

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Uranium-Platinum System

J. J. PARK and D. P. FICKLE, *J. Res. Nat. Bur. Stds.*, 1960, **64A**, (1), 107-117

The phase diagram of the system was constructed from data obtained by thermal, metallographic, and X-ray analysis. The system is characterized by two eutectics and four intermetallic compounds. One eutectic occurs at 1005°C and 12 at.% Pt and a second at 1345°C and 87.5 at.% Pt. The four intermetallic compounds are: UPt_1 , formed peritectoidally at 961°C; UPt_2 , formed peritectically at 1370°C; UPt_3 , melting congruently at about 1700°C; and $UPt_{3.5}$, formed peritectically at 1460°C. Apparent compositions of UPt_1 , UPt_2 , UPt_3 and $UPt_{3.5}$ are 50, 66.7, 75 and 83.3 at.% Pt, respectively. The maximum solubilities are 4.5 at.% U in Pt and 5 at.% Pt in γ -U. The addition of U lowers the γ - β transformation temperature of U from 767° to 705°C, and the β - α transformation temperature from 657° to 589°C.

A Study of the Palladium-Silver-Chromium Alloy System

A. T. GRIGOR'EV, E. M. SOKOLOVSKAYA, M. I. ZARGAROVA and M. V. MAKSIMOVA, *Zhur. Neorg. Khim.*, 1960, **5**, (4), 894-901

The ternary system was studied by the methods of thermal analysis, and examination of hardness, microstructure, electrical resistivity and its temperature coefficient. It was established that the region of separation of eutectics, which exists in the Ag-Cr system, spreads widely in the ternary system up to approximately 42% Pd. The greater part of the phase diagram represents a mechanical mixture. Part of the diagram, adjacent to the Pd corner, represents a ternary solution coming from the binary system Pd-Cr and adjacent in a very narrow strip to the system Pd-Ag.

An Investigation of Alloys in the Palladium-Copper-Chromium System

A. T. GRIGOR'EV, E. M. SOKOLOVSKAYA, L. N. ALTUNINA and M. V. MAKSIMOVA, *Zhur. Neorg. Khim.*, 1960, **5**, (5), 1112-1118

Methods of thermal analysis, measurement of hardness, electrical resistivity and its temperature coefficient, and examination of microstructure after annealing and quenching at 800° and 1000°C were used in the investigation. It was found that the region of separation of eutectics, which exists in the Cu-Cr system, extends into the ternary

system up to 35% Pd. A zone of mechanical mixtures occupies a large part of the phase diagram. Adjacent to the Pd corner, the diagram represents a solid solution in a region which comes from the binary system Pd-Cr and adjoins the Pd-Cu system in a narrow band. With increased temperatures the region of the solid solution increases considerably.

The Structure of the Co-Ge and Rh-Si Systems and Some Related Alloys

S. BHAN and K. SCHUBERT, *Z. Metallkunde*, 1960, **51**, (6), 327-339

The structure of several phases of the systems, which are quasihomologous to brass alloys, was investigated. Lattice structure types were determined for the following phases: $CoGe$, Co_3Ge_5 , Rh_2Si_3 , $Rh_3Si_{2.1}$, $RhSi$, Ir_2Si , Ir_3Si_2 , Ir_4Ge_5 , $IrGe_4$, Pt_4Ga , Pt_3Ga , Pt_2Ga_3 , $PtGa_3$, Pt_3Ge , Pt_3Ge_2 , $PtGe_2$, $Au_{3.5}In$, $Au_{70}Cd_{25}In_5$, $Au_{3.5}In$.

Borides of Rhenium and the Platinum Metals. The Crystal Structure of Re_7B_3 , ReB_3 , Rh_7B_3 , $RhB_{\sim 1.1}$, $IrB_{\sim 1.1}$, and PtB

B. ARONSSON, and E. STENBERG and J. ASELIUS, *Acta. Chem. Scand.*, 1960, **14**, (3), 733-741

The compounds were prepared by arc melting the metal and B powders and the crystal structures were determined by powder photography.

The Thermodynamic Properties of Silver-Palladium Alloys

J. N. PRATT, *Trans. Faraday Soc.*, 1960, **56**, (7), 975-987

Measurements were made of the e.m.f. of cells of the form Ag (pure solid) | Ag^+ | $Ag-Pd$ (solid alloys) at 1000°K with various alloy compositions. Values were obtained by observations at 1000°K and computations at 298°K for the free energies and entropies of formation of the alloys. The negative heats of formation and large negative entropies of formation found are confirmed by the calorimetric studies of Hultgren. The thermodynamic properties are considered in terms of the bond structure of the alloys.

The Importance of Precious Metals in Technology

O. LOEBICH, *Metall*, 1960, **14**, (7), 650-652

The physical and mechanical properties of Ag, Au, Ru, Rh, Pd, Os, Ir and Pt are given in a table. Characteristic properties of the precious metals are their corrosion resistance, high melting points, heat resistance, special electrical properties

and catalytic properties. Because of their chemical stability the precious metals are used for dental alloys, for apparatus in the chemical industry, and for spinnerets. Their oxidation resistance makes Ag, Au, Pt and Pd suitable for electrical contacts. The use of Pt and its alloys in the glass industry and for temperature measurement is described. Industrial uses for Ag, Pt, Pd, Rh and Ru catalysts are mentioned.

