

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### The Phase Diagram and Properties of Palladium-Iridium-Silver Alloys

A. A. RUDNITSKII and V. P. POLYAKOVA, *Zhur. Neorg. Khim.*, 1962, 7, (1), 151-156

The microstructure and properties of the ternary alloys containing up to 50 wt.% Pd were studied and the phase diagram of that part of the system was constructed. Changes in the properties of the alloys in the solid solution region indicate the possibility of ageing. Additions of 1 wt.% Ag to Pd-Ir alloys impairs their mechanical working. Up to 2 wt.% Ir added to Pd-Ag alloys increases their strength and hardness with practically no change in electrical resistivity and its temperature coefficient.

### The Constitution Diagram of the Palladium-Tellurium System

Z. S. MEDVEDEVA, M. A. KLOCHKO, V. G. KUZNETSOV and S. N. ANDREEVA, *Zhur. Neorg. Khim.*, 1961, 6, (7), 1737-1739

The system was investigated by thermal and X-ray analysis, examination of microstructure, and by measurement of microhardness and electrical conductivity. A phase diagram was constructed for the region from 0 to 80 at.% Pd. The intermediate compounds PdTe<sub>2</sub> and PdTe melt at 740°C and 720°C, respectively, while Pd<sub>2</sub>Te, Pd<sub>3</sub>Te and Pd<sub>4</sub>Te are formed by peritectic reactions at 590°, 760°, 820° and ~1000°C, respectively. In the Te-PdTe<sub>2</sub> region there are two-phase alloys which form a eutectic at 440°C near pure Te. Alloys representing an uninterrupted series of unstable solid solutions are formed in the PdTe<sub>2</sub>-PdTe region in the temperature range 640°-690°C.

### The Constitution Diagram of the Niobium-Palladium System

E. M. SAVITSKII, V. V. BARON and A. N. KHOTINSKAYA, *Zhur. Neorg. Khim.*, 1961, 6, (11), 2603-2605

Physico-chemical analysis methods were used to construct the phase diagram. Two chemical compounds found in the system are: Nb<sub>2</sub>Pd, with tetragonal crystal structure, which is formed by a peritectic reaction at 1650°C, and the Kurnakov compound, Pd<sub>3</sub>Nb, which is formed at 1700°C. Nb and Pd are mutually soluble over a wide region in the solid state. Small additions of Nb increase the hardness and strength of Pd alloys and reduce the temperature coefficient of electrical resistivity, but have little effect on the magnitude of the electrical resistivity.

### Phase Relationships in Tantalum-Rich Tantalum-Ruthenium Alloys at 1500°C

C. S. HARTLEY, W. L. BAUN, D. W. FISHER and E. J. RAPPERPORT, *Wright Air Development Division Technical Note WADD-TN-60-288*, Mar. 1961, 18 pp., PB 171823

Alloys containing 10, 20, 30, 40, 45 and 50 at.% Ru were heat-treated for 168 h at 1500°C and quenched. The structure and lattice parameters of the alloys were determined. The solubility of Ru in Ta at 1500°C lies between 20 and 30 at.%. An intermediate phase TaRu exists from between 20 and 30 at.% Ru to 48 ± 2 at.% Ru. The 50 at.% Ru alloy is two-phase.

### The Constitution Diagram of the Ruthenium-Chromium System

E. M. SAVITSKII, V. F. TEREKHOVA and N. A. BIRUN, *Zhur. Neorg. Khim.*, 1961, 6, (8), 1960-1962

The system was investigated by various methods of physico-chemical analysis and the constitution diagram was constructed. Two peritectic reactions occur: liq. + β ↔ σ at 1600°C, and liq. + σ ↔ α at 1470°C. The σ-phase coincides with the compound Cr<sub>2</sub>Ru, α represents the solid solution of Ru in Cr, and β represents the solid solution of Cr in Ru. Cr<sub>3</sub>Ru is formed at low temperatures from α solid solution and σ-phase. The solid solubility of Ru in Cr extends from about 42 wt.% Ru at room temperature to about 47 wt.% Ru at the melting temperature. Hardness and crystallographic data are given for some of the alloys.

### The Order-Disorder Transformation in Iron-Cobalt-Palladium Alloys

A. T. GRIGOR'EV and V. V. KUPRINA, *Zhur. Neorg. Khim.*, 1961, 6, (8), 1891-1901

Phase changes in Fe-Co-Pd alloys were studied at temperatures below 1000°C. Alloys in the following sections of the system were studied: Pd<sub>3</sub>Fe-Co, Pd<sub>2</sub>Fe-FeCo, PdFe-Co, PdFe-FeCo, and FeCo-Pd. Hardness measurements were made on numerous samples in the annealed and quenched states and electrical resistivity data were also obtained. A ternary phase diagram of the systems investigated is given. The microstructure of various alloys is described.

### Nickel-Ruthenium Alloys

E. RAUB and D. MENZEL, *Z. Metallkunde*, 1961, 52, (12), 831-833

The system was studied by thermal analysis and by X-ray and microscopic methods. A peritectic reaction occurs at 1490°C and there is a wide

region of solid solution at this temperature. Between 1490°C and 600°C, the solubility of Ru in Ni decreases from 29.7 at.% to 3.1 at.%, and the solubility of Ni in Ru decreases from 48.7 at.% to 7.2 at.%. Hardness increases with increasing Ru content in the Ni-rich solid solution. Alloys with up to 30 at.% Ru are easily worked by cold-rolling and cold-forging.

