

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

An Investigation of the Silver-Rhodium System

A. A. RUDNITSKII and A. N. KHOTINSKAYA, *Russ. J. Inorg. Chem.*, 1959, 4, (10), 1053-1056 (Transl. of *Zhur. Neorg. Khim.*, 1959, 4, (10), 2308-2312)

The system was studied by differential thermal analysis and examination of microstructure. An equilibrium phase diagram showing limited miscibility in the liquid phase is given. All the alloys were found to be mixtures of the α -solid solution of Ag in Rh and pure Ag. The solid-solubility of Ag in Rh is about 5 wt.% Ag, though it increases slightly with increase in temperature and is about 10 wt.% Ag at 1400°C. Rh is only slightly soluble in Ag; liquid immiscibility was observed in the range 25 to 99.9 wt.% Ag. The hardness, electrical resistivity, temperature coefficient of resistivity and thermoelectric properties of the alloys were examined. Ag-rich alloys have almost the same hardness, electrical resistivity and its temperature coefficient as pure Ag. Small additions of Rh increase the hardness and resistivity of Ag with maximum values at the limit of solubility, while the temperature coefficient of resistivity shows a minimum at the same composition.

The Gold-Rhodium System

A. A. RUDNITSKII and A. N. KHOTINSKAYA, *Russ. J. Inorg. Chem.*, 1959, 4, (11), 1160-1162 (Transl. of *Zhur. Neorg. Khim.*, 1959, 4, (11), 2518-2524)

The constitution of the system was determined by differential thermal analysis and studies of microstructure, Brinell hardness, microhardness, electrical resistivity, tensile strength and thermoelectric properties of annealed and quenched alloys. A phase diagram for the system, which consists of two solid solutions, shows limited liquid miscibility with the miscibility gap extending from 45 to 97.5 wt.% Au. About 5 wt.% Au dissolves in Rh to form the β -solid solution and less than 1 wt.% Rh is soluble in solid Au. These values show some increase at higher temperatures. The microstructures of quenched and annealed alloys show little difference. Small additions of Au increase the hardness of Rh which reaches a maximum at the limit of solid solubility. Additions of up to 5 wt.% Rh scarcely affect the hardness of Au for annealed alloys, but there is an increase in hardness for quenched alloys. For annealed alloys, the electrical resistivity of Au is increased by addi-

tions of Rh up to 10 wt.% and small additions of Au increase the resistivity of Rh to reach a maximum at the β -solid solution boundary.

Silver-Iridium Alloys

A. A. RUDNITSKII and V. P. POLYAKOVA, *Russ. J. Inorg. Chem.*, 1959, 4, (11), 1158-1159 (Transl. of *Zhur. Neorg. Khim.*, 1959, 4, (11), 2515-2517)

The microstructure, microhardness, electrical resistivity, thermo-e.m.f. and melting points of alloys containing up to 10% of either constituent were observed. Limited miscibility in the liquid state was found. The solubilities of Ir in Ag and of Ag in Ir are less than 0.5 and 1 wt.% respectively. Addition of Ir to Ag increases the microhardness and thermo-e.m.f., but has little effect upon melting point, electrical resistivity and its thermal coefficient. The microhardness of Ir is increased by the addition of up to 1 wt.% Ag.

An Investigation of Iridium-Gold Alloys

A. A. RUDNITSKII and V. P. POLYAKOVA, *Russ. J. Inorg. Chem.*, 1959, 4, (10), 1051-1053 (Transl. of *Zhur. Neorg. Khim.*, 1959, 4, (10), 2304-2307)

Alloys with up to 25 wt.% of either Ir or Au were studied. For all alloys, microstructure and microhardness were examined while, for Au-rich alloys, electrical resistivity and its temperature coefficient, thermoelectric power and melting point were measured. Limited miscibility was observed in the liquid state. The solubility of Ir in Au is less than 0.1 wt.% and a maximum of 2 wt.% Au dissolves in Ir. Addition of Ir increases the microhardness and resistivity of Au, but has little effect on its thermoelectric power and melting point. The microhardness of Ir is sharply increased by the addition of Au up to 2 wt.% and then remains constant.