Point Defects in Platinum

G. R. PIERCY, *Phil. Mag.*, 1960, 5, (51), 201-221. Point defects were introduced into pure Pt by deformation in liquid nitrogen, by quenching in H₂O from 1600°C, and by fast neutron irradiation at 50°C. The electrical resistivity, density, lattice parameter, hardness, and X-ray line width were measured before and after the introduction of defects. Mobility of the defects was determined from changes of electrical resistivity due to heat treatment. An interpretation of the results of these measurements and a study of the reaction kinetics is given. Principal defects remaining after irradiation are single vacancies and after quenching are divacancies with activation energies for migration of 1.43eV and 1.13eV, respectively. The two principal defects remaining after deformation in liquid nitrogen are single vacancies and an unknown defect with activation energies for migration of 1.43eV and 0.73eV, respectively.

Ferromagnetism in Pd-rich Palladium-Iron Alloys

J. CRANGLE, *Phil. Mag.*, 1960, 5, (52), 335-342. A series of five alloys containing 1-16 at % Fe was used in this investigation. Intensity of magnetisation in strong fields was measured as a function of temperature and of field. Data on magnetic moments and on Curie points are presented graphically. It was found that ferromagnetism persists in disordered solid solution alloys of Fe in Pd down to 1.25 at.% Fe. Measurements of magnetic moment show that it must be associated in part with the Pd atoms and cannot be completely located on the Fe atoms. It is suggested that the ferromagnetic behaviour is due to an intrinsic tendency to ferromagnetism in Pd or to a resultant moment produced on the Pd atoms by Pd-Fe interactions.

Gas Phase Charged and Electrolytically Charged Beta-Pd-H Alloys

J. P. HOARE, *J. Electrochem. Soc.*, 1960, 107, (7), 635-639

Potential and relative resistance measurements were made on pure Pd cathodes electrolytically charged in hydrogen-stirred 2N H₂SO₄ solution. All experiments were carried out at 23°C. Open-circuit potential vs. time curves were obtained. It is shown that the β -Pd-H alloys obtained differ in their electrochemical properties from those obtained by gas-charging. In a hydrogen

atmosphere a H/Pd atomic ratio of 0.6 is obtained while on removal of the hydrogen atmosphere an H/Pd atomic ratio of about 0.35 is reached. Gas-phase charged β -Pd-H does not similarly lose hydrogen.

The Magnetisation of Ferromagnetic Binary Alloys of Cobalt or Nickel with Elements of the Palladium and Platinum Groups

J. CRANGLE and D. PARSONS, *Proc. Roy. Soc., Series A*, 1960, 255, (1283), 509-519

Binary alloys of Co with Pd, Rh, Ru, Pt, Ir and Os and of Ni with Rh, Ir and Os were prepared by melting in an argon arc furnace. Magnetisation measurements were made using a Sucksmith ring balance; high temperatures were measured by a Pt:13% Rh-Pt thermocouple, while a Pallador thermocouple was used for the Ni alloys. Graphs of spontaneous magnetisation and Curie point against composition for the f.c.c. phases of the alloys are given. The significance of the measurements is discussed in relation to some simple models, none of which explains entirely the behaviour of the alloys measured.

Ordering in CoPt-NiPt Alloys

J. C. WOOLLEY and B. BATES, *J. Less-Common Metals*, 1960, 2, (1), 11-18

Six alloys were prepared to cover the range from CoPt to NiPt in increments of 10 at.% Ni with a constant content of 50 at.% Pt. Lattice parameter values for both the ordered and disordered states were determined. Ordering temperatures were estimated by X-ray techniques. The types of ordering reaction occurring in the various alloys at various temperatures were investigated. On annealing at 500°C, NiPt and the 40 at.% Ni alloy show a continuous reaction, while the other alloys in the series show a discontinuous reaction. These latter alloys show a continuous reaction on annealing at 50°C below the order temperature. The possible percentage disregistry between the ordered and disordered structures were calculated from lattice parameter values. The possibility of producing hard magnetic materials from the alloys of smaller Ni content is discussed.

The Equilibrium Diagram of the System Molybdenum-Rhodium

E. ANDERSON and W. HUME-ROTHERY, *J. Less-Common Metals*, 1960, 2, (1), 19-28

Thermal, microscopical and X-ray methods were used in the investigation of the system above 1500°C in the composition range 40-100 at.% Rh. The hardness of the alloys was determined. An intermediate c.p.h. ϵ -phase extends from 45-82 at.% Rh, with a freezing point maximum of $2075 \pm 10^\circ\text{C}$ at about 67 at.% Rh. A peritectic horizontal at $2000 \pm 10^\circ\text{C}$ corresponds to the reaction: Liquid (92 at.% Rh) + ϵ (81 at.% Rh) \rightleftharpoons Solid solution in Rh (85 at.% Rh). Lattice spacing composition relations for the ϵ -phase are

shown graphically. Both a and c spacings contract with increasing Rh content, but the axial ratio c/a passes through a minimum at about 74 at.% Rh. The ϵ -phase of the W-Ir system shows similar characteristics, in contrast to the ϵ -phases of the Mo-Ir and W-Rh systems. Atomic volume relations of the Mo-Rh system are discussed.