#### Mechanism of the Interaction of Oxygen with Surfaces of Noble Metals

V. V. ANDREEVA and N. A. SHISHAKOV, *J. Appl. Chem.*, 1961, 11, (10), 388-389

In this review the nature of the oxide film formed on Pt, Pd, Au and Ag is discussed. In the case of Pt, the formation of Pt<sub>3</sub>(O<sub>2</sub>)<sub>4</sub> on the surface is proposed. (14 references)

#### Adsorption Properties of Hydrogen and Oxygen on Platinum Black and Carbon-Supported Platinum from 20 to 300 Degrees Kelvin

R. A. FISHER, *Diss. Abs.*, 1961, 22, (2), 441

Oxygen and hydrogen adsorbed on Pt black were removed by a thermally indicated titration using hydrogen and oxygen, respectively. The cleaned Pt black sintered easily at 70-100°C, but the oxygen covered surface showed no sintering at 200°C. Hydrogen chemisorbs on carbon-supported Pt, but chemisorption of oxygen on the same material is not appreciable at 280°K. A carbon-Pt bond which prevents formation of an oxygen-Pt bond is postulated in this latter case.

#### The Preparation and Some Properties of Platinum Hexafluoride

B. WEINSTOCK, J. G. MALM and E. E. WEAVER, *J. Amer. Chem. Soc.*, 1961, 83, (21), 4310-4317

PtF<sub>6</sub> was prepared by burning a Pt wire at about 1000°C in a fluorine atmosphere and condensing the vapour on a Pyrex flask cooled by liquid nitrogen. Yields of up to 70% were obtained. Heats of transition and of fusion were calculated and vapour pressures of the two solid phases were determined. Pt has two triple points, one corresponding to a solid transformation at 3.0°C, and the other to fusion at 61.3°C. The boiling point is 69.14°C. PtF<sub>6</sub> is the most reactive and least stable of the known hexafluorides.

#### Kurnakov Phases in the Palladium-Silver System

E. M. SAVITSKII and N. L. PRAVOVEROV, *Russ. J. Inorg. Chem.*, 1961, 6, (2), 253-254 (Transl. of *Zhur. Neorg. Khim.*, 1961, 6, (2), 499-500)

Alloys of the system were examined by thermal analysis, microstructural analysis, hardness and resistivity measurements. The effect of quenching temperature on resistivity was studied. At high temperatures the Pd-Ag alloys are a continuous series of solid solutions. Changes in physical properties with composition of annealed and quen-

ched alloys indicate the formation of Kurnakov compounds with the compositions Ag<sub>2</sub>Pd<sub>3</sub> and AgPd.

#### The Crystal Structure of Ru<sub>2</sub>Si

B. ARONSSON and J. ÅSELIUS, *Acta Chem. Scand.*, 1961, 15, (7), 1571-1574

Alloys were prepared by arc-melting or sintering mixtures of pure Ru and Si. The crystal structure was elucidated from single crystal data and unit cell dimensions are a=5.27<sub>9</sub>Å, b=4.00<sub>5</sub>Å and c=7.41<sub>8</sub>Å.

#### Conductivity and Hall Constant

##### XVI. Solid Solutions of Palladium with (its) Neighbouring Elements in the Periodic System

W. KÖSTER and D. HAGMANN, *Z. Metallkunde*, 1961, 52, (11), 721-727

Measurements of susceptibility, electrical resistance, Hall coefficient and thermo-e.m.f. were made on binary alloys of Pd with Ag, Au, Cd, In, Rh, Ru, Mo, Nb and Zr. Small additions of the alloying element result in increases in resistance and the absolute value of the negative Hall coefficient, and, with the exception of Rh, in decreased susceptibility. In some cases the thermo-e.m.f. is increased by these small additions, and in others it is decreased. The changes in resistance, Hall coefficient and susceptibility are explained by the simple band model concept.

##### XVII. Application of the Two-Band Model to the Electrical Properties of Palladium

D. HAGMANN, *Ibid.*, 727-735

The parameters for Pd were determined by measurements of electrical resistance, Hall coefficient, susceptibility, thermo-electric power and the Ettinghausen-Nernst coefficient. Data obtained for both bands differ from previous measurements and calculations. These deviations may be due to neglect of interaction of the overlapping bands in use of the A. H. Wilson formula. The influence of scattering by foreign atoms is shown by alloys.

#### Surface Tension of Molten Platinum at 1800°C

P. KOZAKEVITCH and G. URBAIN, *Compt. rend.*, 1961, 253, (20), 2229-2231

The surface tension, measured by the drop method on an Al support, was found to be 1699±20 dynes/cm at 1800°C. The density of Pt at 1800°C, previously determined, is 18.82±0.02 g/c.c.

#### The Density of Silver, Copper, Palladium and Platinum in the Liquid State

L.-D. LUCAS, *Compt. rend.*, 1961, 253, (22), 2526-2528

Density values were studied as a function of temperature at temperatures above the melting

point of each metal and the results obtained are shown graphically.

