

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Tensile Properties of the Platinum Group Metals

F. C. HOLDEN, R. W. DOUGLASS and R. I. JAFFEE, Paper presented at the Third Pacific Area National Meeting, A.S.T.M., San Francisco, Oct. 1959. *A.S.T.M. Special Technical Publication No. 272*.

Tests were carried out in the temperature range -196° to 1000°C on Ru, Rh, Pd, Ir and Pt, all in the annealed condition. With the exception of Pd, material representing different grades of purity or methods of fabrication were used for each metal. Ru was prepared by powder metallurgy techniques; Rh, Pd, Ir and Pt were obtained as rod or wire; electron-beam melted Rh and Ir also were tested. Ru showed rather low ductility at 750° , 1000° and 1200°C and a tensile strength of 31,400 psi at 1000°C . Throughout the range -196° to 1000°C , Rh showed good ductility, and at 1000°C , a tensile strength of about 12,500 psi. Pd, over the whole temperature range, showed low strength and high ductility. Tensile strengths of Ir decreased with increasing temperature to about 45,000 psi at 1000°C ; ductility was good at higher temperatures, but low up to 500°C . Pt resembled Pd with high ductility and low tensile strength. Twinning was observed in all five metals. Strengths plotted *v.* homologous temperature indicate that Rh, Ir and Ru are stronger than Pd and Pt.

Iron-Ruthenium Alloys

E. RAUB and W. PLATE, *Z. Metallkunde*, 1960, **51**, (8), 477-481

A series of Fe-Ru alloys were investigated in the temperature range 400° - 1300°C by X-ray and dilatometer methods, and microscopy. Earlier reports on the stabilisation of γ -Fe by Ru were confirmed. The γ - α and γ - ϵ transformations and their influence on the thermal expansion curves were studied for various alloys up to 30 at. % Ru. The crystal structure of the alloys after heat treatment at various temperatures is given in some detail.

The System Iridium-Tellurium

E. F. HOCKINGS and J. G. WHITE, *J. Phys. Chem.*, 1960, **64**, (8), 1042-1045

Specimens, obtained by heating Ir powder and Te *in vacuo*, were examined by X-ray powder diffraction methods. Two compounds, IrTe_2 and Ir_3Te_8 , were observed and their crystal structures were determined. IrTe_2 has the (C6)

type structure and Ir_3Te_8 has a defect (C2) type structure with approximately one-quarter of the cation sites vacant. The structures are discussed in relation to the arrangement of the electronic energy levels of the metal atoms.

Absorption of Hydrogen by Palladium/Platinum Alloys. Part 3. Some Thermodynamic Factors

A. W. CARSON, T. B. FLANAGAN and F. A. LEWIS, *Trans. Faraday Soc.*, 1960, **56**, (9), 1332-1339

Electrode potential measurements were made on a series of Pt-Pd alloys over a temperature range 0° - 59°C and free energies of solution of hydrogen and hydride vapour pressures were derived as a function of the hydrogen content. Entropies and partial molar heats of formation of β -phase hydrides were derived for alloys containing 2.79, 5.73 and 8.80 at. % Pt. It is suggested that hydrogen absorption in alloys with greater than 35 at. % hydrogen is unlikely to be exothermic. Results indicate that, with increasing Pt content, the critical temperature and pressure for α - β phase coexistence decreases.

Low Temperature Dependence of the Electrical Resistivity and Thermoelectric Power of Palladium and Palladium-Nickel Alloys Containing Absorbed Hydrogen

A. I. SCHINDLER, R. J. SMITH and E. W. KAMMER, *U.S. Naval Research Laboratory Report 5481*, 1960, Jun. 3, 6 pp.

Measurements of electrical resistivity and thermoelectric power were made on wires of Pd, 10% Ni-Pd and 17% Ni-Pd containing various amounts of absorbed hydrogen. At $T=50^{\circ}\text{K}$, a resistivity maximum and, relative to pure Pd, a thermoelectric power minimum were found for samples with $\text{H/Pd} \geq 0.58$. These samples also showed a resistivity minimum at approximately 90°K . The absolute thermoelectric power for Pd-H decreases rapidly as a function of composition in the region $\text{H/Pd} \sim 0.6$ at temperatures $< 85^{\circ}\text{K}$, while above 95°K a maximum is shown at $\text{H/Pd} \sim 0.6$.

On the Contamination of Platinum with Fission Products and the Decontamination of Contaminated Platinum with Acids

T. YANAGIHARA, H. KIMURA and M. CHIBA, *J. Jap. Inst. Metals*, 1960, **24**, (7), 413-417 (English summary)

Pt plates were soaked in a solution of fission products and maximum contamination was

reached in about 3 hours. It was shown by autoradiography, electron microscopy and optical microscopy that the contamination is affected by the surface condition of the Pt. The plates were decontaminated with tap water, HCl, HNO₃, H₂SO₄, H₃PO₄, HF and fused salts. Of those investigated hot HCl and fused KHSO₄ were the most effective decontaminating agents. The degree of contamination of Pt with fission products is very low.

Mass-Spectrometric Study of the Osmium-Oxygen System

R. T. GRIMLEY, R. P. BURNS and M. G. INGRAM, *J. Chem. Phys.*, 1960, **33**, (1), 308-309

The main ionic species produced from a Knudsen cell in the temperature range 1100-1750°K were OsO₃⁺ and OsO₄⁺. The ratio OsO₃⁺:OsO₄⁺ is a function of the oxygen pressure and the temperature and confirms the presence of OsO₃ and OsO₄ molecules in the vapour phase. Above 1700°K, evidence supports the existence of a stable OsO₂ molecule.