Elastic Constants of Palladium from 4.2-300°K

J. A. RAYNE, *Phys. Rev.*, 1960, **118**, (6), 1545-1549
Measurements were made on a single crystal of Pd. Extrapolation of the data to 0°K gives the values $c_{11} = 2.341 \pm 0.027 \times 10^{12}$ dyne cm^{-2} , $c_{12} = 1.761 \pm 0.027 \times 10^{12}$ dyne cm^{-2} , and $c_{44} = 0.712 \pm 0.003 \times 10^{12}$ dyne cm^{-2} . The corresponding value of the Debye temperature is $\theta_0 = 275 \pm 8^\circ\text{K}$ in agreement with calorimetric data. Both shear constants show an anomalous temperature dependence which may be correlated with the temperature variation of the contribution to $C = c_{44}$ and $C' = \frac{1}{2}(c_{11} - c_{12})$, resulting from holes in the d band of Pd.

ELECTROCHEMISTRY

Effect of Hydrogen Pressure on the Hydrogen Overvoltage on Bright Rhodium

S. SCHULDINER, *J. Electrochem. Soc.*, 1960, **107**, (5), 452-457

A Rh cathode, mounted in a Teflon rod, was activated by repeated anodic and cathodic polarisation. Measurements were made at each partial pressure of hydrogen under both cathodic and anodic polarisation. The investigation was carried out at $27^\circ \pm 1^\circ\text{C}$ in pre-electrolysed 1M H_2SO_4 using a Pt anode and a Pt reference electrode. Results obtained indicate that the overvoltage mechanism is controlled by the $2\text{H}_{\text{ads}} \rightarrow \text{H}_2$ step. Kinetic parameters for the mechanism were calculated. The relationship between surface coverage with atomic hydrogen at equilibrium and the partial pressure of molecular hydrogen above the solution is interpreted by a Langmuir adsorption isotherm.

A Study of the Oxidation of Hydrogen at Platinised Platinum Electrodes

T. C. FRANKLIN and S. L. COOKE, *J. Electrochem. Soc.*, 1960, **107**, (6), 556-560

The investigation was carried out using bright Pt wire plated with Pt black as electrodes in solutions in the pH range between 2N H_2SO_4 and 2N NaOH at 25°C. Current-voltage curves obtained show three maxima which correspond to two forms of hydrogen adsorbed at the surface of the Pt and one form of adsorbed hydrogen. Hydrogen is absorbed into Pt more rapidly from NaOH solutions than from H_2SO_4 solutions. The effect of pH on the current-voltage curves suggests that adsorbed hydrogen is present as a charged species, probably H_3^+ . Results obtained by the

current-voltage curve technique are in agreement with those obtained by charging curve and a.c. bridge methods.

New Types of Platinum-Tantalum Electrodes

P. MÜLLER and H. SPEIDEL, *Metall*, 1960, **14**, (7), 695-696

The use of Ta or Ta-sheathed current-carrying members for Pt electrodes used in the manufacture of H_2O_2 and other "per" compounds is discussed, and the behaviour of a simple electrode, comprising a rod of Ta bearing a thin strip of Pt, is considered. The advantages are shown of a new form of electrode consisting of a main support of Ta-sheathed Al or Cu rod, to which are attached five Ta cross-bars which, in turn, carry four thin strips of Pt parallel with the main rod. Such electrodes provide a more uniform current and voltage distribution which permits the current density to be increased; they also give a longer service life—both of which factors help to make the process more economic.

METAL WORKING

Attempts to Improve the Forming of Rhodium and Iridium by Cladding with Platinum

G. REINACHER, *Metall*, 1960, **14**, (7), 664-668

It was found that bimetal material could be produced by cladding Rh or Ir on both sides with Pt, using a hot-rolling technique. Experiments were carried out to compare the use of the bimetal material with that of unclad Rh and Ir in a cupping method for the manufacture of laboratory apparatus. Starting with discs 0.2 x 55 mm diameter of each material, it was found that whereas the unclad Rh and Ir required 4-5 and 17 intermediate annealings, respectively, to produce cups 16 x 33 mm diameter, the Pt-clad metals required only half as many annealings. Possible applications of the bimetal materials in laboratories and the glass industry are discussed.

LABORATORY APPARATUS AND TECHNIQUE

Permeability and Diffusivity of Hydrogen through a Palladium Tube

O. M. KATZ and E. A. GULBRANSEN, *Rev. Sci. Instr.*, 1960, **31**, (6), 615-617

The construction of the Pd tube for use in a high vacuum glass system is described. Diffusion measurements were made in the temperature range 213-379°C and back pressures of 1 to 2 atm Hg were used. The tube was kept above 150°C while exposed to the hydrogen and purified hydrogen was drawn off from within the metal. Under the experimental conditions permeability is proportional to the square root of pressure and

an exponential function of reciprocal temperature. The equation for diffusion is $D_{HPd} = 4.31 \times 10^{-3} e^{-5600/RT}$. Results were reproducible to $\pm 2\%$ of the mean.