Research on the Alloys of Noble Metals with the More Electropositive Elements. II. Micrographic and Roentgenographic Examination of the Magnesium-Palladium Alloys

R. FERRO, *J. Less-Common Metals*, 1959, 1, (6), 424-438

Thirty-nine alloys with Pd content ranging from 27.4 to 99.3 wt.% were prepared and examined. Alloys with less than 90 wt.% Pd were hard and those in the range 30-70 wt.% Pd are very brittle. Intermediary phases with compositions corresponding to $MgPd_3$, $MgPd$ (2 modifications), $Mg_{2-7}Pd$, Mg_3Pd , Mg_4Pd and Mg_6Pd were detected, and the crystallographic structure of each is described.

The Temperature Coefficient of Resistance of Pd-H Alloys

R. J. FALLON and G. W. CASTELLAN, *J. Phys. Chem.*, 1960, **64**, (1), 160-161

The hydrogen content of a Pd wire was determined at 49.3°C as a function of relative resistance. From these values and from others previously obtained at 20°C, the values of the temperature coefficient of resistance were calculated.

Evolution of Atomic Oxygen from a Platinum Surface Treated Previously with Discharged Oxygen Gas

K. MITANI and Y. HARANO, *Bull. Chem. Soc. Japan*, 1960, **33**, (2), 276

A Pt ribbon was treated with discharged oxygen. It was found on heating to 1400°C *in vacuo* that atomic oxygen was evolved. This oxygen results from the decomposition of PtO₂ on the surface of the ribbon.

Thermodynamics of the Gaseous Oxides of the Platinum-Group Metals

C. B. ALCOCK and G. W. HOOPER, *Proc. Roy. Soc., Series A*, 1960, **254**, (1279), 551-561

Experiments carried out in the temperature range 1000°-1600°C have served to identify the volatile oxide species of Pt and Rh formed in the presence of oxygen. Vapour pressures of the oxides, used to calculate the thermodynamics of their formation, were measured by means of the "transportation" technique, an oxygen/nitrogen mixture being used as carrier gas. The oxide species were found to be Pt_xO₂ and Rh_xO₂ respectively. The value of x was determined as unity by varying the activity of the metal at constant oxygen pressure by alloying with Au and Pt, respectively, and by measuring weight loss of the alloys on oxidation. Ru, Ir and Pd were studied less thoroughly by similar techniques and thermodynamic data were obtained for the proposed oxide molecules, Ir₂O₃, IrO₃ and RuO₃.

Rates of Adsorption of Hydrogen on Palladium and on Rhodium

M. J. D. LOW, *Canad. J. Chem.*, 1960, **38**, (4), 588-595

The effects of temperature and initial gas pressure on the adsorption of hydrogen on Pd/Al₂O₃ and Rh/Al₂O₃ catalysts were studied. There exist, for both gas-solid systems, three distinct and consecutive stages, each of which may be described by the Elvoich equation. Low initial pressures and high temperatures favour the early appearance of each stage. The amounts of hydrogen adsorbed on both catalysts decrease on increasing the temperatures from 0° to 400°C. Above 400°C, with increasing temperature, the rate of adsorption on Pd decrease, while those on Rh increase. An increase in the initial gas pressure over the range 10-60 mm Hg results in increased rates and extents of adsorption.

On the Preparation of Platinum Black with a Clean Surface. Preliminary Heats of Adsorption of Hydrogen

H. CHON, R. A. FISHER and J. G. ASTON, *J. Amer. Chem. Soc.*, 1960, **82**, (5), 1055-1057

A thermal titration technique (the catalytic recombination of chemisorbed oxygen with hydrogen) was used to prepare a sample of Pt black with a clean surface. Results show that the Pt black sample was originally covered with a complete monolayer of oxygen. Heats of adsorption were measured using an adiabatic Pt calorimeter, temperatures being measured with a Pt resistance thermometer. Preliminary heats of adsorption of hydrogen as a function of coverage are reported at 0°C.