### Deviations from Matthiessen's Rule for Platinum

P. G. KLEMENS and G. C. LOWENTHAL, *Austral. J. Physics*, 1961, 14, (3), 352-358

An investigation of the resistivity-temperature relationship of seventeen Pt resistors at temperatures down to 50°K indicates that the observed deviations from Matthiessen's rule may be due to the presence of small concentrations of impurities. Thus the behaviour of a resistor depends on the nature as well as the total amount of impurities and imperfections.

### Determination of the Emissivity, for Total Radiation, of Small Diameter Platinum - 10% Rhodium Wires in the Temperature Range 600 - 1450°C

D. BRADLEY and A. G. ENTWISTLE, *Brit. J. Appl. Phys.*, 1961, 12, (12), 708-711

Two lengths of 0.00057 in. diameter 10% rhodium-platinum wire, 1.425 in. and 1.064 in. long, were heated electrically *in vacuo*. The net rate of radiant energy loss from the wires, and thus the emissivity of the wire, was obtained by measurement of wire resistance and current. The resistance-temperature relationship was found for wire immersed in a horizontal electric furnace, the temperature being measured by a sheathed Pt: 13% Rh-Pt thermocouple. Emissivity values are compared with those for pure Pt.

### The Reversible Temperature Coefficient of Remanence of a Pt-Co Permanent Magnet

W. L. ZINGERY and T. M. WIRT, *Canad. J. Phys.*, 1961, 39, (9), 1384-1385

50 : 50 at. % Pt-Co magnets, operating at a permeance coefficient of 20, were temperature-cycled five times from 100°C to -60°C. Measurements then made gave a reversible temperature coefficient of -0.042%.

### Vapour Pressures of Platinum Metals. II. Rhodium

L. H. DREGER and J. L. MARGRAVE, *J. Phys. Chem.*, 1961, 65, (11), 2106-2107

Values found for the heat of sublimation of Rh at 298°K and for the normal boiling point are  $134.2 \pm 0.8$  Kcal/mole and  $3900 \pm 100^\circ\text{K}$ , respectively.

### Resistance and Hall Constant. XXI. Gold-Palladium Alloys

W. KÖSTER and T. HALPERN, *Z. Metallkunde*, 1961, 52, (12), 821-825

The dependence of resistance and Hall coefficient of the alloys on mechanical and thermal pre-treatment was measured. Changes of state were followed by this temperature dependence, and the effective mobility was also calculated. Short-

range order resulting from slow cooling or annealing of quenched and deformed samples is associated with an increase of resistance and Hall coefficient. Cold-working causes a decrease in resistance and Hall coefficient. The temperature coefficient of the Hall constant is negative for alloys with 12-95 at. % Pd.

## ELECTROCHEMISTRY

### The Effect of Organic Molecules on the Adsorptive Properties of Platinum Electrodes

M. W. BREITER, *J. Electrochem. Soc.*, 1962, 109, (1), 42-48

Impedance measurements and quasistationary potentiostatic current potential curves were used in the study of the effect of addition of amyl alcohol, caprylic acid and diphenylamine to 1 M HClO<sub>4</sub> on the adsorption of hydrogen and oxygen by a Pt wire electrode. Hydrogen adsorption decreases with increasing amyl alcohol concentration in the potential range +0.1 to +0.4 V. In the double layer region, +0.4 to +0.8 V, capacity decreases with increasing amyl alcohol concentration at constant potential. Adsorbed organic molecules are oxidised at potentials at which oxygen is adsorbed simultaneously.

### Hydrogen Overvoltage at Cathodes of 77 per cent Palladium and 23 per cent Rhodium

J. C. BARTON and F. A. LEWIS, *Nature*, 1961, 192, (Nov. 11), 549-550

23% Rh-Pd wire cathodes were used in the investigation in which  $R/R_0$  ( $R_0$  = resistance in the hydrogen-free alloy) was recorded and plotted against electrode potential. Measurements were made in 0.002 N and 0.01 N HCl. The electrodes were preactivated by (i) preflaming near white heat, (ii) plating Pd black, or (iii) plating bright Pd.

### Performance of Fractional Watt Ion Exchange Membrane Fuel Cells

E. J. CAIRNS, D. L. DOUGLAS and L. W. NIEDRACH, *Amer. Inst. Chem. Engrs. J.*, 1961, 7, (4), 551-558

The performance of about 100 hydrogen-oxygen cells with electrode areas of 11.4 sq. cm was studied. Two basic cell designs, one with a bonded Pt gauze current collector and the other with external collectors in contact with the Pt or Pd catalyst electrode layer, were investigated. Pt, Pd, Ir and Rh are suitable electrode materials for room temperature operation. Characteristic open circuit voltages are 1.07 for Pt and 0.97 for Pd electrodes. The typical current density at 0.5 V is about 30 mA/sq. cm. In the load range 8.5 to 230 ohm/sq. cm at room temperature, about 40 amp-hr./sq. cm of active area may be expected before failure due to pinhole formation in the resin electrolyte. In the temperature range 0° to 85°C, cell performance shows a maximum at 55°C.