An Internally Wound Platinum-Rhodium Furnace for Use in Air up to 1900°C

P. D. S. ST. PIERRE, *Bull. Am. Ceram. Soc.*, 1960, **39**, (5), 264-266

The construction of the furnace, which may be run in neutral or oxidising atmospheres, is described in detail. A 40% Rh-Pt wire is used as the heating element because of its high melting point (1920°C) and easy workability. At 1500°C the temperature is constant to $\pm 5^\circ\text{C}$ along 3 in. of the 5 in. of the central axis of the heating chamber. It is recommended that specimens should be placed on coils of 40% Rh-Pt to avoid the effects of contamination and hot spots. A 20% Rh-Pt : 40% Rh-Pt thermocouple may be used with the furnace for temperatures up to approximately 1850°C.

CATALYSIS

The Mechanism of Hydrogenation of Benzoquinone on Platinum, Palladium-on-Calcium Carbonate, and Raney Nickel

N. M. POPOVA and D. V. SOKOL'SKII, *Russ. J. Phys. Chem.*, 1959, **33**, (11), 527-530 (Transl. of *Zhur. Fiz. Khim.*, 1959, **33**, (11), 2573-2578)

Quinone is hydrogenated to hydroquinone on Pt and Pd/CaCO₃ (except with Pt in CH₃COOH) in a zero-order reaction with a shift of potential towards the anodic region of 0.66-0.68V. The potential shift is caused by the removal of adsorbed hydrogen from the catalyst surface. On complete hydrogenation of the quinone the catalyst again becomes a hydrogen electrode. Quinone is hydrogenated to cyclohexane diol on Raney Ni. The apparent energy of activation for the hydrogenation of quinone on Pt and Pd/CaCO₃ is 1-2 kcal/mole. It is suggested that in the hydrogenation the catalysts act as electron donors, and as electron acceptors in the activation of hydrogen. In contrast to Raney Ni, the activity of Pt and Pd/CaCO₃ is not reduced by repeated hydrogenation of quinone.

Catalytic Reduction of Phenylcarbinols into Aromatic Hydrocarbons

N. I. SHUIKIN and I. F. BEL'SKII, *J. Gen. Chem. U.S.S.R.*, 1959, **29**, (3), 859-861 (Transl. of *Zhur. Obshchei Khim.*, 1959, **29**, (3), 875-877)

C₆H₅CH₂OH and ethylphenylcarbinol were hydrogenated in a flow system at 250°C and normal pressure. Catalysts used were Pt/C, Pd/C, Ni/ZnO and skeletal Ni-Al. Under these conditions, ethylphenylcarbinol may be reduced to propylbenzene in 88-95% yields. On skeletal Ni-Al, small amounts of C₆H₆ and C₆H₅CH₃ are formed in addition to insignificant amounts of

ethyl phenyl ketone. C₆H₅CH₂OH is reduced to C₆H₅CH₃ and dehydrogenated to C₆H₅CHO under the same conditions. Under the experimental conditions, aliphatic alcohols are not reduced to hydrocarbons. Pentanol-2 and heptanol-1 are dehydrogenated to pentanone-2 and heptanal respectively, the latter being decarbonylated to n-hexane.

The Role of Supports in Catalytic Hydrogenation. Part I. Specific Effects of Various Oxide Carriers on the Activity of Platinum

E. B. MAXTED and S. AKHTAR, *J. Chem. Soc.*, 1960, (May), 1995-1998

Catalysts for the liquid-phase hydrogenation of cyclohexene were prepared by depositing 0.00625 g Pt on varying amounts of ZrO₂, ThO₂, Cr₂O₃, CeO₂, MgO and ThO₂.2Cr₂O₃. A well-defined maximum for catalyst activity, characteristic for each support, was observed. The maximum activities occur at different ratios of support to Pt for each of the supports used. ZrO₂ and ThO₂ are highly active promoters; the activation effect of the other supports decreases in the order Cr₂O₃ > CeO₂ > ThO₂, 2Cr₂O₃ > MgO. There is no direct correspondence between the surface areas of the supports and their effectiveness. Electron-microscopic studies of the disposition of the Pt on the support showed that the Pt occurs centrally on the support grains.

High Temperature Changes in Alumina Structure and Activity of Platinum-Alumina Catalysts

R. F. WATERS, J. B. PERI, G. S. JOHN and H. S. SEELIG, *Ind. & Eng. Chem.*, 1960, **52**, (5), 415-416

The catalysts were heated in dry air or air saturated with water vapour and the effects of temperature and water vapour on surface area and transformation were measured. Surface areas were measured by the Brunauer-Emmett-Teller method and the structure was examined by an electron microscope. Catalyst activities were measured in a naphtha reforming test. It was found that, at high temperatures, Pt/Al₂O₃ catalysts prepared from γ -Al₂O₃ retain surface area and activity and resist transformation of the Al₂O₃ better than those prepared from ϵ -Al₂O₃. Water catalyses the effects of temperature on surface area and Al₂O₃ type, but it has less effect on the γ -catalyst.