Absorption of Hydrogen by Palladium-Platinum Alloys. Part I. Electrical Resistance as a Function of Hydrogen Content, and One-Atmosphere Isobars

A. W. CARSON, T. B. FLANAGAN and F. A. LEWIS, *Trans. Faraday Soc.*, 1960, **56**, (3), 363-370

A series of six Pd-Pt alloy wires with Pt content ranging from 2.79 to 18.99 at.% (5 to 30 wt.%) was used in the investigation. Hydrogen was absorbed directly from hydrogen-saturated acidic solutions or was introduced by electrolysis. Relationships between relative resistance, R/R₀, and hydrogen content, H/Me, were established at 25°C and the temperature dependence of these relationships were examined over the range 0-59°C. Values for the solubility of hydrogen in the alloys at 1 atm pressure were determined over the temperature range 0-59°C. The relationships between R/R₀ and H/Me indicate that the bonding and conduction mechanisms in the Pd-Pt alloy hydrides are similar to those operating in the Pd-H system. The relationships which were established at 25°C are applicable in the range 0-59°C.

Part 2. Kinetic Studies of Absorption from Acidic Solutions

Ibid., 371-381

The absorption of hydrogen from HCl solutions by the above series of Pd-Pt alloys was followed by the measurement of relative electrical resistance and electrode potentials. At 25°C, the rate of absorption in alloys in the range 2.79-8.80 at.% Pt is constant over a considerable range of hydrogen contents and is similar to that for Pd. On increasing the Pt content to 12.03 at.%, the absorption rate is reduced and variable. The absorption rate for the alloys is not significantly altered by changes in acid concentration over the range 0.02-1.0N HCl or by electrolytic co-conduction phenomena associated with the bridge current. For a 2.79 at.% Pt alloy, the absorption rate has a hydrogen pressure dependence of 1.00 ± 0.05 over the region of constant rate. The absorption mechanism is discussed.

Absorption of Hydrogen by Palladium-Silver Alloys

F. A. LEWIS and W. H. SCHURTER, *Naturwiss.*, 1960, **47**, (8), 177-178 (In English)

Hydrogen was absorbed at 25°C from hydrogen-saturated HCl solutions by Ag-Pd alloy wires containing 10, 20, 26, 40 and 50% Ag respectively. The course of absorption was followed by measurement of electrode potential and of relative electrical resistance, R/R_0 , of the specimens. Potential plateaux observed appear to be associated with ranges of hydrogen content over which two phases (analogous to the α - and β -phases of the Pd-H system) coexist. The plateau potential increases with addition of up to 26% Ag. The value of 6 mV for 40% Ag is lower than that found by other workers. With increase in Ag content, the equilibrium hydrogen content decreases.

The Palladium-Hydrogen Equilibrium at High Pressures and Temperatures

P. L. LEVINE and K. E. WEALE, *Trans. Faraday Soc.*, 1960, **56**, (3), 357-362

The solubility of hydrogen in Pd was determined at six temperatures between 326° and 477°C and at pressures from 25 to 990 atm. At the highest pressures, the solid phase atomic ratio H/Pd exceeds 0.59. Isotherms of the Pd-H system plotted from the results are compared with those obtained by other workers for the critical region temperatures in the same pressure range. The general features of the supercritical isotherms are reproduced by Lacher's equation for isotherms below 313°C. The electrical resistance of the solid phase with hydrogen pressures up to 1000 atm was determined at 366°, 396° and 456°C. It increases with hydrogen content until a maximum value $R/R_0 = 1.490$ is reached at $H/Pd \approx 0.4$.

Permeability and Diffusion of Hydrogen through Palladium

M. VAN SWAAY and C. E. BIRCHENALL, *Trans. Met. Soc. A.I.M.E.*, 1960, **218**, (2), 285-289

A series of steady-state permeability studies were carried out using Pd membranes 0.005, 0.010 and 0.020 in. thick. A temperature rise after establishing constant permeability resulted in a permeability increase followed by a slow loss. On cycling the temperature, no further change in permeability value for a given temperature occurred, provided the maximum temperature previously attained was not exceeded. Oxidation followed by hydrogen reduction restored initial high permeabilities and the square-root dependence on hydrogen pressure. The effect of contaminants was examined. Permeability decreased with time below 155°C at 1 atm applied pressure and was slowly restored by evacuation or heating in hydrogen at about 200°C. The formation of the intermediate β -phase Pd-H explains in part the hysteresis observed on cycling the temperature.

