI₂, PtI₃ and PtI₄ were prepared. Crystallographic studies showed that PtI₃ was cubic with $a = 11.3\text{Å}$. Magnetic susceptibility studies showed that PtI₂ was diamagnetic. The temperature dependence of the susceptibility of PtI₃ and PtI₄ was taken to indicate impurities. The bonding of all three compounds was thought to be covalent.

A General Synthesis of Tetraphenylcyclobutadiene-Metal Complexes by Ligand Transfer

P. M. MAITLIS and M. L. GAMES, *J. Am. Chem. Soc.*, 1963, **85**, (12), 1887-1888

The first examples of the conversion of one hydrocarbon-transition metal complex into another by direct ligand transfer and of reactions involving cyclobutadienes where the cyclobutadiene groups remained intact were those of tetraphenylcyclobutadiene Pd bromide with

Fe(CO)₅ or Ni(CO)₃ to give tetraphenylcyclobutadiene Fe(CO)₃ and tetraphenylcyclobutadiene NiBr₂ respectively. The reaction mechanisms are discussed.

Rh₆(CO)₁₆ and its Identity with Previously Reported Rh₄(CO)₁₁

E. R. COREY, L. F. DAHL and W. BECK, *J. Am. Chem. Soc.*, 1963, **85**, (8), 1202-1203

Crystal structure analysis showed that the compound reported to be Rh₄(CO)₁₁ is really Rh₆(CO)₁₆. Each Rh atom is situated at the vertex of an octahedron and is bonded to four Rh atoms, two terminal CO groups and two CO groups bridging the Rh atoms. The molecule is the first-known hexanuclear metal carbonyl and has two electrons in excess of xenon configuration. Like CH₄, it has idealised T_d symmetry. Similar work corrected the formulas of Os₂(CO)₉ and Ru₂(CO)₉ to trinuclear Os₃(CO)₁₂ and Ru₃(CO)₁₂.

Complexes in the Rhodium (III)-Chloride System in Acid Solution

W. C. WOLSEY, C. A. REYNOLDS and J. KLEINBERG, *Inorg. Chem.*, 1963, **2**, (3), 463-468

Complexes were prepared between Rh(III) and Cl⁻ ion in dilute HCl solution and were separated by ion exchange technique. RhCl₂²⁺, RhCl₂⁺, *cis*- and *trans*-RhCl₃, RhCl₄⁻, RhCl₅²⁻ and RhCl₆³⁻ were identified. Their molar absorption spectra were plotted. Each of these possessed two maxima with a shift towards longer wavelengths as the number of Cl ligands increased. Formation constants at 120°C for 6M solutions of the complexes were determined as $k_1 > 10^3$, $k_2 > 10^8$, $k_3 \sim 10^3$, $k_4 = 250 \pm 120$, $k_5 = 25 \pm 8$, $k_6 = 0.56 \pm 0.18$.

Production of Iridium Carbonyl

N. S. IMYANITOV and D. M. RUDKOVSKII, *Zhur. Obshch. Khim.*, 1963, **33**, (4), 1053-1054

Iridium carbonyl, Ir(CO)₃, was prepared from anhydrous IrCl₃ and CO. The reaction was accelerated in the presence of Cu. The pressure of CO was 230 to 250 atm. and the temperature was 240°C.

On Oxoosmate (VII)

R. SCHOLDER and G. SCHATZ, *Angew. Chem.*, 1963, **75**, (9), 417

The preparation of the osmate (VII) compounds Li₃OsO₆, Na₃OsO₆, Na₃OsO₅, K₃OsO₆ and Ba₃(OsO₆)₂ is reported. They are black substances. In H₂O they decompose into OsO₄ and osmate (VI). CH₃OH and C₂H₅OH reduce them to osmium (VI).

A Novel Type of Arene Complex

J. CHATT and J. M. DAVIDSON, *I.U.P.A.C. XIXth Internat. Congress, London, 1963*, (abs. A), 188-189, abs. AB4-52

A new class of ruthenium (0) complex [Ru(PP)₂

(arene)], where PP = ditertiary phosphine, arene = benzene, naphthalene, anthracene, phenanthrene, has been prepared by the reduction of octahedral ditertiary phosphine complexes of type $[\text{RuCl}_2(\text{PP})_2]$ by arene negative ions such as $[\text{C}_{10}\text{H}_8]^-$. This class of compound is unusual and its structure is discussed with reference to its reactions and n.m.r. spectrum. Osmium forms analogous compounds.