A Low Pressure Process for the Reduction of Nitriles. Use of Rhodium Catalyst

M. FREIFELDER, *J. Amer. Chem. Soc.*, 1960, **82**, (9), 2386-2389

Basic nitriles were hydrogenated at room temperature and 2-3 atm in the presence of ammonia using a 5% Rh/Al₂O₃ catalyst. Due to the selectivity of the catalyst, hydrogenolysis of the benzyl grouping did not occur. 3-indoleacetonitrile was successfully converted to tryptamine.

Palladium Catalysts. IX. Kinetic Studies

R. W. MESCHKE and W. H. HARTUNG, *J. Org. Chem.*, 1960, **25**, (1), 137-140

Pd/C catalysts were used in the investigation. Results indicate that the hydrogenation of phenylcarbonyl compounds is a two-stage process. Reduction to the carbinol is a zero order reaction which is followed by hydrogenolysis to the hydrocarbon, a reaction of indeterminate order. The hydrogenolysis is progressively inhibited by the hydrocarbon which is formed. The substances reduced were $C_6H_5NO_2$, $C_6H_5COCH_2CH_3$, C_6H_5CHO and $C_6H_5CH_2OCOCH_3$.

Palladium Catalysts. X. Substrate-Specific and Stereospecific Centres

R. L. BEAMER, J. DOYLE SMITH, J. ANDRAKO and W. H. HARTUNG, *J. Org. Chem.*, 1960, **25**, (5), 798-801

Hydrogenation experiments were carried out on a mixture of equimolar amounts of benzyl acetate and of fumaric acid, 4-methyl-2-pentene and Schiff base using Pd/C catalysts. It was found that the mixture of benzyl acetate and fumaric acid reduces at a faster rate than for the two substrates separately. Also, the Schiff base of the racemic acyloin is reduced more quickly than the Schiff base of the D-(-)-acyloin under identical conditions. The results agree with the postulate that each substrate has an affinity for a particular site on the catalytic surface and that these sites may be different for specific compounds and specific isomers.

Reduction of 7 α -Bromosteroids with Tritium

M. GUT and M. USKOKOVIC, *J. Org. Chem.*, 1960, **25**, (5), 792-794

7 α -bromocholesterol acetate was reduced with tritium in the presence of a 5% Pd/CaCO₃ catalyst to give cholesterol-7-H³. The isotope distribution is described and a possible mechanism for this distribution is proposed.

Bonding Energy between the Surface of Metallic Catalysts and Carbon

S. L. KIPERMAN and A. A. BALANDIN, *Russ. J. Phys. Chem.*, 1959, **33**, (9), 277-281 (Transl. of *Zhur. Fiz. Khim.*, 1959, **33**, (9), 2045-2052)

A kinetic method suggested for determining the bonding energies of Ni, Fe, Pt and Pd catalysts uses the reactions of isotopic exchange, hydrogenation, and hydrogenolysis of the lower homologues of organic compounds. Calculations were made with C adjacent to single, double and triple bonds and in three-membered and aromatic rings. There is a regular increase in stability of the bonding between catalyst and C as the multiplicity of the linkage adjacent to the latter increases. The formation of three-membered and aromatic rings increases the stability of the link between catalyst and C in comparison with

the corresponding values for single—or double—bonded C. Changes in bonding energy corresponding to small variations in activity and on changing from one metal to another are comparatively low.

Catalytic Hydrogenation of Vinylacetylene for the Preparation of Butadiene. I. General Kinetic Rules of Selective Hydrogenation of Vinylacetylene in Solution

I. V. GARMONOV, A. L. KLEBANSKII and K. K. CHEVYCHALOVA, *J. Gen. Chem. U.S.S.R.*, 1959, **29**, (3), 809-814 (Transl. of *Zhur. Obshchei Khim.*, 1959, **29**, (3), 824-829)

Experimental work was carried out in a glass rocking vessel in C₂H₅OH solution using a Pd/SiO₂ gel catalyst. It was established that in the initial stages of the process and up to about 30% degree of hydrogenation (calculated on the acetylenic bond), the addition of hydrogen occurs mainly at the triple bond. Further hydrogenation with simultaneous hydrogenation of the resulting butadiene results in a difficulty separable hydrocarbon mixture. Initially the hydrogenation reaction is of zero order with respect to vinyl acetylene and of first order with respect to hydrogen. In the kinetic region (rocking rate >300 cycles/min), the reaction rate is directly proportional to the amount of catalyst and independent of the intensity of agitation. In the diffusional region of the reaction with respect to hydrogen, the reaction rate is directly proportional to the intensity of agitation and independent of the amount of catalyst. The reaction rate in both the kinetic and diffusional regions of hydrogenation is directly proportional to the partial pressure of hydrogen.