The Mechanism of Occlusion of Hydrogen by Palladium in Contact with Sulphuric Acid Solution

R. J. FALLON and G. W. CASTELLAN, *J. Phys. Chem.*, 1960, **64**, (1), 4-9

Experiments were carried out with Pd wire electrodes of various sizes. Attempts to obtain a stable 0.05 V potential were unsuccessful. It was found the concentration of hydrogen in Pd increases linearly with time and that the length of the potential-time plateau is dependent on wire size and hydrogen flow rate. An over-all mechanism for the occlusion is postulated as a result of a study of open circuit concentration-time and potential-time relationships. It is concluded that the diffusion of hydrogen in solution is the rate-determining step. The contributions in the mechanism of gas solution and dissociation at the surface are discussed.

Effects of γ -Radiation on the Absorption of Hydrogen in Metals

K. YOKOGAWA and T. SUGENO, *J. Jap. Inst. Metals*, 1960, **24**, (2), 113-117 (English summary)

The amount of hydrogen absorbed in Pd was estimated by change in electrical resistance. When Pd wires were immersed in acidic or alkaline solutions, no hydrogen absorption was observed during irradiation. In dilute H_2SO_4 or dilute HCl, a large amount of hydrogen was absorbed by Pd with thin oxide films formed either by anodic treatment or by γ pre-irradiation in aerated H_2O or in H_2O_2 . It is concluded that a thin oxide film is necessary for hydrogen absorption by Pd in acidic solution. The oxide film formed by heating in air did not show this effect. The results are interpreted by the photovoltaic theory of semi-conductors.

Investigations of the Electron Spin Resonance and the Electrical Resistivity of Platinum-Carbon Catalysts

C. S. NICOLAU and H. G. THOM, *Z. Anorg. Allgem. Chem.*, 1960, **303**, (3/4), 133-140

Measurements were made on Pt/C (5Pt:100C) catalysts which had been previously heated at temperatures between 50° and 1000°C. The variation with increasing temperature of the parameters of the electron spin resonance lines as well as that of the resistivity is shown to add further support to the hypothesis of "pseudo-sandwich" complexes of Pt with C.

Brunauer-Emmet-Teller (BET)-Surface Area and Morphological Investigations of Platinum-Carbon Catalysts

C. S. NICOLAU, *Z. Anorg. Allgem. Chem.*, 1960, **303**, (3/4), 127-132

The alterations of the BET-surface areas and morphological changes in the catalysts after heating in a limited supply of air to 50°-100°C

were shown to be in agreement with previously reported electron spin resonance and electrical resistivity measurements. The role of oxygen in these changes is emphasised. Results of catalytic investigations support the conclusion that, for certain reactions, concentration of free electrons is the essential part of the catalytic activity of these catalysts. Electron micrographs are reproduced.

Where to Use Platinum Group Metals

S. S. RICE, *Materials in Design Eng.*, 1960, 51, (2), 126-129

Physical and mechanical properties of the Pt metals and some of their alloys are given. Because of their corrosion resistance, Pt and its alloys are used for glass manufacturing equipment, laboratory apparatus and spinnerets. Pt metal catalysts are used extensively in the petroleum and chemical industries. The uses of the Pt metals in electrical engineering and for temperature measurement are among the other applications described.

ELECTROCHEMISTRY

Investigation on the Influence of Platinum in Mercury Electrodes on Certain Electrode Processes

W. KEMULA, Z. GALUS and Z. KUBLIK, *Bull. Acad. Pol. Sci., Ser. Sci. Chem., Geol., Geog.*, 1959, 7, (10), 723-728 (In English)

A hanging drop Hg electrode and a Pt wire electrode electrolytically coated with Hg were immersed in the same electrolyte and voltammetric curves were recorded. Solutions of Zn^{2+} , Cd^{2+} , Sn^{2+} , Sb^{3+} , Pb^{2+} , Cu^{2+} and Tl^{+} were added to the 0.1M KCl basic electrolyte. For a solution containing Zn and Sn the cathode processes for the two electrodes differ slightly. Zn does not oxidise from the amalgam anode and oxidises smoothly at the Hg electrode. The oxidation curves for Cd on the two electrodes differ slightly. Differences in the cyclic voltammetric curves were observed for solutions containing Sn^{2+} and Sb^{3+} ions separately, but not for Pb^{2+} , Cd^{2+} , Cu^{2+} , and Tl^{+} . The behaviour of the amalgam electrode is possibly due to the formation in it of intermetallic compounds with Pt.