ELECTROCHEMISTRY

Radiochemical Method for the Investigation of Electrode Processes on Metal Electrodes

W. W. LOSSEW, M. A. DEMBROWSKI, A. I. MOLODOW and W. W. GORODEZKI, *Electrochim. Acta*, 1963, **8**, (5), 387-397

Two radiochemical techniques are described. The first permitted the determination at amalgam electrodes of electrode kinetic parameters. The second facilitated measurement of the very low rate of anodic dissolution of passive Pt. The Pt anode was irradiated by a neutron flux of 10^{13} neutrons/cm² sec and was then immersed in 270 g/l NaCl solution. The corrosion rate was determined by periodic measurements of the radioactivity of the electrolyte using a 100-channel scintillation spectrometer and reached a stable value of 3.6×10^{-6} to 9.1×10^{-6} mg/cm² hour.

The Anodic Formation of *per*-Compounds on Platinum

M. W. BREITER, *Chem.-Ing.-Techn.*, 1963, **35**, (5), 376-378

Persulphate forms anodically on Pt in two steps. First the SO_4^{2-} and HSO_4^- ions are altered to SO_4^- and then SO_4^- anions combine to form $\text{S}_2\text{O}_8^{2-}$. Current-voltage curves illustrate these processes in sulphate solutions. Labelling with ^{18}O showed that O_2 from water present does not take part in the reaction and that O_3 in H_2O_2 formed when persulphate solutions are hydrolysed originates in the persulphate. (21 references).

Hysteresis of the Relationships between Electrical Resistance and the Hydrogen Content of Palladium

J. S. BARTON, F. A. LEWIS and I. WOODWARD, *Trans. Faraday Soc.*, 1963, **59**, (5), 1201-1207

Evidence favours the existence of absorption and desorption isotherms for H_2 in Pd, once steady state conditions are reached, which are independent of the time of measurement. The relation between the H/Pd ratio and R/R_0 , where R_0 is the electrical resistance of H-free Pd, was studied at 0, 25 and 50°C during H_2 absorption and desorption. Resistance measurements and X-ray studies were made on Pd wires and the magnetic susceptibility was determined on Pt sheet. R/R_0 , susceptibility and lattice parameters of Pd returned to pure Pd values after desorption of H_2

by oxidation at 25°C. They do not retain hydride values as believed previously.

On the Electrochemical Formation and Decomposition of Oxygen and Hydrogen Layers on Platinum in Aqueous Solution

H. DIETZ and H. GÖHR, *Electrochim. Acta*, 1963, **8**, (5), 343-359

Low current density charging curves were used to study the chemisorption of O_2 and H_2 on Pt during anodic and cathodic polarisation. The mechanism of gas layer formation indicated that, during cathodic polarisation of an O_2 layer, chemisorption of H_2 commenced before all the O_2 is reduced and a loose layer of Pt atoms remained, which only gradually resumed the normal lattice pattern. This appears to explain increased activity of Pt electrodes in partly cathodic redox reactions after anodic pre-treatment.

Formation and Dissolution of Platinum Oxide Film: Mechanism and Kinetics

S. W. FELDBERG, C. G. ENKE and C. E. BRICKER, *J. Electrochem. Soc.*, 1963, **110**, (7), 826-834

Pt is oxidised in two stages, a slow and a fast step. Reduction reverses these steps but the second is so slow that a half-reduced state usually occurs, making the oxidation apparently irreversible. The three states of the Pt electrode - reduced Pt, oxidised $\text{Pt}(\text{O})_x$ and half-reduced $\text{Pt}(\text{OH})_x$ - were studied by constant current and controlled potential techniques with a Pt foil electrode, an H_2 reference electrode and a Pt counter electrode, in 0.8 M HClO_4 . A single kinetic equation relating current, potential and time was derived and suggested that the oxide is a chemisorbed film.