Equilibrium Measurements in the Iridium-Oxygen System. Gaseous Iridium Trioxide

H. SCHAFER and H. J. HEITLAND, *Z. Anorg. Allgem. Chem.*, 1960, **304**, (5/6), 249-265

Measurements made by the carrier gas method have shown that Ir and IrO₃ heated in currents of oxygen or oxygen-nitrogen are volatilised with the formation of gaseous IrO₃, which is stable up to 1700°C. This confirms previous hot wire experiments. The interpretation of published hot wire experiments with Pt and Rh indicates the existence of Pt_xO₂ and Rh_xO₂. Thermodynamic data for IrO₂(s) and IrO₃(g) have been obtained.

Equilibrium Measurements in the Platinum-Oxygen System. Gaseous Platinum Dioxide

H. SCHAFER and A. TEBBEN, *Z. Anorg. Allgem. Chem.* 1960, **304**, (5/6), 317-321

Pt was volatilised as the dioxide by heating in an oxygen atmosphere. The equilibrium Pt + O₂ = PtO₂(g) was measured in the range 1107°-1208°C and the following data were obtained: ΔH₂₉₈ = 41.30 kcal; ΔS₂₉₈ = 3.01 cal; S(PtO₂(g), 298) = 62.0 cal.

Changes in Resistance on the Chemisorption of Gases on Thin Metal Films

W. M. H. SACTLER and G. J. H. DORGELO, *Z. Phys. Chem. (Frankfurt)*, 1960, **25**, (1/2), 69-74

The Pt-H system was investigated. It was found that, as with other metals, chemisorption of hydrogen effects a sharp initial increase in the electrical resistance of the films. Absorption of hydrogen in the metal lattice often causes a decrease in resistance. A temperature as low as -210°C is necessary for suppressing the absorption of hydrogen in Pt.

Kinetics of Hydrogen and Oxygen Adsorption and Their Reaction on Platinum

P. K. MIGAL' and V. A. TSIPLYAKOVA, *Zhur. Fiz. Khim.*, 1960, **34**, (6), 1153-1160 (English summary)

The adsorption of hydrogen and oxygen and their interaction in the presence of As, Hg and of (CN)' ions were investigated. The adsorption rate for hydrogen on non-poisoned Pt was found to be of zero order. The effect of the poisons on the hydrogen adsorption rate diminishes in intensity in the order (CN)' > Hg > As. It is suggested that the reaction between adsorbed hydrogen and molecular oxygen takes place according to the "impact" mechanism with redistribution of hydrogen on the surface. A similar mechanism without surface redistribution of oxygen is suggested for the reaction between adsorbed oxygen and molecular hydrogen. The effect of As, Hg, and (CN)' ions on the reaction rates was studied.

Modern Industrial Uses of the Platinum Metals

W. BETTERIDGE and D. W. RHYS, *Metal Industry*, 1960, **97**, (9, 10 and 11), 163-166, 183-185 and 203-205

The physical and chemical properties of the Pt metals upon which many of their applications depend are given. Major uses of the metals in the metallurgical, chemical, petroleum, electrical, glass, synthetic fibre and atomic energy industries are reviewed.

The Thermal and Magnetic Properties of Some Transition Element Alloys

D. W. BUDWORTH, F. E. HOARE and J. PRESTON, *Proc. Roy. Soc., Series A*, 1960, **257**, (1289), 250-262

Magnetic measurements were made on 40 different Pd-Rh, Pt-Ir and Pt-Au alloys. The specific heats of Pd-Rh and Pt-Au alloys and the pure metals Rh, Pt and Au were measured in the range 1.8 to 4.2°K and the electronic heats and Debye temperatures were computed. Tables of results are given. Similarities between alloys of Pd and Ag or Rh with alloys of Pt and Au or Ir are noted.

Magnetic Properties of the Pd and Pt Group Transition Metal Complexes

H. KAMIMURA, S. KOIDE, H. SEKIYAMA and S. SUGANO, *J. Phys. Soc. Japan*, 1960, **15**, (7), 1264-1272

Magnetic susceptibilities and g-values are calculated by means of the intermediate coupling scheme. The effect of the d_γ orbitals is neglected because of the cubic symmetry of the crystalline field. The effect of the Coulomb repulsion is regarded as comparable to that of the spin-orbit interaction. The results are compared with experimental data.

Vapour Pressures of Platinum Metals. I. Palladium and Platinum

L. H. DREGER and J. I. MARGRAVE, *J. Phys. Chem.*, 1960, **64**, (9), 1323-1324

Vaporisation studies were carried out by the Langmuir free evaporation technique. Results obtained for Pt are: $\log P_{\text{mm}}^{\text{solid}} = 10.362 - 29,100/T$; $\Delta H_{298}^{\circ} = 135.2 \pm 0.8$ kcal/mole; estimated boiling point $\approx 4100 \pm 100^{\circ}\text{K}$. For Pd: $\log P_{\text{mm}}^{\text{solid}} = 9.075 - 19,425/T$; $\Delta H_{298}^{\circ} = 91.0 \pm 0.8$ kcal/mole; estimated boiling point $\approx 3200 \pm 100^{\circ}\text{K}$.

Investigation of Adsorption on Platinised Carbon by Change of the Gaseous Atmosphere

A. N. MOSEVICH, B. P. NIKOL'SKII, V. I. PARAMONOVA and E. L. MORDBERG, *Zhur. Phys. Khim.*, 1960, **34**, (9), 1900-1906 (English summary)

The adsorption of Cs and Br ions from aqueous solutions in hydrogen and air atmospheres was investigated. Adsorption and desorption studies were carried out both in the presence and absence of a buffer and of foreign ions. The adsorption of Cs and Br ions was shown to have an electrostatic character and to conform to the basic laws of ion exchange.