Mechanism of the Electro-oxidation of Alcohols and Aldehydes on Platinum. III. On the Shape of the Polarisation Curves for the Oxidation of Ethyl Alcohol

G. A. BOGDANOVSKII and A. I. SHLYGIN, *Zhur. Fiz. Khim.*, 1960, 34, (1), 57-62 (English summary)

The shape of the polarisation curves obtained using platinised Pt electrodes in H_2SO_4 is determined by the condition of the electrode surface. With active electrodes a single depression in

current, associated with the appearance of adsorbed oxygen, is observed. Electrodes of low activity also give a single depression, caused by the inhibiting action of the intermediate, CH_3CHO . Two current depressions, caused by both the intermediate and by adsorbed oxygen, are observed in the case of electrodes of moderate activity.

LABORATORY APPARATUS AND TECHNIQUE

Use of a Platinum Filament in the Electron Microscope

F. W. BISHOP, *Rev. Sci. Instr.*, 1960, 31, (2), 124

A Pt filament, its top coated with a mixture of oxides, has been used to replace the W filament in the microscope. Advantages of the filament are that its low emission temperature results in a slow evaporation rate, the electron source is small, the field of illumination uniform, and the drift of illumination is small. Oxidation of the Pt is negligible.

Direct Determination of Traces of Total Oxygen in Naphthas

I. J. OITA, *Anal. Chim. Acta*, 1960, 22, (5), 439-443

In a modification of the Schütze method, the sample in a quartz spiral is pyrolysed in a SiO_2 tube. The oxygen is converted to CO_2 over Pt/C which is retained at the ends of the tube and divided into two portions by Pt gauze. A roll of Pt gauze minimises deposition of pyrolytic C on the Pt/C. Solid, highly oxygenated, non-volatile samples are contained in a Pt boat instead of a quartz spiral.

Osmium Tetroxide as General Catalyst for Oxidations in Alkaline Media

F. SOLYMOSI and J. CSIK, *Chemist-Analyst*, 1960, 49, (1), 12-13

The influence of OsO_4 on the oxidation reactions of hypochlorite, hypobromite, hypiodite, permanganate and chloramine was studied. In addition, the effect of various complex-forming substances on the rate of the reactions catalysed by OsO_4 was examined.

CATALYSIS

Nitric Acid Manufacture—Theory and Practice

H. A. SORGENT and G. F. SACHSEL, *Ind. & Eng. Chem.*, 1960, 52, (2), 101-104

NH_3 oxidation processes described are the atmospheric pressure process, the complete pressure process and the atmospheric oxidation-pressure absorption method. The three fundamental steps in the production of HNO_3 by NH_3 oxidation—oxidation of NH_3 to NO , oxidation

of NO to NO₂ and absorption of NO₂ in H₂O—are described in detail. The effects on the oxidation of NH₃ of increased temperature, pressure and gas velocity and the composition of the Rh-Pt catalyst used are stated. Factors influencing the absorption reaction are indicated. Three recently developed HNO₃ production methods—the Wisconsin process, the nuclear nitrogen fixation method and the MgNO₃ concentration process—are outlined.

Catalytic Production of N,N-Dimethylhydrazine

K. KLAGER, E. M. WILSON and G. K. HELMKAMP, *Indust. & Eng. Chem.*, 1960, **52**, (2), 119–120

N,N-dimethylhydrazine was prepared by the hydrogenation of N-nitrosodimethylamine (NDMA) using a 10% Pd/C catalyst. The effects of catalyst and NDMA concentrations, temperature, hydrogen pressure and solvent were investigated. With increasing catalyst concentration, hydrogen absorption rates increase, but there is a decrease in the yield of the hydrazine. Between 25° and 63°C the reaction is independent of the temperature. The hydrogen consumed at the completion of the reaction is inversely proportional to the temperature.