ELECTRODEPOSITION

Electroless Plating with Precious Metals

R. N. RHODA, *Plating*, 1963, **50**, (4), 307-309

This review describes how uniform deposits of Au, Ag and the Pt metals can be made on surfaces difficult to electroplate. The displacement technique requires the article to be plated to be immersed in a solution of a complex of the precious metal. Precious metal atoms then plate out as the substrate goes into solution. The process can continue until all surface sites are filled or until the solution strength drops too low. Pt metal coatings are possible up to 65 μ in. Pt, 50 μ in. Pd, 30 μ in. Rh and 100 μ in. Ru. The chemical reduction technique consists of dipping the article into a precious metal salt solution and reducing the metal out on to it. At present only Pd of the Pt metals can be done this way, using Pd (II) tetra-ammine chloride in 1:1 NH_4OH solution with the di-Na salt of EDTA as stabiliser and controlling the thickness of the coating with N_2H_4 or by solution exhaustion. For Pd on Cu, an underplate of Ni or Au is needed. (31 references.)

LABORATORY APPARATUS AND TECHNIQUE

Palladium-Diaphragm Hydrogen Pump

J. R. YOUNG, *Rev. Scient. Instrum.*, 1963, **34**, (4), 374-377

Pumping of H₂ towards a region of higher H₂ concentration can occur at a heated Pd or Ag-Pd diaphragm. This region must have an oxidising atmosphere. The region of lower H₂ concentration needs a reducing atmosphere or a good vacuum. The membrane catalyses the oxidation of H₂ to H₂O. A pumping speed of 0.25 l H₂ per sec. per cm² of 0.004 in. Pd or 25% Ag-Pd is possible at 500 to 600°C. It has been possible to pump down to 10⁻⁹ mm Hg while the hot diaphragm was exposed to air. The theoretical maximum pumping speed is over 180 times that achieved so far. Ti and Ni also can pump but at a slower rate.

Alloys for High Temperature Strain Gauges

K. E. EASTERLING, *Br. J. Appl. Phys.*, 1963, **14**, (4), 225

8% W-Pt is more suitable than 3% W-35% Ag-Pd and 5% Cu-5% W-Pt as a high temperature strain gauge alloy. The gauge factors of the ternary alloys are 1.25 and 3.0 respectively and their strain temperature coefficients were found to be 81.0×10^{-6} and 50.2×10^{-6} in. per in. per °C respectively. More drift occurred in the ternary alloys due to oxidation as the W content increased but the overall zero-drift rate for 8% W-Pt was the lowest of several alloys tested.

METAL WORKING

How to Weld Bi-Metal Tape

J. D. EYESTONE, *Metalworking Production*, 1963, **107**, (9), 57-58

Details are given of methods used by the Western Electric Co., U.S.A., to weld Pd to Ni or Cu-Ni base metal. Both components are continuously fed into an automatic machine which produces uniform welds and the tape is then rolled to its final shape. Another technique welds groups of contacts to springs in one operation. Bi-Metal strips with Au, Ag and Pt as the contact metal can be made in similar ways.

The Activated Sintering of Tungsten with Group VIII Elements

W. W. HAYDEN and J. H. BROPHY, *J. Electrochem. Soc.*, 1963, **110**, (7), 805-810

Sintering of W powder with small additions of Group VIII activating elements showed that Pd increased the rate of densification the most, followed in order by Ni, Rh, Pt and Ru. 0.25 wt.% Pd gave densities 93.5 and 99.5% of theoretical after 30 min. and 16 hr, respectively, at 1100°C in H₂, whereas with no addition only presintering of W occurred at 1100°C. A carrier phase layer

is believed to have formed on the W surface, into which the W dissolved, so decreasing the distance between particle centres and compacting the powder. Results for each activating metal are discussed in relation to the mechanism of carrier phase sintering.

CATALYSIS

A New Process for the Industrial Synthesis of Isoprene

M. DE MALDÈ, *Chim. e Ind.*, 1963, **45**, (6), 665-673

Isoprene is produced in three stages from acetone and acetylene. Acetylation of acetone in NH₄OH under pressure produces methylbutynol. This is selectively hydrogenated to methylbutenol over Pd catalyst in the liquid phase. This process occurs at <10 atm. pressure and at mild temperatures with up to 99.95% efficiency. Control of the reaction speed is unnecessary. The final stage is dehydration of methylbutenol to form isoprene. The industrial plant for these processes is described and the properties of natural and synthetic rubbers are compared.