## ELECTRODEPOSITION

### The Electrodeposition of Iridium

E. L. MACNAMARA, *J. Electrochem. Soc.*, 1962, **109**, (1), 61-63

Deposits of Ir were obtained from an aqueous solution of chloriridic acid throughout a concentration range of 1-120 g Ir/l and a current density range of 2.2 - 10.8 amp/dm<sup>2</sup>. The deposition is temperature dependent, and, depending on the temperature, the appearance of the deposits is markedly affected by the current density. Optimum operating conditions were found to be: metal concentration, 10 g/l; bath temperature, 60°C; current density, 6.6 amp/dm<sup>2</sup>; pH, approximately 2. These conditions produce a cathode efficiency of 6%, while decreasing the current density to 2.2 amp/dm<sup>2</sup> increases it to 14%. Deposits may also be obtained from sodium and potassium chloroiridates and bromoiridates. A Pt anode-Cu cathode system was used predominantly in the experimental work.

### Palladium Plating

J. E. PHILPOTT, *Electroplating & Metal Finishing*, 1962, **15**, (1), 20

The properties of Pd electrodeposits obtained from a tetrammino palladium nitrate bath are described. Details are given of hardness, specific gravity, specific resistance, electrical and thermal conductivity, and thermal e.m.f. against Pt.

### Rhodium Plating Thickness Measurements

L. MAISEL, *Metal Finishing*, 1961, **59**, (12), 50-52, 56

Methods of measurement at present used depend on metallographic mounting of a plated sample or on determination of the cathode efficiency of the plating bath at the operating current density. Suggested methods involve the use of eddy currents, X-ray fluorescence, or radioisotopes (20 references)

## LABORATORY APPARATUS AND TECHNIQUE

### A Hot-Stage Petrographic Microscope for Glass Research

T. W. BROCK, *J. Amer. Chem. Soc.*, 1962, **45**, (1), 5-7

The construction and operation of the microscope are described in detail. The magnification is  $\times 70$  and the maximum operating temperature is 2000°F. Two pieces of 10% Rh-Pt foil welded at two opposite ends to 20% Rh-Pt bars form the heating element which is suspended within a carbon block on the microscope stage. The instrument is of particular value in the measurement of glass crystal growth rates.

## CATALYSIS

### Studies on the Silk-Platinum Catalyst. I. Its Preparation and Activity

A. AKAMATSU, Y. IZUMI and S. AKABORI, *Bull. Chem. Soc. Japan*, 1961, **34**, (8), 1067-1072

A silk-Pt chelate was prepared by boiling silk fibroin with an aqueous 0.75% K<sub>2</sub>PtCl<sub>4</sub> solution for 14 to 20 min. The most active catalyst was obtained by reduction of the chelate in 1% CH<sub>3</sub>COOH with 90 kg/cm<sup>2</sup> of hydrogen at 160°C. Activity is affected by the solvent, temperature and time of activation. The catalyst may be stored in the dry state for several weeks without loss of activity. In the hydrogenation of C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>, the catalyst is about 250 times as active as a PtO<sub>2</sub> catalyst with the same Pt content.

### II. General Properties

*Ibid.*, 1302-1306

The catalyst was found to be less active in the hydrogenation of some aldehydes, unconjugated aliphatic ketones, C=C double bonds, and aliphatic nitro groups than in the hydrogenation of aromatic nitro groups. It is poisoned by CO, benzyl mercaptan, and the cupric ion. Differences in the behaviour of the catalyst from that of other Pt catalysts are attributed to the spacing of the active centres due to the structure of the silk fibroin protein.

### Catalysis of the Hydration of Acetylenic Compounds by Ruthenium (III) Chloride

J. HALPERN, B. R. JAMES and A. L. W. KEMP, *J. Amer. Chem. Soc.*, 1961, **83**, (19), 4097-4098

An aqueous Ru(III) chloride solution was used to catalyse the hydration of C<sub>2</sub>H<sub>2</sub> and several mono- and di- substituted acetylenes under mild conditions. The rate law for the conversion of C<sub>2</sub>H<sub>2</sub> to CH<sub>3</sub>CHO is  $-d[C_2H_2]/dt = k[C_2H_2][Ru(III)]$ .  $k$  varies with HCl concentration, showing a maximum value at about 4 M HCl, and depends on Cl<sup>-</sup> concentration. A reaction mechanism involving the formation of an intermediate  $\pi$ -complex is proposed.

### Reactions of Cyclanes and Alkanes in the Presence of Metals of Group VIII of the Periodic System under Hydrogen Pressure

N. I. SHUIKIN, *Ind. J. Appl. Chem.*, 1961, **24**, (1), 7-13

A study was made of the performance of supported Pt, Pd, Rh and Ru catalysts in the conversion of the ethylcyclopentane, methylcyclohexane and *n*-heptane constituents of the methylcyclohexane fraction of straight-run gasolines. Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> gel were used as catalyst supports. Experiments were carried out at 460°C and 20 atm hydrogen pressure with rapid flow rates and a 1:5 molal hydrocarbon-hydrogen ratio. The products of the processes of aromatisation, isomerisation and

hydrogenolysis were analysed and the properties of the various catalysts was compared. It is concluded that under these conditions the direction of the reactions may be influenced by the choice of catalyst.

#### Valence State of Platinum/Alumina Catalysts

R. J. BERTOLACINI, *Nature*, 1961, 192, (Dec. 23), 1179-1180

Ultra-violet and reflectance spectrophotometric measurements made on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts indicated that Pt in the soluble form is present in the octahedral plus-four valence state.