II. Effect of Various Factors on the Rate and the Selectivity of Hydrogenation of Vinylacetylene

Ibid., 815-819 (Transl. of *Zhur. Obshchei Khim.*, 1959, **29**, (3), 830-835)

The factors investigated were the nature of the catalyst support and solvent, the reaction temperature, the intensity of stirring of the solution and the pH of the medium. Catalysts used were prepared by precipitating Pd on SiO₂ gel, BaSO₄ and polyvinyl alcohol. Temperatures were in the range -16° to +20°C. It was found that the reaction proceeds unselectively at low stirring intensity. In alcoholic solution with pH >7 the reaction proceeds at a greater rate but with less selectivity than in acid or neutral media. The rate of hydrogenation with various catalyst supports corresponds to the order polyvinyl alcohol > SiO₂ gel > BaSO₄. Selectivity is unaltered by changes in the support or the solvent. The hydrogenation rate varies with the solvent used. Hg (C₂H₅O₂)₂, Cu (C₂H₅O₂)₂ and H₂S introduced into the catalyst suspension decreased the selectivity and the reaction rate.

III. Hydrogenation of Vinylacetylene by a Continuous Method

Ibid., 820-824 (Transl. of *Zhur. Obshchei Khim.*, 1959, 29, (3), 836-840)

A process used for continuous hydrogenation on a laboratory scale is described. It was shown that under conditions of uniform gas distribution and intensive stirring of the solution and with a definite proportion of hydrogen and vinyl acetylene and velocity of the gaseous mixture, the reaction products consist almost entirely of butadiene and unreacted vinyl acetylene. The catalyst retains its activity for over 200 hours. Two methods of regenerating the catalyst without loss of activity or selectivity are described.

Catalytic Oxidation. XIV. Catalytic Oxidation of Primary and Secondary Hydroxy-Compounds with Oxygen on Platinum in the Liquid Phase

K. HEYNS and L. BLAZEJEWICZ, *Tetrahedron*, 1960, 9, (1/2), 67-75

Primary alcohols may be oxidised to aldehydes or carbonic acids and secondary alcohols to ketones on Pt/C or PtO₂ catalysts under mild conditions in aqueous solution or in organic solvents. The oxidation of various alcohols was investigated systematically. The method is especially suitable for the preparation of long-chain aldehydes.

Hydrogenation and Hydrogenolysis. III. Rhodium-Platinum Oxide as a Catalyst for the Hydrogenation of the Aromatic Nucleus

S. NISHIMURA, *Bull. Chem. Soc. Japan*, 1960, 33, (4), 566-567

A PtO₂/RhO₂ catalyst was prepared and reduced with hydrogen in neutral C₂H₅OH or CH₃COOH suspension. The Rh/Pt black obtained was found to be very effective for the hydrogenation of various aromatic compounds in CH₃COOH. The catalyst is superior to Adams' Pt catalyst both in activity and in selectivity in the hydrogenation of the aromatic nucleus.

Mixed Catalysts Pd-Ag, Pd-Cu and Pd-Au in the Hydrogenation of Benzene. III. Pd-Au Catalysts

A. A. ALCHUDZHAN and E. T. KRISTOSTURYAN, *Izvest. Akad. Nauk. Armyan. S.S.R., Khim., Nauki*, 1959, 12, (5), 305-312 (*Chem. Abs.*, 1960, 54, (12), 11670 c)

Six Pd-Au catalyst samples containing 2.8-75.62 at. % Au were investigated. In the hydrogenation of C₆H₆, Au does not deactivate Pd, but hydrogen, Ag, and Cu do. Au affects the magnetic susceptibility of Pd in the same way as hydrogen, Ag, and Cu, which weaken or completely destroy it. An explanation suggested is that although the energy levels available in Pd are filled with the electrons of Au, and thus the magnetic suscepti-

bility is decreased, this occurs only at the expense of a very high heat of hydrogenation of C₆H₆. Electron pairs, formed when the energy levels of Pd are filled with the electrons of Au, decouple, so that Au does not deactivate Pd.

The Mechanism of Hydrogen Isotope Exchange on Platinum Films

G. K. BORESKOV and A. A. VASILEVITCH, *Kinetika u Kataliz*, 1960, 1, (1), 69-82

The isotopic exchange in molecular hydrogen and the exchange of adsorbed hydrogen with deuterium and tritium on Pt films at 78° and 90°K were investigated. The heterogeneous surface appears to be related to the adsorption of hydrogen. The partition coefficients of hydrogen isotopes on adsorption were determined. The kinetics of the isotopic effect were established for the molecular reaction of exchange and possible mechanisms for the process are discussed.

Contact Catalytic Oxidation in the Liquid Phase of Organic Compounds on Precious Metals. I. Oxidation of the Monophenyl Ether of Ethylene Glycol to Phenoxyacetic Acid

I. I. IOFFE, JU. T. NIKOLAEV and M. S. BRODSKII, *Kinetika u Kataliz*, 1960, 1, (1), 125-128

It was established that phenoxyethanol may be oxidised to phenoxyacetic acid with a yield up to 85% by oxygen at atmospheric pressure or air at increased pressure using Pt catalysts. The catalysts used were 5% Pt/Al₂O₃/SiO₂, 8% Pt/C, 5% Pt/αAl₂O₃ and 5% Pt/pumice. The influence of various kinetic factors on the velocity of the reaction in the liquid phase oxidation was investigated.