Catalytic Hydrogenation and Hydrogenolysis of Furan Compounds

I. F. BEL'SKII and N. I. SHUIKIN, *Uspekhi Khim.*, 1963, **32**, (6), 707-736

The Pt metals are used as catalysts in many of the reviewed reactions. Pd or Pt on C or Al₂O₃ are referred to most frequently. (92 references.)

Investigation of the Thermal and Catalytic Changes of Hydrofuran Compounds

N. I. SHUIKIN, I. F. BEL'SKII and R. A. KARACHANON, *Z. Chem.*, 1963, **3**, (6), 222-226

2,3-Dihydrofurans were isomerised at 450 to 480°C to carbonyl compounds of the cyclopropane series but 2,5-dihydrofurans were dehydrogenated to the corresponding furans. Both groups were dehydrogenated to the corresponding furans over Pt metal catalysts at 200 to 300°C. The H₂ produced further reacted with both furans and dihydrofurans to form tetrahydrofurans and aliphatic ketones. Isomerisation of tetrahydrofurans to aliphatic carbonyl compounds increased with increasing temperature and was more marked when there were long alkyl groups in the α -position. Tetrahydrofuran conversions over Os, Ru, Rh and Ir catalysts from 300 to 400°C showed that most tetrahydrofurans can be dehydrogenated to furans. Isomerisation (at the C-O bond) and hydrogenolysis of 2-alkyl-2,2- and 2-alkyl-2,5-tetrahydrofuran occurred simultaneously at 350°C in the vapour phase over platinised C.

Kinetic Isotope Effect of Ethylene Oxidation by Palladium Chloride

I. I. MOISEEV, M. N. VARGAFIYK and YA. K. SYRKIN, *Izv. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk.* 1963, (6), 1144-1145

The speed of C₂H₄ oxidation in aqueous PdCl₂

solution was studied for H₂O and D₂O. In H₂O, with 0.396 M/l, NaCl and 0.113 M/l HCl at 25°C, the velocity constant was $15.2 \pm 0.3 \times 10^{-2} \text{ l. M}^{-1} \text{ sec}^{-1}$ and in D₂O (98.92 at. % D₂) under similar conditions the constant was $3.75 \pm 0.07 \times 10^{-2} \text{ l. M}^{-1} \text{ sec}^{-1}$. The ratio of the constants was 4.05 ± 0.15 . There was practically no change in the kinetic isotope effect for acid concentrations up to 0.285 M/l. It was doubtful whether PdCl₂C₂H₄⁻ reacted with OH⁻ ions.

The Mechanism of Isomerisation of Hexanes on Platinum Catalysts

Y. BARRON, D. CORNET, G. MAIRE and F. G. GAULT, *J. Catalysis*, 1963, 2, (2), 152-155

Hydrogenolysis of methylcyclopentane on 0.2% Pt/Al₂O₃ in the 270-330°C range gave mainly *n*-hexane, 2-methylpentane and 3-methylpentane. Isomerisation of any of these hexane isomers on the same catalyst gave the other two at a lower rate than by hydrogenolysis and some dehydrocyclylation to methylcyclopentane occurred. Results suggested that the same catalyst sites promoted all these processes and that a common 5-membered cyclic intermediate was involved. The latter may have been a π -bonded complex. Isomerisation was not due to carbonium ion rearrangement.

Activation of Platinum-Alumina Catalyst by Water. Part 2. Dehydrogenation of Cyclohexane

I. I. LEVITSKI, M. G. GONIKBERG, KH. M. MINACHEV and D. A. KONDRAT'EV, *Izv. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1963, (5), 798-801

The change in activity of 0.005% Pt/Al₂O₃ catalyst was studied after its treatment at 420°C by H₂ with steam at 60-80 atm. pressure and after treatment at 500°C by H₂ free of O₂ and H₂O. H₂O activated both the hydrogenation of C₆H₆ and the dehydrogenation of cyclohexane. Deactivation of the catalyst for both reactions occurred after dehydration at 550°C by H₂ free of O₂ and H₂O.