Increasing the Stability of the Passive State in Titanium

N. D. TOMASHOV, G. P. TSHCHERNOVA and R. M. ALTOWSKI, *Z. Phys. Chem. (Leipzig)*, 1960, **214**, (5/6), 312-323

The behaviour of Ti and its alloys with 1% and 2% of Pt and Pd on cathodic and anodic polarisation in H_2SO_4 and HCl solutions was studied by potentiostatic methods. It was shown that the complete passivation of Ti is made more difficult by increasing the temperature and concentration of the acid solution. The alloys of Ti with Pt and Pd have a substantially higher corrosion stability than Ti. Ti may be protected anodically in H_2SO_4 and HCl of all concentrations and may be passivated by cathodic depolarisers such as ions of Pt^{4+} , Cu^{2+} and Fe^{3+} in the corrosive medium.

Some Aspects of the Structural Chemistry of Platinum

E. G. COX, *J. Roy. Inst. Chem.*, 1960, **84**, (Aug.), 283-284

The historical development of the study of the stereochemistry of Pt co-ordination compounds is outlined. The structure of derivatives of $\text{Pt}(\text{CH}_3)_3\text{I}$ is discussed.

The Melting Point of Osmium

A. G. KNAPTON, J. SAVILL and R. SIDDALL, *J. Less-Common Metals*, 1960, **2**, (5), 357-359

The melting point was redetermined as $3045 \pm 30^{\circ}\text{C}$ by direct measurement of the black-body radiation from a hole near the centre of an electrically heated bar.

Miscibility Curves and Critical Point of the Gold-Platinum System

A. MÜNSTER and K. SAGEL, *Z. Phys. Chem. (Frankfurt)*, 1960, **23**, (5/6), 415-425

Miscibility curves and the critical point of the system were determined by measurement of electrical conductivity. The critical temperature, t_k , is given as $1252 \pm 1.5^{\circ}\text{C}$ and the critical atomic fraction of Pt, x_k , is 0.40 ± 0.007 . The results of a study of the shape of the miscibility curves were compared with the Fuchs theory of lattice models.

Nitrides of Iron with Nickel, Palladium, and Platinum

H. H. STADELMAIER and A. C. FRAKER, *Trans. Met. Soc. A.I.M.E.*, 1960, **218**, (3), 571-572

Nitrides were prepared as powders and their crystal structure was determined with a powder camera. A perovskite structure is assumed for Fe_3PdN with Pd and the interstitial nitrogen fully ordered.

New High-Coercivity Alloys in the Binary Systems Fe-Pt, Fe-Pd and Ni-Pd

Z. I. ALIZADE, *Bull. Acad. Sci. U.S.S.R., Phys. Series*, 1959, **23**, (3), 399-400 (*Izvest. Akad. Nauk S.S.S.R., Ser. fiz.*, 1959, **23**, (3), 416-417)

The magnetostriction of alloys with a wide range of Pt and Pd concentrations was investigated. Results obtained for the three systems of the relationship between saturation magnetostriction and alloy composition are shown graphically. Fe-Pt and Fe-Pd alloys have a positive maximum saturation magnetostriction. The Ni-Pd system, however, comprises a number of alloys with a high negative magnetostriction.

Elastic Constants of Palladium from 4.2 to 500°K

J. A. RAYNE, *Phys. Rev. Letters*, 1960, **4**, (8), 437-438

Extrapolation to absolute zero of the data obtained on a single crystal gives the following results:

$$c_{11} = (2.341 \pm 0.027) \times 10^{12} \text{ dyne cm}^{-2}, \quad c_{12} = (1.761 \pm 0.027) \times 10^{12} \text{ dyne cm}^{-2}, \quad c_{44} = (0.712 \pm 0.003) \times 10^{12} \text{ dyne cm}^{-2}.$$

Research on the Alloys of Noble Metals with the More Electropositive Elements. III. Micrographic and X-Ray Examination of Some Magnesium-Platinum Alloys

R. FERRO and G. RAMBALDI, *J. Less-Common Metals*, 1960, **2**, (5), 383-391

Alloys in the range 0-30 at.% Pt were prepared and examined by chemical analysis, specific gravity determination, micrographic and X-ray examination. The eutectic composition and temperature were estimated to be about 7.5-7.6 at.% Pt and 575°C , respectively. Intermediary ζ - and δ -phases were detected. The ζ -phase,

corresponding to Mg_3Pt , is face-centred cubic and the δ -phase, corresponding to Mg_3Pt , is hexagonal Na_3As type.

ELECTROCHEMISTRY

Proton Transfer between Pd/H and Pd/Pt/H Electrodes

Part 1. Equilibrium Hydrogen Electrodes

A. W. CARSON, T. B. FLANAGAN and F. A. LEWIS, *Trans. Faraday Soc.*, 1960, **56**, (9), 1311-1323

The investigation was carried out in 1N HCl without evolution of hydrogen using continuous and separated wire electrodes of Pd and Pt-Pd alloys containing 2.79, 5.73, 8.80 and 12.03 at.% Pt. It was found that polarisation of proton transfer is related to imposed changes of the hydrogen content of the electrodes. The activation energy for proton transfer was determined as 4.9 kcal/mole. The effect of proton transfer in solution upon electrical resistance measurements was studied.

Part 2. Incomplete Polarisation of Proton Transfer

Ibid., 1324-1328

Studies on specimens as above showed that when the hydrogen content of the electrodes corresponds to the coexistence of α - and β -phases, reversible concentration polarisation of proton transfer may be incomplete. Effects of the incomplete polarisation on the measurement of electrical resistance in acidic solutions were observed for the series of Pt-Pd alloys and reasons for errors are discussed.