Development of Gas-Recombination Catalysts Palladium as a Catalyst

J. P. MCBRIDE and L. E. MORSE, *U.S.A.E.C. HRP Progress Report*, Oct. 31, 1959, ORNL-2879, 174-175 and 177

Two methods—the Westinghouse and dispersion methods—of preparing the Pd/ThO₂ slurry catalyst are described. The activity of the catalyst prepared by the latter method was found in hydrogen-oxygen recombination studies to be 10 to 20 times that of the Westinghouse-type catalyst. Results showing the activity of the dispersion-prepared catalyst in terms of reaction rate and catalyst performance index are given in a table.

Ibid., *HRP Quar. Prog. Rep.*, Jan. 31, 1960, ORNL-2920, 92

Reaction rates were measured at 280°C in aqueous ThO₂-8% U₃O₈ slurries containing Pd/ThO₂ catalyst and pressurised with oxygen. With Pd concentrations of 60 and 120 p.p.m.,

based on ThO_2 , the rates were equivalent to CPI's of 0.4 and 1.2 w/ml at 280°C and a partial pressure of 100 psi hydrogen. Studies were also made of the effect of oxygen overpressure on the reaction rate of the hydrogen-oxygen mixtures in slurries containing 120 p.p.m. Pd.

A Contribution to the Study of the Hydrogenolysis of Cyclopentane Hydrocarbons

F. GAULT, *Ann. Chim.*, 1960, 5, (5/6), 645-706

A Pt/ Al_2O_3 catalyst was used in the hydrogenolysis of methylcyclopentane and dimethyl-1-3-cyclopentane and of polymethylated cyclopentane hydrocarbons. The experimental conditions are described in detail in the case of simple hydrocarbons. The composition of the catalyst was studied as a function of the dispersion of Pt on the support and the effects of temperature and pressure on the properties of catalysts of high and low Pt content were investigated. The mechanism of the isomerisation and demethylation reactions which occur with the polymethylated hydrocarbons is discussed. The effect of thermal treatment on dispersion of the Pt and the relationship between the speed of cleavage of γ and α bonds and the Pt content of the catalyst were studied. The temperature has no influence on the composition in the case of low concentration catalysts, but in the case of high concentration catalysts the speed of secondary-tertiary bond cleavage increases with temperature. When the catalyst is very strongly poisoned, the speed of cleavage diminishes. Steric effects explain these results.

Precious Metal Catalysts. Industrial Uses, Research and Production Control. A Survey

E. KOBERSTEIN, *Metall.*, 1960, 14, (7), 669-676

This survey covers compact, homogeneous and supported catalysts and their applications in chemical industry. Among the supported Pt catalysts are those used in reforming, isomerisation, gas purification and isotope exchange processes. Methods of determining the structure, texture and mechanical properties of the catalysts are surveyed. The characterisation of catalytically active surfaces, and the chemical analysis and activity tests of the catalysts are also described. (77 references.)

Effect of Nitrogen or Sulphur Compounds on the Poisoning of Platinum Reforming Catalyst

T.-Y. LIN and Y.-C. CHENG, *Wu Han Ta Hsueh, Tzu Jan K'o Hsueh Hsueh Pao*, 1959, 5, 32-56 (*Chem. Abs.*, 1960, 54, (6), 5987c)

It was found that Pt loses its basic catalytic activity in the presence of 0.3% N or S, but that the poisoned catalyst may be reactivated by fresh hydrocarbons. The poisoning of Pt obeys the mechanism of selective adsorption. N compounds have higher selectivity to the isomerisation centre and S has higher selectivity to the

hydrogenation centre. Increased temperature increases the resistance of Pt to poisoning, but, in the presence of S and cyclohexane, its activity decreases with increased pressure. The relation between pressure and dehydrogenation activity is: $A = -ap + b$, where $A = \%$ dehydrogenation activity, $p =$ pressure in mm, $a = -3.272 \times 10^{-1}$, and $b = 16.2$. In *n*-octane containing N, the isomerisation activity of Pt increases with the increased pressure. The activity of Pt decreases with increased flow rate. Greater poisoning of Pt is shown by elements with higher atomic weight and more free electrons and by compounds with greater complexity for the non-poisonous portion of the molecule.

A Study of the Catalytic Hydrogenation of Hydroxybenzenes over Platinum and Rhodium Catalysts

B. L. STUMP, *Diss. Abs.*, 1959, 20, (4), 1197

Adams' Pt and 5% Rh/ Al_2O_3 catalysts were used in the study. The kinetics of the hydrogenation are first order in hydrogen pressure, zero order in acceptor concentration and directly proportional to catalyst weight. With Pt catalyst, there is extensive hydroxyl cleavage, but with Rh catalyst there is little. The extent of the cleavage is influenced by the reaction temperature and structure of the acceptor. A mechanism for the hydrogenation involving the formation of hydroxycyclohexane intermediates is proposed. A method for the preparation of 1,3-cyclohexanedione was developed.