Hydrogenation and Hydrogenolysis. VII. Selective Hydrogenation of Aromatic Compounds Containing C-O Linkages Liable to Hydrogenolysis with a Rh-Pt Oxide under High Pressures

S. NISHIMURA and H. TAGUCHI, *Bull. Chem. Soc. Japan*, 1963, 36, (3), 353-355

High pressure hydrogenation of aromatic compounds with 7:3 Rh-Pt oxide was shown to avoid hydrogenolysis of C-O linkages and results for several compounds are tabulated. The solvent was CH₃COOH and the pressure was 100-150 kg/cm². Principal products were the corresponding saturated alcohols and ethers. At atmospheric pressure less of the saturated compounds was produced and there was twice as much hydro-

genolysis. The synthesis of *cis*-alicyclic compounds is possible by the method.

The Synthesis of Tritium-Labelled 9, 10-Oleic Acid

K. S. TENNY, S. C. GUPTA, R. F. NYSTROM and F. A. KUMMEROW, *J. Am. Oil Chem. Soc.*, 1963, 40, (5), 172-175

Tritium-labelled *cis*-9, 10-oleic acid is reported with better than 90% specificity at the 9 and 10 positions. Oleic acid was prepared by hydrogenation of stearolic acid over 5% Pd/C in ethyl acetate solution containing 20% C₆H₅N. Specific labelling was confirmed by bromination and subsequent dehydrodehalogenation of the oleate. 5% Pd/C was also stereospecific in the reduction of stearolic to oleic acid, using tritiated stearolic acid. Radioassay by liquid scintillation spectrometer showed specific radioactivities of 1000 mc/g and 927 mc/g of T for oleic and stearic acids respectively.

The Conditions of Preparation and the Dispersion of Platinum in Platinised Silica Gels

V. S. BORONIN, V. S. NIKULINA and O. M. POLTORAK, *Zh. Fiz. Khim.*, 1963, 37, (5), 1174-1177

The dispersion of Pt in Pt/SiO₂ catalysts depends on their mode of preparation. The chemisorption of H₂ by the catalysts was used to measure the Pt dispersion, which varied from almost the atomic state in the best conditions to a crystalline form of Pt. At constant temperature the ratios H:Pt reached steady values depending on the different conditions of preparation. The ratios slowly decreased as the Pt content of the silica gel increased.

Adsorption of Hydrogen on Platinised Silica Gel

V. S. BORONIN, V. S. NIKULINA and O. M. POLTORAK, *Vestnik Mosk. Univ., Ser. II, Khim.*, 1963, (3), 24-28

The amount of H₂ adsorbed on Pt/SiO₂ depends on the preparation of the catalyst as it affects the dispersion of Pt. Catalysts with from 0 to 2% Pt were studied at pressures from 0 to 1.7 mm Hg and over a wide range of temperature but especially at -196° and +20°C.

Dehydrogenation and Hydrogenolysis of Cyclohexane on Ru/SiO₂ Catalyst

F. B. GONEIM, A. A. BALANDIN and T. A. SLOVOKHOTOVA, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1963, (7), 1203-1210

5% Ru/SiO₂ was used as catalyst in studies of these reactions in the 250 to 350°C range. The reactions were temperature dependent. Curves of % conversion against temperature showed inflections at 300 to 320°C for dehydrogenation and 300 to 330°C for hydrogenolysis. Activation

energies for dehydrogenation were 9.2 and 16.65 kcal/M at 250 to 300°C and 320 to 350°C respectively. For hydrogenolysis they were 12 and 26.6 kcal/M respectively. Adsorption coefficients of benzene for dehydrogenation of cyclohexane were determined in the 250 to 300°C range. The rate of hydrogenolysis of cyclohexane is given by $v = kP_{C_6H_{12}}^{0.675} P_{H_2}^{0.955}$, where P is the pressure and k is a constant.

Hydrogenation of Diels-Alder Adducts of Anthracene

M. KOLOBIELSKI, *J. Org. Chem.*, 1963, **28**, (7), 1883-1885

Only one aromatic ring in 9, 10-dihydroanthracene-9,10-endo- α,β -succinic anhydride was hydrogenated in the presence of Ru/Al₂O₃ but the reaction was nonselective in the presence of Raney Ni. Several diesters and an N-substituted imide were prepared from the hydrogenation product. Both aromatic rings of 11-methylol-9, 10-dihydro-9, 10-ethanoanthracene were attacked by H₂ in the presence of Ru/Al₂O₃. This difference was attributed to steric effects.