#### Isotope Exchange between Hydrogen and Liquid Ammonia in the Presence of Platinum Catalysts

R. HAUL and D. BLENEMANN, *Naturwiss.*, 1961, 48, (20), 644

Pt/C and Pt/SiO<sub>2</sub> catalysts were used in experiments to measure the exchange velocity. Measurements were made in the temperature range -70°C to +25°C and at hydrogen pressures up to 150 atm. Results obtained were compared with those obtained in the gaseous state.

#### Catalytic Exchange of *n*-Hexane and Deuterium and Some Allied Reactions on Films of Palladium and Rhodium

F. G. GAULT and C. KEMBALL, *Trans. Faraday Soc.*, 1961, 57, (10), 1781-1794

Mass spectrometric analysis was used to study the exchange of deuterium with C<sub>2</sub>H<sub>6</sub>, *n*-C<sub>5</sub>H<sub>12</sub> and *n*-C<sub>6</sub>H<sub>14</sub> on Pd films and with *n*-C<sub>6</sub>H<sub>14</sub> on Rh films. It is suggested that αβγ- triadsorbed alkanes, in addition to monoadsorbed and αβ-diadsorbed species, are involved as intermediates in the mechanism. An alternative mechanism of exchange on Rh involves the direct formation of diadsorbed hexane. Self-poisoning of the exchange by dissociated hydrocarbons occurs above 100°C on Pd, and at 0°C or above on Rh. Both oxygen and diethyl ether poison the exchange reactions on Pd and Rh. The experimental results are discussed in detail.

#### Oxidation of Olefins with Palladium Chloride Catalysts

J. SMIDT, *Chem. & Ind.*, 1962, (Jan. 13), 54-61

The history of the discovery of the reaction: C<sub>2</sub>H<sub>4</sub> + PdCl<sub>2</sub> + H<sub>2</sub>O → C<sub>2</sub>H<sub>4</sub>O + Pd + 2HCl is outlined. Complex formation and complex hydrolysis, the two main steps of the reaction, are discussed. Their mechanism involves the formation of a π-complex between the olefin and PdCl<sub>2</sub>. Non-oxidative reactions between Pd salts and unsaturated compounds, including transesterification and saponification, are also described. For the continuous direct oxidation of olefins to carbonyl compounds, CuCl<sub>2</sub> is added to the PdCl<sub>2</sub> to accelerate the reoxidation of the precipitated Pd. In the continuous oxidation of C<sub>2</sub>H<sub>4</sub> either a one-

step or a two-step process may be carried out. The commercial application of the two-step process is described.

#### The Role of Supports in Catalytic Hydrogenation. Part I. Activation Effects of Various Oxide Carriers on Palladium

E. B. MAXTED and S. I. ALI, *J. Chem. Soc.*, 1961, (Sept.), 4137-4140

A study was made of the activation effects of ZrO<sub>2</sub>, ThO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, MgO, and V<sub>2</sub>O<sub>5</sub> as supports for 6 mg Pd in the hydrogenation of 1 ml cyclohexene in alcohol at 20°C. In all cases the activity of the supported catalysts increases to a maximum and subsequently falls as the amount of the support is increased. The peak activities occur at different catalyst : support ratio for each support and vary for different specimens of the same support. Surface areas and total pore volumes of the oxide supports were measured.

#### Part II. Further Effects of Various Oxide Supports on the Activity of Palladium

E. B. MAXTED and J. S. ELKINS, *J. Chem. Soc.*, 1961, (Dec.), 5086-5090

Catalysts consisting of 6.25 mg Pt supported on various amounts of Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and Cr<sub>2</sub>O<sub>3</sub> were used in the liquid-phase hydrogenation of 1 ml cyclohexene (or 1.5 ml ethyl crotonate) dissolved in C<sub>2</sub>H<sub>5</sub>OH. ZrO<sub>2</sub> and fine-grained Al<sub>2</sub>O<sub>3</sub> were the most active supports tested. Specific surface areas and micropore volumes were measured for the supports. It is concluded that the observed difference in activity for the hydrogenation of cyclohexene and ethyl crotonate is dependent on the mean pore radius of the support. The relative surface areas of the supported Pt were determined by a poisoning method.

#### Azomethine Chemistry. I. Formation of Optically Active α-Amino Acids by Asymmetric Induction

R. G. HISKEY and R. C. NORTHROP, *J. Amer. Chem. Soc.*, 1961, 83, (23), 4798-4800

10% Pd/C or Pd(OH)<sub>2</sub>/C catalysts were used in the hydrogenation of four α-keto acids in the presence of D-(+)- and L-(-)-α-methylbenzylamine. The corresponding optically active α-amino acids were obtained.

#### Rhodium-Platinum Oxide as a Catalyst for the Hydrogenation of Organic Compounds II. Catalyst Preparation and Effects of Platinum in Rhodium-Platinum Oxide

S. NISHIMURA, *Bull. Chem. Soc. Japan*, 1961, 34, (10), 1544-1545

The Rh-Pt (7:3) oxide is prepared by fusing a mixture of the chlorides of the metals corresponding to 0.30 g Rh and 0.13 g Pt with 20 g NaNO<sub>3</sub>, raising the temperature of the mixture to 460~480°C for 10 min, and leaching the cooled melt with distilled H<sub>2</sub>O. The resulting

Rh-Pt oxide is washed with 0.5% NaNO<sub>3</sub> solution and dried over CaCl<sub>2</sub>. The activity and selectivity of Rh-Pt oxide catalysts of various compositions was studied in the hydrogenation of toluene and acetophenone and results are shown in a table. Catalysts containing 70 to 90% Rh are the most active and selective.