CHEMICAL TECHNOLOGY

Bursting Discs Protect Chemical Plant

J. E. PHILPOTT, *Metall.*, 1960, 14, (7), 662-664

The function of bursting discs in the protection of closed vessels is outlined. Materials which may be used for bursting discs include Al, Ni, Cu, Monel metal, stainless steel, Ag, Au, Pd, Pt and graphite. Bursting disc assemblies and their location in the plant to be protected are described.

TEMPERATURE MEASUREMENT

The Total Radiation Pyrometer, the Immersion Thermocouple and Temperature Measurement in a Steel Foundry

I. HARVENG and J. MAROT, *Silicates Indust.*, 1960, 25, (5), 235-242 and 1960, 25, (6), 297-303

A total radiation pyrometer was used for measuring the bath temperature of a Thomas static converter. Calibration of the pyrometer was effected by comparing its record at the end of the blowing of the charge with measurements obtained with a Pt:13% Rh-Pt immersion thermocouple. With the aid of the pyrometer, the final temperature of the bath was estimated to $\pm 18^\circ\text{C}$ in the

range 1560–1670°C. The causes of errors in the pyrometer measurements are explained. Precautions to be taken in the use of immersion thermocouples in steelworks are described and causes of error in their use are also given in detail. (16 references.)

Modern Trends in Resistance Thermometry
P. H. STIRLING and H. HO, *Ind. Eng. Chem.*, 1960, **52**, (7), 49A–51A

Developments which have improved the performance of noble metal and other thermocouples and resistance thermometers are described.

NEW PATENTS

Low-stress Electrodeposited Rhodium

SEL-REX CORP. *British Patent* 836,475

Rhodium is deposited from an aqueous sulphuric acid bath containing rhodium sulphate and magnesium sulphamate—preferably 30 g/l, dissolved therein.

Hydrogenation of Aromatic Amino Compounds

ABBOTT LABORATORIES *British Patent* 836,951

A ruthenium hydrogenation catalyst is used in a process of catalytically hydrogenating aromatic amino compounds to produce the corresponding alicyclic amino compounds by passage of the aromatic compound through a reaction zone for reaction with hydrogen at 200–260°C in the presence of the catalyst. Ruthenium metal supported on activated carbon pellets or an oxide or salt of ruthenium may be used.

Spinning Nozzles

W. C. HERAEUS G.M.B.H. *British Patent* 837,236

A spinning nozzle is composed of an alloy of palladium with 7–15% iridium and 15–30% rhodium. Up to 15% of the palladium may be replaced by other platinum group metals. The alloy is easily machinable and polishable, chemically and mechanically stable and heat-treatable.

Electrodeposition of Platinum

THE MOND NICKEL CO. LTD. *British Patent* 838,350

Platinum is deposited from an aqueous acidic chloride-chloroplatinate electrolyte containing 180–300 g of anhydrous hydrogen chloride per l and 10–50 g of platinum per l at 45–90°C, the conditions of electrolysis being such as to maintain the rate of deposition of platinum on the cathode such that, when plotted against the hydrogen chloride concentration, it lies within a specified area shown on the drawing.

Brazing and Alloys therefor

THE MOND NICKEL CO. LTD. *British Patent* 838,949

A brazing alloy contains 10–60% copper, 10–50% nickel, 1–30% manganese and balance of at least 10% palladium. The alloy is stated to be superior to existing alloys used for joining metal parts at temperatures of 550°C and above.

Brazing and Alloys therefor

THE MOND NICKEL CO. LTD. *British Patent* 838,950

A ternary copper-palladium-manganese brazing alloy has a composition falling within an area A-B-C-D of a ternary diagram, the area being bounded by lines joining the following points:

Pd	Cu	Mn
20	36	44
35	28	37
44	30	26
47	38.5	14.5
43	47	10
40	50	10
10	48	42

Brazing

THE MOND NICKEL CO. LTD. *British Patent* 838,951

Metal parts for use at 550°C and above are brazed with a ternary copper-palladium-nickel alloy falling within a specified area of a ternary Cu-Pd-Ni diagram shown, the area being bounded by lines joining the following points:

Pd	Ni	Cu
21	10	69
50	10	40
56	20	24
49	40	11
30	57	13
15	60	25
10	55	35
10	25	65

Catalytic Reforming

SOCONY MOBIL OIL CO. INC. *British Patent* 839,106

A hydrocarbon mixture boiling in the gasoline range is reformed by contacting it with a catalyst consisting of a mechanical mixture of particles of less than 10 microns diameter of (1) a porous inert carrier on which is deposited a platinum group metal in amount to give 0.05–5% by wt. of the metal in the final catalyst and (2) eta alumina activated with halogen in amount to give a final halogen content of 0.1–0.9%. The resulting mixture has a dehydrogenation activity of at least 50 and an acid activity of at least 0.2.

Isomerisation of Alkanes

ENGELHARD INDUSTRIES INC. *British Patent* 839,421

A catalyst composition for isomerisation of light normal alkanes consists of 0.05–5% by wt. palladium (based on total catalyst wt.) on a support of 5–25% borica and remainder alumina. The alumina consists of gamma-alumina modi-