A Study of the Adsorption Phenomena of Rhodium, Iridium, Palladium and Gold with the Potentiostatic Triangle Method

F. G. WILL and C. A. KNORR, *Z. Elektrochem.*, 1960, **64**, (2), 270-275

The adsorption of hydrogen and oxygen on the precious metals was studied. It was found that the maximum hydrogen coverage of the roughened surface was 62% for Rh, 45% for Ir, and 30% for Au. The surface coverage is dependent on the potential velocity and preliminary treatment. For each metal oxygen evolution and layer-formation commences at a different value of potential. With the exception of Ir, in the range investigated oxygen layer-formation increases up to 2.2V. Some characteristic measurements for each precious metal studied are given in a table.

The Determination of Diffusion Coefficients D_{H_2} , D_{H^+} and D_{OH^-} with a Platinum Disc Electrode

M. BREITER and K. HOFFMANN, *Z. Elektrochem.*, 1960, **64**, (4), 462-467

The apparatus with the Pt disc electrode is described. The diffusion coefficients were determined by means of the Lewitsch formula from

measurements of anodic or cathodic limiting current densities. D_{H_2} was measured in 0.5N H_2SO_4 , 5N H_2SO_4 and 0.1M Na_2SO_4 in the temperature range -10° to $60^\circ C$ from the anodic limiting current density of hydrogen molecules. D_{H^+} was obtained in weakly acid 0.1M Na_2SO_4 at $20^\circ C$ from the cathodic limiting current density of H^+ ions and D_{OH^-} was obtained in weakly alkaline 0.1 M Na_2SO_4 from the anodic OH^- ion limiting current density.

The Electrolytic Formation and Dissolution of Oxide Films on Platinum

H. A. LAITINEN and C. G. ENKE, *J. Electrochem. Soc.*, 1960, **107**, (9), 773-731

An electrolytic cell consisting of a Pt foil indicator electrode, a Pt gauze counter electrode and $HClO_4$ electrolytes of varying strengths was used in conjunction with a calomel reference electrode. The formation of surface PtO was believed to be an irreversible reaction due to a mechanism which involves a hydroxyl radical intermediate. It was concluded that the steady-state evolution occurs on a surface which has at least one atom of oxygen per surface Pt atom. A first order reduction of the surface oxide was shown experimentally. The surface oxide is reduced at potentials several hundred mV cathodic to the oxide formation potential and the rate of dissolution increases with increasing cathodic electrode potential.

Catalytic Activity and Electronic Structure of Rhodium-Palladium-Hydrogen Cathodes in Acid Solution

J. P. HOARE, *J. Electrochem. Soc.*, 1960, **107**, (10), 820-825

Hydrogen overvoltage measurements were made on Rh-Pd cathode beads containing 1, 2, 5, 10, 15, 20, 50 and 90 at.% Rh hydrogen stirred in 2N H_2SO_4 at $25^\circ C$. α - and β -phases, similar to those existing in the Pd-H system, were investigated. The mechanisms of the reactions on the various cathodes are discussed. The catalytic activity of the cathode surface for the hydrogen reaction was determined at low current densities. It is suggested that vacancies in the d -band of the cathodes make possible the strong chemical bonds between the absorbed hydrogen and the surface and that there is a direct relationship between the heat of absorption of hydrogen and the catalytic activity. The density of states at the Fermi level determines the strength of the bonds.

Electrochemical Phenomenon at the Glass-Refractory Material Interface

L. LEGER, M. BOFFE and E. PLUMAT, *Glass Technol.*, 1960, **1**, (4), 174-179

Measurements of the e.m.f. developed at the glass-refractory contact served to record continuously alkali penetration of the refractory and

to study the kinetics of the refractory attack by the molten glass. Solid-solid, solid-liquid, and liquid-liquid systems were investigated and in each case, Pt connecting plates or wires were used. The influence of the atmosphere was studied by introducing different atmospheres around two Pt wire electrodes dipping in molten glass. Both static and dynamic tests were carried out and the experimental procedures are described in detail.

Hydrogen Evolution on Platinum Electrodes. The Heats of Activation for the Component Reactions

R. PARSONS, *Trans. Faraday Soc.*, 1960, **56**, (9), 1340-1350

Measurements were made at various temperatures in 0.5M HCl of steady-state current-voltage curves in the range 4×10^{-1} to 10 Acm^{-2} using a Pt sphere electrode. The heat of activation at the reversible potential was found from the polarisation curves to be 5.2 kcal. The impedance of the electrode was measured as a function of frequency and temperature. It is estimated that the exchange current of the discharge reaction is more than 100 times that of the overall reaction, but the heat of activation is approximately the same.

Investigation of Surface Changes of a Platinum Electrode

H. GRUBITSCH and K. HECKEL, *Werkstoffe u. Korrosion*, 1960, **11**, (5), 271-273

The surface changes of a polished electrode, used as a cathode in the galvanic cell $-\text{Cd} | 0.1\text{N NaCl} || 0.1\text{N NaCl} | \text{Pt} | -$, were investigated by electron microscopy. The circuit was alternately completed and broken every 15 mins. Observed changes in the surface of the Pt electrode apparently correspond to a reconstruction of the surface and to a lessening of its activity. This decrease in surface activity explains the slow current decrease with ventilating elements, the cathodes of which are immersed in an electrolyte with constant oxygen content.

ELECTRODEPOSITION

Peculiarities of Cathodic Reduction of Platinum Metals from Complex Electrolytes

A. I. LEVIN and B. A. PANKRATOV, *J. Appl. Chem. U.S.S.R.*, 1959, **32**, (8), 1825-1831 (Transl. of *Zhur. Priklad. Khim.*, 1959, **32**, (8), 1787-1793)

Shifts of potential in absence of current in various electrolytes containing Pt metals were investigated. The potentials depend on the salt content and concentration of the electrolyte and shift in the negative direction with increasing dilution. Electrode polarisation accompanying simultaneous discharge of Pt metals from complex mother liquors was studied. It was found that

this polarisation is diminished in the presence of Cu in the electrolyte due to the simultaneous discharge of the Cu cations with the Pt metals.