### The Stereochemistry of the Addition of Silicchloroform to Acetylenes. A Comparison of Catalyst Systems

R. A. BENKESER, M. L. BURROUS, L. E. NELSON and J. V. SWISHER, *J. Amer. Chem. Soc.*, 1961, **83**, (21), 4385-4389

The addition of SiHCl<sub>3</sub> to 1-pentyne, 1-hexyne, 1-heptyne, 3-methyl-1-butyne, and 3, 3-dimethyl-1-butyne was studied in the presence of Pt/C, H<sub>2</sub>PtCl<sub>6</sub>, and benzoyl peroxide catalysts. With both Pt/C and H<sub>2</sub>PtCl<sub>6</sub>, and benzoyl peroxide catalysts. With both Pt/C and H<sub>2</sub>PtCl<sub>6</sub>, stereoselective *cis* additions result in the formation of *trans* products. It is suggested that the H<sub>2</sub>PtCl<sub>6</sub> is reduced by the SiHCl<sub>3</sub> to a black solid which is the active catalyst. A *trans* addition occurred in the presence of benzoyl peroxide with four of the acetylenes. In the case of 3, 3-dimethyl-1-butyne, a mixture of *cis-trans* adducts, with the *trans* isomer predominating, and a diadduct were formed.

### Methods for the Oxidation of Propylene

P. W. SHERWOOD, *Brennstoff-Chem.*, 1961, **42**, (12), 375-377

Industrial processes for the preparation of acrolein, acetone, propylene oxide and acrylonitrile are described. A PdCl<sub>2</sub> oxidation catalyst is suggested for the oxidation of propylene according to the reaction: C<sub>3</sub>H<sub>6</sub> + PdCl<sub>2</sub> + H<sub>2</sub>O → CH<sub>3</sub>-C-CH<sub>3</sub> + Pd + 2HCl.

### Review of Recent U.S.A. Patents on Catalysts

E. SOLOMON and P. A. LEFRANCOIS, *World Petroleum*, 1962, **33**, (1), 42-44

Seventy-five catalyst patents are discussed in this review, which deals with various aspects of petroleum refining. The processes concerned are those of reforming, dehydrogenation, cracking, hydrocracking, hydrotreating, isomerisation, polymerisation, alkylation, and oxidation. Both Pt metal and base metal catalysts are discussed.

### Denmark's First Major Refinery

S. ROWBOTTOM and E. D. QUINEY, *World Petroleum*, 1962, **33**, (1), 46-49

Details of the construction of the 20,000 b/sd Dansk-Veedol Kalundborg refinery are given. The process units are an atmospheric crude distillation unit, a vacuum distillation unit, gasoline and kerosene treating units, a naphtha hydrodesulphuriser and a Platformer, a vacuum gas-oil hydrodesulphuriser, and gas recovery and LPG facilities.

### The Kinetics of Sintering of Platinum Supported on Alumina

R. A. HERRMANN, S. F. ADLER, M. S. GOLDSTEIN and R. M. DE BAUN, *J. Phys. Chem.*, 1961, **65**, (12), 2189-2194

Pt/Al<sub>2</sub>O<sub>3</sub>/Cl catalyst samples were heat-treated in air for 1 h at 593°C and then heat-treated at 564°C, 594°C and 625°C for various lengths of time up to 353 h. Fresh and heat-treated samples were examined by hydrogen chemisorption and X-ray line broadening techniques and by measurement of Pt solubility in HF. Results obtained for the chemisorptive capacity for hydrogen, rate of hydrogen chemisorption and Pt crystallite size are given. These indicate that Pt in the original catalyst is in a highly dispersed form and that the formation of Pt crystallites is a result of heat treatment.

### The Deurag-Nerag Oil Refinery at Misburg near Hanover

H. WELLER, *Erdöl u.-Kohle*, 1961, **14**, (10), 821-823

The development of the refinery since 1931 is described. The various units are described and a flow sheet of the refining processes is given. New units completed in 1961 include a Unifiner/Platformer and a top-cracking plant.

### Catalytic Decomposition of Nitric Oxide

R. R. SAKAIDA, R. G. RINKER, Y. L. WANG and W. H. CORCORAN, *Amer. Inst. Chem. Engrs. J.*, 1961, **7**, (4), 658-663

An Al<sub>2</sub>O<sub>3</sub>-supported catalyst containing 0.1% Pt and 3.0% Ni as the oxides was used in the study of the decomposition of NO in a stainless steel tubular flow reactor. The NO concentration in nitrogen was 0.404 or 0.432 vol.%. Pressures of 1 to 15 atm and temperatures in the range 800° to 1000°F were used. The decomposition rate was found to be second order with respect to NO, and retarded by atomic oxygen and excess nitrogen in the system. A reaction mechanism is proposed.

### Platinum/Charcoal Catalysts

K.-H. SCHNABEL, *Z. Chem. (Leipzig)*, 1961, **1**, (9), 274-275

The activity of various Pt catalysts supported on birch charcoal in the dehydrocyclisation of *iso*-octane to 1, 1, 3-trimethylcyclopentane is compared with that of Pt/Al<sub>2</sub>O<sub>3</sub>, Pt/C/Al<sub>2</sub>O<sub>3</sub>, Pt/SiO<sub>2</sub> and Pt/C/SiO<sub>2</sub> catalysts.