GLASS TECHNOLOGY

Improved Counterbalanced Sphere Viscometer for Use to 1750°C

E. F. RIEBLING, *Rev. Scient. Instrum.*, 1963, **34**, (5), 568-572

This viscometer incorporates a linear variable differential transformer and recorder which permit more accurate measurement of the vertical speed of the bob through the melt. Molten oxides at temperatures up to 1750°C can now be measured as low as the 1 to 5 poise range. Vertical constant-temperature environment is provided by a 50% Rh-Pt wound furnace. Crucible, bob and suspension are 40% Rh-Pt and the thermocouple is 6% Rh-Pt:30% Rh-Pt. Correction for surface tension effects is necessary. Standardisation, sensitivity and possible errors are discussed. The apparatus can be adapted to measure conductivity below 1400°C when melts contain large amounts of SiO₂ or related compounds.

Silver-Palladium Alloys as Crucible Materials in Studies of Low-Melting Iron Silicates

A. MUAN, *Am. Ceram. Soc. Bull.*, 1963, **42**, (6), 344-347

Consideration of temperature conditions and thermodynamic data from the ternary system Ag-Pd-Fe showed that Ag-Pd alloys were possible crucible materials for equilibrium studies on molten Fe oxides and silicates at controlled O₂ potentials above those of Fe stability. Pd alloyed to Ag raised the melting point without much increase in Fe solubility. The alloy loss was <5% of that using Pt crucibles. Limiting temperatures and O₂ potentials were derived

for Fe oxides. Fe silicates showed lower Fe activity than oxides. The amount of noble metal dissolved was tolerable while the O₂ potential $> 10^{-6}$ atm at 1200°C. Ag-Pd alloys are expected to be useful for studies on low-melting synthetic iron silicates and low O₂ potential basalts.

Glass in Space

R. C. REMINGTON, *Glass Ind.*, 1963, **44**, (4), 198-201, 230

The principles and construction of vertical sensing elements (V.S.E.s) for use in space instruments are described. A typical V.S.E. consists of a moulded glass body containing a stable electrolyte and a gas bubble. Pt electrodes are separated by the bubble and the electrolyte. A change in the attitude of the vehicle causes the bubble to move and a change of resistance between the electrodes is detected and used to restore the original position. The V.S.E. replaces the mechanical pendulum and is more reliable. Sealing glass-Pt joints is simple and no leaking occurs.

ELECTRICAL ENGINEERING

The Use of Susceptors in Induction Heating

J. F. LIBSCH and P. CAPOLONGO, *Metal Progress*, 1963, **83**, (4), 77-81, 114-118

This review surveys the indirect heating of metallic and non-metallic parts by susceptors, which are themselves heated by induction. The three main types of susceptor are "complete", i.e. heating by radiation alone, "slit", i.e. heating by the induction coil as well as the susceptor, and "integral", i.e. forming part of the assembly to be fabricated. Materials used, with examples of their uses, are tabulated. Susceptors are made from graphite, Ni alloys, Pt, Rh, Ir, Mo, Ta, W, Al alloys and stainless steel. Although expensive, Pt metals are easily formed and chemically stable and are used for melting non-conducting materials. The use of a Pt slit susceptor for fusing glass beads on to metal wires is illustrated.

The Use of Radioactive Contact Electrodes in the Measurement of Metal Migration in Electrical Contacts

M. R. HOPKINS and C. H. JONES, *Br. J. Appl. Phys.*, 1963, **14**, (3), 137-140

The migration of electrode material between electrical contacts of Ag, Pt, 10% Ir-Pt or 25% Ir-Pt depends on the circuit inductance, even in the low range 10⁻⁸ to 3 × 10⁻⁶H. Only 10³ contacts operations were sufficient to transfer enough radioactive material at the investigated contact to measure with a Geiger-Muller counter. Irradiated Pt contacts were compared against a standard irradiated Pt foil. Ag^{110m} and Ir¹⁹⁴ tracers were used in the other cases. Only micro-arc transfer was observed. Graphs illustrate the variation of metal migration with inductance.