LABORATORY APPARATUS AND TECHNIQUE

Compact Palladium Diffusion Leak for Hydrogen

L. A. NOBLE, W. H. SAIN and R. K. WAITS, *Rev. Sci. Instr.*, 1960, **31**, (7), 789-790

A Pd thimble ($\frac{3}{8}$ in. diameter, 0.005 in. wall thickness) is brazed to an inner Heliarc ring which is brazed to a stacked ceramic arrangement. The heater, a spiral of thoriated W wire, is located concentrically within the Pd thimble. An outer Heliarc weld ring brazed to the inlet tubulation forms the outlet assembly. The heater requires a maximum of about 5.5 amp at 5V and the Pd temperature is about 270°C at 20W with 1 atm inlet and 5-10 mm Hg outlet pressures.

Infrared Absorption Spectra of Alkali Metal Nitrates and Nitrites Above and Below the Melting Point

J. GREENBERG and L. J. HALLGREN, *J. Chem. Phys.*, 1960, **33**, (3), 900-902

Spectra of fused LiNO_3 , NaNO_3 , KNO_3 , RbNO_3 , CsNO_3 , NaNO_2 and KNO_2 were obtained by supporting the salts in the interstices of a 32 mesh Pt screen. Spectra below the melting points were obtained by allowing the salt to solidify on the screen. The screen was heated by the passage of an electric current and temperatures were measured by a Pt : 10% Rh-Pt thermocouple.

Platinum-to-Pyrex Tubular Housekeeper Seals

B. B. GRAVES, *Rev. Sci. Instr.*, 1960, **31**, (3), 349-350

A modification of the Housekeeper technique for sealing Pt to Pyrex entails reduction of the included angle of the feather edge of the Pt from 9° to between 1° and 1½°. Methods of producing the edges and of testing the seals are described.

CATALYSIS

Hydrogenation of Unsaturated Compounds in the Presence of Colloidal Palladium. XI. Hydrogenation of Vinylacetylene

KH. V. BAL'YAN and N. A. BOROVIKOVA, *J. Gen. Chem. U.S.S.R.*, 1959, **29**, (8), 2516-2519 (Transl. of *Zhur. Obshchei Khim.*, 1959, **29**, (8), 2553-2556)

The hydrogenation was carried out with ratios of vinylacetylene to hydrogen of 1:1, 1:0.75, and 1:0.5 (in moles) and the effect of various additives on the composition of the hydrogenation products was studied. It was found that without additives and at any ratio of the reactants, buty-

lenes and butane were formed together with a predominant amount of butadiene. Butylene formation falls with a decrease in the amount of hydrogen used. $Pb(C_2H_3O_2)_2$ and $Cu(C_2H_3O_2)_2$ slow the hydrogenation reaction, decrease the butylene content, and increase the yield of butadiene.

XII. Hydrogenation of Alkylacetylenes and Phenylacetylene

KH. V. BAL'YAN and N. A. BOROVIKOVA, *J. Gen. Chem. U.S.S.R.*, 1959, **29**, (8), 2520-2523 (Transl. of *Zhur. Obshchei Khim.*, 1959, **29**, (8), 2557-2559)

Some monoalkylacetylenes and phenylacetylene were hydrogenated with colloidal Pd in a CH_3COOH solution. It was found that hydrogenation proceeds selectively at the triple bond to form the corresponding olefins and styrene. After the addition of the first two atoms of hydrogen, the hydrogenation rate increases sharply and then decreases again.

Hydrogenation and Dehydrogenation

J. T. BRADBURY, W. M. KEELY, F. J. O'HARA and R. F. VANCE, *Ind. Eng. Chem.*, 1960, **52**, (9), 803-806

In this review of recent literature on hydrogenation and dehydrogenation processes, the many uses of Pt metal and other catalysts are outlined. Fundamental studies as well as many industrial processes are reviewed. (111 references.)

Purifying Hydrogen by Selective Oxidation of Carbon Monoxide

M. L. BROWN, A. W. GREEN, G. COHN and H. C. ANDERSEN, *Ind. Eng. Chem.*, 1960, **52**, (10), 841-844

Laboratory and pilot plant work in which CO in NH_3 synthesis gas was oxidised catalytically to CO_2 with air or oxygen is described. The selective oxidation process was studied in relation to hydrogen and CO content of the gas stream, oxygen/CO ratio, catalyst composition, space velocity and temperature. Effective catalysts for the reaction in the temperature range 250-320°F are supported Pt, Rh, Rh-Pt and Ru. The temperature is held within the selective range by steam dilution. In CO_2 -free gas streams, 2% CO may be reduced to 10 p.p.m. Proposed single- and two-stage oxidation units are illustrated.

A New Catalyst System for the Polymerisation of Acetylenic Compounds

L. B. LUTTINGER, *Chem. & Ind.*, 1960, (36), 1135
The system consists of a freshly prepared mixture of an hydridic reducing agent (e.g. an alkali borohydride, $LiAlH_4$ or B_2H_6) with a salt or complex of a Group VIII metal (e.g. Co, Ni, Ru, Os, Pt or Pd). This system is effective under wide variations in composition and conditions.