### Kinetics of the Platinum-Catalysed Hydrogen Reduction of Aqueous Cobalt Sulphate-Ammonium Acetate Solutions

R. T. WIMBER and M. E. WADSWORTH, *Trans. Met. Soc. A.I.M.E.*, 1961, **221**, (6), 1141-1148

The solutions containing H<sub>2</sub>PtCl<sub>6</sub> were reduced by hydrogen in a Pyrex-lined autoclave in the temperature range 170°-232°C and in the hydrogen partial pressure range 115-830 p.s.i.a. The reduction rate is independent of the amount of

H<sub>2</sub>PtCl<sub>6</sub> added initially and directly proportional to the hydrogen partial pressure and surface area of the Pyrex glass exposed to the solution. It is suggested that the reducible Co complex is probably Co(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O. The role of the Pt catalyst is discussed.

### Reductions with Ruthenium. II. Its Use in the Hydrogenation of Pyridines

M. FREIFELDER and G. R. STONE, *J. Org. Chem.*, 1961, **26**, (10), 3805-3808

Abstract in *Platinum Metals Review*, 1961, **5**, (3), 115

### Hydrogenation of Substituted Pyridines with Rhodium on Carbon Catalyst

M. FREIFELDER, R. M. ROBINSON and G. R. STONE, *J. Org. Chem.*, 1962, **27**, (1), 284-286

Abstract in *Platinum Metals Review*, 1962, **6**, (1), 36

### The Effect of the Method of Preparation of Platinised Charcoal on its Activity in C<sub>5</sub>-Dehydrocyclisation of Paraffins and Dehydrogenation of Cyclohexane Hydrocarbons. II. Effect of Conditions during Reduction of Platinum

A. L. LIBERMAN, K.-KH. SHNABEL' and B. A. KAZANSKII, *Kinetika i Kataliz*, 1961, **2**, (4), 547-552

The effect of various reagents (formalin, KOH) used in the preparation of platinised charcoal on its activity was studied and the existence of an activity optimum for each reagent was established. Small amounts of KOH activate the catalyst in C<sub>5</sub>-dehydrocyclisation, but deactivate it when added in larger quantities. Additions of KOH deactivate the platinised charcoal in reactions for the expansion of 5-membered rings. The results obtained indicate that C<sub>5</sub>-dehydrocyclisation of paraffins and expansion of 5-membered rings take place on different active centres.

### The Effect of $\gamma$ -Irradiation on the Activity of Platinum-Containing Catalysts

KH. M. MINACHEV and YU. S. KHODAKOV, *Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk*, 1961, (8), 1430-1432

1% Pt/Al<sub>2</sub>O<sub>3</sub> and 10% Pt/Al<sub>2</sub>O<sub>3</sub> catalysts were subjected to  $\gamma$ -irradiation before use in the decomposition of H<sub>2</sub>O<sub>2</sub> solution. It was found that the decrease in catalytic activity resulting from  $\gamma$ -irradiation increased with the amount of Pt present in the catalyst. A 1% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst which had been roasted at 1000-1050°C for 10 h did not show any change in activity after  $\gamma$ -irradiation.

### The Effect of Sulphur on the Activity and Selectivity of Platinum Reforming Catalysts

N. R. BURSIAN and G. N. MASLYANSKII, *Khim. i Tekhnol. Topliv i Masel*, 1961, (10), 6-9

The investigation was carried out at a pressure of 40 atm using an 80°-180° straight distilled benzine

fraction which contained 0.01 to 0.27% S. It was shown that an increase in the amount of S in the raw material results in increased deactivation of the catalyst and in decreases in the yield of aromatic hydrocarbons and hydrogen and in the octane rating of the gasoline produced. Removal of H<sub>2</sub>S from the circulating gases increases the stability of the Pt catalyst in the reforming process.

## GLASS TECHNOLOGY

### World's Largest Direct Melt Fibre Glass Plant

G. L. VINCENT, *Ceramic Industry*, 1961, **77**, (1), 44-50

The equipment and operating procedures of the Pittsburgh Plate Glass plant at Shelby, N.C., is described and illustrated by fifteen photographs. Twenty-four continuous-melting furnaces each contain fourteen Pt bushings. The bushings have 200-400 orifices, the diameter of which is controlled to within  $\pm 0.00025$  in. in their forming by the use of binocular microscopes. An elaborate electronic system is used to control the orifice size, orifice temperature and speed of fibre drawing.

### Further Studies of the Crystallisation of a Lithium Silicate Glass

G. E. RINDONE, *J. Amer. Ceram. Soc.*, 1962, **45**, (1), 7-12

Beads of a Li<sub>2</sub>O.4SiO<sub>2</sub> glass with varying concentrations of Pt were reheated at 600°C and 650°C and rates of crystallisation of Li<sub>2</sub>O.2SiO<sub>2</sub> were determined. Maximum crystallisation occurs with about 0.005% Pt at both temperatures. The addition of 0.005% Pt lowers the activation energy for crystallisation from 120 kcal/mole without Pt to 50 kcal/mole. Li-rich clusters in the glass 250Å in size increase up to 500Å in the presence of Pt nuclei. A silica O phase is present in glasses containing 0.025% Pt. The effectiveness of Pt as a nucleating agent in Li<sub>2</sub>O.4SiO<sub>2</sub> glass is discussed.