TEMPERATURE MEASUREMENT

An Electrical Deep-Sea Thermometer with Short Adjustment Time

H. HINKELMANN and H. M. IHME, *Z. angew. Phys.*, 1963, 15, (5), 429-435

A Pt resistance thermometer has been designed for deep sea work. It has a time constant of only 0.2 sec. The construction of the apparatus and the control circuit are fully described. The Pt wire is about 1 m long, 0.06 mm diameter and about 30 ohm resistance. It is protected by a Au capillary pressure housing. The accuracy of the arrangement is better than 0.01°C.

Problems Encountered Using IrRh-Ir Thermocouples for Measuring Combustion Gas Temperatures.

C. M. STANFORTH, *Soc. Automotive Eng*, 1962, (524F), 1-3

An Ir:Rh-Ir thermocouple was flame-sprayed with Al₂O₃ and then registered temperatures close to calculated values at a jet engine burner using JP-4 fuel. A similar unsprayed thermocouple gave much higher results. Catalytic action at the

metal surface was suspected in the second case although it had been believed that this did not take place above 1200°F. The thermocouples are required as jet engine control devices operating up to 3500°F. Possible errors due to radiation, conduction and slow recovery are discussed.

Relationship between the Real and Ideal Resistivity of Platinum

R. J. BERRY, *Canad. J. Phys.*, 1963, 41, (6), 946-982

Data on 138 Pt resistance thermometers were correlated to find a relation between the real and ideal resistance functions of Pt by Matthiessen's Rule. Kohler's expression for deviations from this rule was not applicable in general but in the range 20 to 90°K held fairly well for about $\frac{1}{3}$ of the resistors examined. Values for the ideal resistance function were found by extrapolation of measurements on many thermometers. A special method in the range 20 to 90°K gave more accurate results than previously. Methods for determining the residual resistance ratio at 0°K were studied. To extend the Pt resistance temperature scale below 90.19°K some differences in interpolating the real resistance function between fixed calibration points were outlined and compared with previous methods.

NEW PATENTS

Carotenoid Compounds

ROCHE PRODUCTS LTD. *British Patent* 924,255

A palladium/lead (calcium carbonate) catalyst is used in a hydrogenation step in a method of making carotenoid and dehydro-carotenoid compounds of given formula.

Pyridoxal Derivatives

LEPETIT S.p.A. *British Patent* 924,514

A palladium-on-charcoal or a platinum oxide catalyst is used in a process of preparing new pyridoxal derivatives of given general formula.

Pyridine Bases

THE DISTILLERS CO. LTD. *British Patent* 924,527

A catalyst of silica and/or alumina and palladium may be used in a process of producing pyridine bases by heating crotonaldehyde, ammonia and a saturated aliphatic ketone.

Removing Acetylene Hydrocarbons from Gaseous Mixtures

FARBWERKE HOECHST A.G. *British Patent* 924,627

For the removal of acetylene hydrocarbons and butadiene from gaseous mixtures containing hydrogen and olefines, the mixture is passed over a palladium-silica catalyst containing less than 1 wt. % of palladium at 150°-300°C and at a rate of 150-500 litres per litre of catalyst per hour.

Electrolysis of Salt Solutions

RUHRCHEMIE A. G. *British Patent* 925,079

The counter electrode of a mercury amalgam cell is formed of a double skeleton material, from 1-10% of the iron group metal carrier material of which is replaced by platinum, palladium, iridium or ruthenium.

Titanium-cored Electrode

AMALGAMATED CURACAO PATENTS CO. N.V. *British Patent* 925,080

A platinum group metal coated-titanium electrode having a titanium oxide barrier layer has this barrier layer formed electrolytically or by oxidation before the platinum coating is applied.

Preparation of Alkanediols

E. I. DU PONT DE NEMOURS & CO. *British Patent* 925,404

An alkanediol having 5 or more carbon atoms in the molecule is made by reacting together at 100°C or above and at least 1000 atm pressure an acyclic diene hydrocarbon, carbon monoxide, formaldehyde and hydrogen in the presence of a catalyst formed of a salt, organic chelate or carbonyl of a Group VIII noble metal, e.g. rhodium (III) or ruthenium (III).