Derivation of an Equation for the Kinetics of Hydrogenation of Benzene by Hydrogen in the Presence of Palladium Catalysts

I. M. KOLESNIKOV, *Zhur. Fiz. Khim.*, 1960, **34**, (7), 1528-1533 (English summary)

The derived equation was applied to experimental results previously obtained using catalysts containing 1.4, 1.03, 0.49 and 0.18% Pd. It was shown that the adsorption of C_6H_6 on the catalyst is considerable. "Faiquability" of the catalyst varies inversely with the Pd content. The concept of the uniformity of the catalytic surface of Pd is shown to be applicable to this reaction.

Progress in the Study of Heterogeneous Catalysis

C. KEMBALL, *Proc. Chem. Soc.*, 1960, (Aug.), 264-274

The course of catalytic reactions has been followed by using the mass spectrometer to analyse reaction products. Types of reactions studied were (i) exchange reactions with deuterium, (ii) reactions involving deuteration, and (iii) reactions with hydrogen. Metal catalysts used in the various reactions included films of Ni, Mo, W, Pd, Pt, and Rh and some supported and wire types. In order to explain the experimental results it was necessary to consider the types of adsorbed species present on the catalysts and the manner in which the relative stabilities or reactivities of the species affect the mechanism of heterogeneous catalysis. Examples of each type of reaction are discussed. (28 references.)

Hydrogenation of Methyl Oleate in Solvents

E. R. COUSINS and R. O. FEUGE, *J. Amer. Oil Chem. Soc.*, 1960, **37**, (9), 435-438

Hydrogenation was carried out to an iodine value of about 50 at 30°C and under atmospheric pressure with the methyl oleate alone or dissolved in C_2H_5OH , C_6H_{14} , CH_3COOH or *n*-butyl ethyl ether. Of the total double bonds produced with a 10% Pd/C catalyst, with or without a solvent, 76.6-79.1% were *trans* bonds. With Raney Ni and solvents, *trans* bonds obtained were in the range 20.7-34.8%. When Raney Ni without a solvent and the Pd catalyst were used, positional isomers were formed extensively. Raney Ni with solvents gave products with a large proportion of double bonds in the 9-position.

Hydrogenation of Fatty Oils with Palladium Catalysts. V. Products of the Tall Oil Industry

M. ZAJCEW, *J. Amer. Oil Chem. Soc.*, 1960, **37**, (10), 473-475

Tall oil distillate was reduced to an iodine number of 22 using a 5% Pd/C catalyst with a pressure of 2600 psi at 200°C. The resulting tall oil fatty acids were reduced using a Pd/C catalyst and the linoleic acid, *cis*-oleic acid,

saturated acid and *trans*-isomers produced were determined. Pt, Ir, Rh and Ru were also examined for activity, selectivity and tendency to form *trans*-isomers and were found to be less suitable catalysts.

Development of Gas-Recombination Catalysts. Palladium Catalyst Development

J. P. MCBRIDE and L. E. MORSE, *U.S.A.E.C. Homogeneous Reactor Programme Quarterly Progress Report*, Apr. 30, 1960, ORNL-2947, 87-90
The sol method of preparing the Pd/ThO₂ catalyst is described. The effects of catalyst concentration and pretreatment with oxygen or hydrogen and of ThO₂ slurry concentration on catalytic activity in the hydrogen-oxygen reaction were studied. Specific activity of the sol-prepared catalyst appears to be independent of the type and concentration of the slurry solids. Pretreatment of the slurry catalyst system with hydrogen or maintaining an excess hydrogen overpressure results in a greatly increased specific activity.

Kinetics of the Reaction between Hydrogen and Oxygen on Platinum

E. N. KHAR'KOVSKAYA, G. K. BORESKOV and M. G. SLIN'KO, *Proc. Acad. Sci. U.S.S.R., Phys. Chem. Section*, 1959, **127**, (1-6), 563-566 (Transl. of *Doklady Akad. Nauk S.S.S.R.*, 1959, **127**, (1), 145-148)

A stationary flow method was used to measure the catalytic activity of a Pt wire working in the temperature range 20 to 180°C and at pressures from 50 to 750 mm with various initial reaction mixtures. The gases were circulated at 400-1100 l/hr. It was found that with a large excess of hydrogen in the gas mixture the reaction was first order with respect to oxygen. With a large excess of oxygen and with high Pt activity the reaction is first order with respect to hydrogen, but with low Pt activity the order with respect to hydrogen is reduced to 0.1-0.2. The relationship between reaction rate and the concentration of oxygen and hydrogen was studied. Results are discussed in terms of the various forms of chemisorption which occur.

Hydrogenation of Furan Compounds on Platinum and Rhodium Catalysts

N. I. SHUIKIN and I. F. BEL'SKII, *J. Gen. Chem. U.S.S.R.*, 1959, **29**, (4), 1063-1065 (Transl. of *Zhur. Obshchei Khim.*, 1959, **29**, (4), 1093-1095)
The furans were hydrogenated on Pt/C and Rh/C in the vapour phase at various temperatures. It was found that with α -alkenyl furans at 150°C, reduction of the olefin bond in the side chain gives the corresponding α -alkyl furans in 90-95% yield. On Pt/C at 150°C the furan ring reacts slowly with hydrogen, undergoing hydrogenolysis at the double bonds (20-25%) and hydrogenolysis at the 1-5 C-O bond (75-80%). At 200°C

on Rh/C, the furan ring undergoes hydrogenation into tetrahydrofuran (40%) and hydrogenolysis at the 1-5 C-O bond with the formation of the corresponding ketone (60%). On Rh/C at 300°C there is only hydrogenolysis of the furan ring.