## TEMPERATURE MEASUREMENT

### Temperature Measurement with Resistance Thermometers

K. H. CLEMENS, *Angew. Mess- u. Regeltechnik*, 1962, **2**, (1), a1-a2 (*Sprechsaal*, 1962, **95**, (1))

The use of Pt, Ni and some semi-conductor materials in resistance thermometry is described. Pt is recommended for measurements in the temperature range -220° to 750°C and Ni for the range -60° to 180°C.

### Temperature Measurement

K. H. CLEMENS, *Angew. Mess- u. Regeltechnik*, 1961, **1**, (1), a1-a6 (*Sprechsaal*, 1961, **94**, (20))

Physical phenomena upon which methods of

temperature measurement depend are described briefly. The principles underlying the operation of thermocouples and the range of some common base metal and Pt metal thermocouple combinations are discussed. Among the other topics

discussed are the insulation and protection of thermocouple wires by ceramic materials and metal sheaths, the measurement of thermal e.m.f., errors of measurement, and calibration of thermocouples.

## NEW PATENTS

### Titanium Alloys

UNION CARBIDE CORP. *British Patent 882,184*

A titanium alloy capable of withstanding the corrosive action of non-oxidising acid contains 50% or more of titanium, a total of 0.005–5% by wt. of one or more of gold, rhenium and a platinum group metal and balance titanium alone or an alloy thereof with molybdenum or manganese or with aluminium and vanadium.

### Non-emissive Electrode

"PATELHOLD" PATENTVERWERTUNGS- & ELEKTROHOLDING A.G. *British Patent 882,480*

A non-emissive electrode for electric discharge vessels has at least part of its surface covered first with a layer of rhenium and then with a layer of a platinum group metal, both layers being of a thickness of about 1  $\mu$ . The layers may be applied electrolytically to a core of tungsten, molybdenum, tantalum, indium, zirconium or hafnium.

### Treatment of Gases

ENGELHARD INDUSTRIES INC. *British Patent 882,536*

The preferential oxidation of carbon monoxide mixed with a hydrogen-containing gas is effected by first adding water to the gaseous mixture of carbon monoxide, hydrogen, nitrogen and carbon dioxide, and then air sufficient to provide an oxygen to CO volume ratio of 3 : 1 to 0.25 : 1. The resulting mixture is then passed over a supported platinum catalyst at elevated temperature to convert the CO to CO<sub>2</sub>.

### Preparation of Cyclohexylsulphamic Acid

ABBOTT LABORATORIES *British Patent 882,752*

In the preparation of cyclohexylsulphamic acid and physiologically acceptable salts thereof, phenylsulphamic acid and salts thereof are hydrogenated in the presence of a catalytic amount of rhodium; 5% rhodium on alumina may be used.

### Purification of Waste Gases

ENGELHARD INDUSTRIES INC. *British Patent 883,944*

Waste gases containing free oxygen and oxides of nitrogen are purified by the combustion of the gases and a gaseous fuel in a first reaction zone (less than the stoichiometric amount of fuel for complete reaction being used) and in the presence of a platinum group metal – containing catalyst, cooling of the effluent gases and then the com-

bustion, in a second reaction zone, of a mixture of these gases and additional gaseous fuel also in the presence of a similar catalyst. The catalyst is preferably palladium and the fuel methane or natural gas. Inlet temperature in each zone is 200–900°C.

### Removal of Free Oxygen and Reduction of Oxides of Nitrogen in Waste Gases

ENGELHARD INDUSTRIES INC. *British Patent 883,945*

Free oxygen is removed from waste gases, and the oxides of nitrogen therein reduced, by contacting a mixture of the gases and a fuel gas containing saturated and unsaturated hydrocarbons and COS, CS<sub>2</sub> and/or H<sub>2</sub>S with a palladium, platinum, rhodium or ruthenium catalyst. Palladium or platinum, supported on a carrier, is preferably used. Inlet temperature of the gases to the catalyst is 400°–900°F.

### Selective Reduction Reactions of Oxide-containing Gases

ENGELHARD INDUSTRIES INC. *British Patent 883,946*

Selective reduction reactions of gases containing oxides of nitrogen and free oxygen are effected by combustion in a reaction zone of a mixture of the gases and ammonia in contact with a platinum group metal catalyst to reduce the oxides of nitrogen. The catalyst is preferably palladium, rhodium, ruthenium or platinum deposited on a carrier. The reaction is carried out at 150–400°C.

### Acetylene Transition Metal Carbonyl Derivatives

UNION CARBIDE CORP. *British Patent 885,514*

A stable organo-metallic carbonyl reaction product is formed by heating in a non-aqueous medium a transition metal carbonyl, e.g. ruthenium, rhodium, palladium, osmium or iridium with an acetylenic compound at a suitable temperature.

### Anodes for Electrolytic Cells

IMPERIAL CHEMICAL INDUSTRIES LTD. *British Patent 885,817*

An anode is formed of a foraminated titanium metal sheet wholly or partly covered with a platinum metal or an alloy of two or more such metals. Expanded titanium metal sheet is preferably used with platinum or rhodium.