Reaction of Polyhalomethanes with Enol-ethers of Δ^4 -3-Ketosteroids. A New Pathway to 6 α -Methylsteroids

S. LIISBERG, W. O. GODTFREDSEN and S. VANGEDAL, *Tetrahedron*, 1960, **9**, (3/4), 149-155

Reaction of enol ethers of Δ^4 -3-ketosteroids with CBr₄ affords via 6-tribromomethylsteroids the corresponding 6-dibromomethylene- Δ^4 -3-ketosteroids. Upon catalytic hydrogenolysis over Pd/SrCO₃ these are smoothly transformed into 6-methyl- Δ^6 -3-ketosteroids. Other polyhalomethanes react in a similar way with enol ethers of Δ^4 -3-ketosteroids.

The Heterogeneous Catalysis by Metals of Electron-Transfer Reactions in Solution

M. SPIRO, *J. Chem. Soc.*, 1960 (Sep.), 3678-3679

The catalytic action of Pt, Ru, Ir, Pd, and Au in the reaction $2\text{Fe}(\text{CN})_6^{3-} + 3\text{I}^- \rightarrow 2\text{Fe}(\text{CN})_6^{4-} + \text{I}_3^-$ was observed. Pt and Hg were also exposed to the reactions $2\text{Fe}^{3+} + 3\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_3^-$ and $\text{S}_2\text{O}_8^{2-} + 3\text{I}^- \rightarrow 2\text{SO}_4^{2-} + \text{I}_3^-$. Results may be explained on the hypothesis that iodide ions and oxidant ions are adsorbed on the metal surface and that electrons may be transferred between them through the metal.

The Mechanism of the Reactions between Palladium Salts and Olefins in Hydroxyl-Bearing Solvents

I. I. MOISEYEV, M. N. VARGAFK and YA. K. SYRKIN, *Doklady Akad. Nauk S.S.S.R.*, 1960, **133**, (2), 377-380

Four types of reaction studied were: (i) interaction between the $(\text{PdCl}_2 \cdot \text{C}_2\text{H}_4)_2$ complex and non-aqueous solvents; (ii) interaction between PdCl₂ and C₂H₄ in glacial CH₃COOH containing CH₃COONa; (iii) oxidation of C₂H₄ by *n*-benzoquinone in glacial CH₃COOH in the presence of PdCl₂; (iv) oxidation of C₂H₄ by *n*-benzoquinone in alcohol solution in the presence of PdCl₂. It is suggested that the decomposition of the π -complex in hydroxyl-bearing solvents entails intermediate formation of vinyl compounds. Methods of preparation of complex vinyl esters and of acetals are indicated.

Evolution of Atomic Oxygen from Platinum Surface Treated Previously with Nitrous Oxide

K. MITANI and Y. HARANO, *Bull. Chem. Soc. Japan*, 1960, **33**, (8), 1147

Atomic oxygen was evolved *in vacuo* on heating to 1400°C a Pt surface previously treated at

1100°C with N₂O at pressures of 10~50 mm Hg. A dark brown film of PtO₂ deposited on the wall of the reaction vessel. It is believed that PtO₂ formed on the Pt surface is the source of the atomic oxygen.

The Treatment of Nitric Acid Plant Tail Gas
W. FLETCHER, *Brit. Chem. Eng.*, 1960, 5, (11), 789-790

The tail gas, which usually contains 0.3-0.5% NO₂, 2-4% excess oxygen and nitrogen, may be catalytically reduced by hydrogen, CH₄ or other fuel gases. Four types of catalyst at present in use are: (i) Pt metals deposited on Al₂O₃ spheres or pellets; (ii) Pt metals on ceramic pellets; (iii) supported Ni-Cu; (iv) Pt metals deposited on crimped Ni-Cr ribbon. The designs of the reactors is discussed and operating conditions are described in detail.

Thermal and Catalytic Decomposition of Hydrocarbons

A. J. DE ROSSET and C. V. BERGER, *Ind. Eng. Chem.*, 1960, 52, (8), 711-716

Recent literature concerning the processes of thermal decomposition, catalytic cracking, catalytic reforming and dehydrogenation in petroleum refining is reviewed. Both industrial methods and research work are outlined. (100 references.)

Heterogeneous Catalysis in the Petroleum Industry

H. PICHLER, *Trans. Instn. Chem. Engrs.*, 1960, 38, (4), 225-233

The history of the development of the processes of hydrogenation, oxidation, cracking, dehydrogenation, isomerisation, reforming and polymerisation is given briefly in this review. Fundamental properties of catalytic reactions are discussed. Reaction mechanisms and properties of the Pt metal and base metal catalysts for CO-hydrogenation, catalytic cracking, reforming and Ziegler reactions are examined. (20 references.)

Kinetics of *n*-Pentane Isomerisation over Pt/Al₂O₃ Catalyst

J. H. SINFELT, H. HURWITZ and J. C. ROHRER, *J. Phys. Chem.*, 1960, 64, (7), 892-894

The investigation was carried out at 372°C in a flow reactor in the presence of added hydrogen. Pressures varied from 7.7 to 27.7 atm and the hydrogen/*n*-pentane ratio varied from 1.4 to 18. The isomerisation rate was found to be independent of the total pressure at a fixed *n*-pentane/hydrogen mole ratio and to be correlated with the *n*-pentane/hydrogen mole ratio. A mechanism by which isomerisation proceeds via an olefin intermediate, *n*-pentene, which migrates to acidic sites to isomerise, is supported by these results. The isomerisation of the intermediate olefin is the rate-controlling step.

The Correlation between the Activity of a Platforming Catalyst and Certain Physical Properties

I. V. NICOLESCU, A. POPESCU, C. FOREDA, A. PAPIA and I. BALLY, *J. Chim. Phys.*, 1960, 57, (5), 409-415

An active and thermally deactivated 1% Pt/Al₂O₃ catalyst was studied by X-ray and electrical methods. It was found that the active support material is η-Al₂O₃ and not γ-Al₂O₃. The decrease in catalyst activity results from a decrease in the degree of dispersion of the Pt as well as from deformation of the crystal lattice of the Pt. In the temperature range 429°-500°C, the specific electrical conductivity of the active catalyst in air and in hydrogen is greater than that of the deactivated catalyst. The energy of activation of the electrical conductivity increases on deactivation of the catalyst. The existence of a correlation between physical properties of the catalyst and its activity in the Platforming process are indicated.

An Investigation of Thiophene Poisoning Effect on a Platinum Catalyst under Reforming Conditions. 3. Effect of Temperature and Hydrogen Pressure

KH. M. MINACHEV, D. A. KONDRAT'EV and O. K. SHCHUKINA, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1960, (7), 1263-1266

The deactivation of a 1% Pt/Al₂O₃ catalyst in the dehydrogenation of C₃H₁₂ containing 2.65% thiophene was studied at a constant hydrogen pressure of 20 atm with pressures of 10-40 atm and temperatures of 450° and 475°C. It was found that the degree of hydrogenation increases with increase of temperature and diminishes with increasing pressures. The specific surface area of the deactivated catalysts diminishes with increased temperature, but in practice is not changed with alteration of pressure.

A Study of the Effect of the Specific Surface Area of Platinised Alumina-Silica on the Degree of *n*-Nonane Conversion. 2. Change in the Catalytic Activity of Platinised Alumina-Silica in the Course of the Carrier Treatment by Water Vapour

KH. M. MINACHEV, N. I. SHUIKIN and M. A. MARKOV, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1960, (8), 1466-1470

The investigation was carried out using 0.5% Pt/Al₂O₃/SiO₂ catalysts with varying specific surface area at temperatures of 360-450°C and a hydrogen pressure of 10 atm in a fluid system. It was found that the degree of hydrocracking is reduced with decreasing specific surface area of the catalyst. A yield of 54% *i*-C₉H₂₀ was obtained at 380°C and at 450°C with catalysts having specific surface areas of 320 m²/g and 60 m²/g, respectively.

ELECTRICAL ENGINEERING

An Investigation of the Effect of Materials Used for the Construction of Telephone Exchanges on Contact Materials Containing Silver and Palladium

H. LIPKE and W. CLEMENT, *Nachrichtentech. Z. (N.T.Z.)*, 1960, **13**, (9), 431-435

Contact materials investigated at constant temperature and humidity levels were Ag, Pd, 50% Pd-Ag and 30% Pd-Ag. Resistance changes with time were the basis for conclusions on the effects of the various materials on the contacts. Organic substances such as oil of turpentine and linseed oil mainly affect Pd-containing contacts.

CHEMICAL TECHNOLOGY

The Use of Precious Metals in Plant Construction

M. WITTUM, *Metall*, 1960, **14**, (9), 897-901

Uses of Ag, Au, Pt and their alloys in the construction of chemical plant are described. The suitability of these metals for this purpose is shown by a study of their corrosion resistance and mechanical and physical properties.

NEW PATENTS

Thermocouples

ELECTROFLO METERS CO. LTD. *et al.* *British Patent* 845,031

A thermocouple consists of an insulating sheath formed as a solid elongated block of high-refractory ceramic, the hot junction being embedded in the block close to one end and the thermocouple wires emerging from the other end. A metal cladding is provided around the block leaving the hot junction end exposed. The thermocouple wires are of platinum-rhodium 20% alloy and platinum-rhodium 40% alloy.

Purification of Ethylene

ENGELHARD INDUSTRIES INC. *British Patent* 846,077

Carbon monoxide is removed from a mixture thereof with ethylene and oxygen by passing the mixture over a rhodium-containing catalyst at 25-150°C. The catalyst is preferably rhodium on activated alumina. Another platinum group metal, e.g. platinum, may also be included.

Electrical Contacts

NORTON GRINDING WHEEL CO. LTD. *British Patent* 847,200

For the purpose of inhibiting the detrimental effects of disruption at the points of contact,

GLASS TECHNOLOGY

The Increasing Use of Platinum in the Glass Industry

KASWANT, *Sprechsaal*, 1960, **93**, (18), 473-477

Economic aspects of the world supply and consumption of the Pt metals are reviewed. The principal physical properties of these metals are given in graphical and tabular form. Examples given of the applications of Rh-Pt alloys include feeders, crucibles for melting optical glass and bushings for glass fibre manufacture. Mention is made of the use of a Be-Pt alloy for silicate melts.

TEMPERATURE MEASUREMENT

Techniques in Calorimetry. I. A Noble-Metal Thermocouple for Differential Use

E. D. WEST, *Rev. Sci. Instr.*, 1960, **31**, (8), 896-897

A 40% Pd-Au:10% Rh-Pt thermocouple for use in an adiabatic calorimeter up to 600°C is described. The e.m.f. of the thermocouple together with dE/dT values are shown on a graph.

electrical make-and-break members have, at the point of contact, a flame-sprayed coating of platinum or of an alloy of platinum with another metal of the same group.

Hydroforming Process

THE BRITISH PETROLEUM CO. LTD. *British Patent* 847,728

The first stage of a two-stage platinum reforming process for treating petroleum hydrocarbons boiling within the gasoline and naphtha ranges is carried out at at least 450°C with a catalyst of platinum on a normally acidic support rendered non-acidic by the addition of sodium; the second stage is carried out at a similar temperature using a catalyst of platinum on an acidic support. Support preferably consists of alumina.

Dehydrogenation of Alicyclic Alcohols

ENGELHARD INDUSTRIES INC. *British Patent* 849,135

An alicyclic alcohol is dehydrogenated to an alicyclic ketone by passing the alcohol at a pressure from subatmospheric to atmospheric over a catalyst consisting of ruthenium supported on carbon preferably at a temperature of 50-700°C.