Dehydrogenation of Cyclohexane as a Function of Flow Rate and Grain Size of the Catalyst (0.5% Pt/Al₂O₃)

N. F. KONONOV, KH. M. MINACHEV and N. I. SHUIKIN, *Zhur. Priklad. Khim.*, 1959, **32**, (9), 2107–2115

The investigation was carried out at 450–470°C and 20 atm. It was found that the degree of conversion of cyclohexane changed little with variation of flow rate. Increased flow rate resulted in a slow increase in the temperature gradient between the centre and peripheral layers of the catalyst. There was evidence of a temperature gradient along the axis of the upper layers of the catalyst. The degree of conversion decreased on changing the grain size of the catalyst from 2 × 2 mm to 6 × 6 mm.

Low Pressure Hydrogenation of Ketones with Platinum Metal Catalysts

E. BREITNER, E. ROGINSKI and P. N. RYLANDER, *J. Org. Chem.*, 1959, **24**, (12), 1855–1857

Pd, Pt, Rh and Ru on high-surface C were used as catalysts for the hydrogenation, in various solvents, of aliphatic, aromatic and α,β -unsaturated ketones. Ru catalysts were activated with hydrogen before use, but the other catalysts were used directly. Rate measurements were made at 25°C and an initial pressure of 1 atm and a large ratio of catalyst to substrate was used. Pd is ineffective in the hydrogenation of aliphatic ketones, Pt is effective in aqueous acid solution and Rh and Ru were most active in neutral or basic solution. The reduction of mesityl oxide, in competition with methyl isobutyl ketone was

found to be highly selective in all cases. Hydrogenolysis and reduction of the ring occur readily with aromatic ketones. With C₆H₅COCH₃ it was found that Pd is the most effective catalyst for side-chain hydrogenation.

The Hydrogenation of Fatty Oils with Palladium Catalyst. III. Hydrogenation of Fatty Oils for Shortening Stock

M. ZAJCEW, *J. Amer. Oil Chem. Soc.*, 1960, **37**, (1), 11–14

Four Pd/C catalysts (1%, 5%, 2% and 0.5% Pd) and four Pd/C catalysts containing 1% Pd, with 0.9%, 1.0%, 0.35% and 0.5% Ag, and 0.6%, 0.35%, 0.25% and 0.35% Bi, respectively, were used in this laboratory investigation. It was found that natural unsaturated oils may be hydrogenated to give the desired low content of *trans* isomers by using very mild operating conditions. The operating variables studied were agitation, pressure, temperature, catalyst deactivation, concentration of Pd on the carrier and in the oil, and type of feed.

IV. Pilot-Plant Preparation of Shortening Stocks

M. ZAJCEW, *J. Amer. Oil Chem. Soc.*, 1960, **37**, (3), 130–132

2% and 5% Pd/C catalysts were used for the hydrogenation of soybean and 70/30 soybean/cotton-seed oils. The hydrogenation procedure is described. Results of the pilot-plant work differ slightly from those obtained in the laboratory. Selectivity is lower, but remains constant though catalyst activity decreases with re-use. The *trans* content is somewhat higher than that obtained in the laboratory, but the rate of increase with increased operating temperatures is lower. With re-use of catalyst the processing time is increased, but it decreases sharply with increase of temperature. It is possible by controlled processing to produce a commercially acceptable shortening.

The Catalytic Decomposition of Ammonia on Evaporated Metal Films

S. R. LOGAN and C. KEMBALL, *Trans. Faraday Soc.*, 1960, **56**, (1), 144–153

Films of Ni, Rh, Co, Pd, Pt, Ru, Re, V, W and Ta were used in this investigation. Activation energies and pressure dependences were determined for Ni, Rh, Co, Pt, Ru and Re. Nitride formation was observed with V, W, and Ta. An activation energy was found for W, but results for Ta and V were not reliable. With all the metals, sintering occurred in the presence of gases as they were heated to the reaction temperatures (300–500°C). Additional sintering occurred with Pt during reactions above 550°C. Values for the pressure dependences support the theory of Temkin and others that the rate-determining step of the decomposition is the desorption of nitrogen from the catalyst surface.

The Catalytic Decomposition of Cyclohexylamine and Allied Reactions on Evaporated Platinum Films

R. L. MOSS and C. KEMBALL, *Trans. Faraday Soc.*, 1960, **56**, (1), 154-160

The decomposition of $C_6H_{11}NH_2$ to NH_3 , C_6H_6 and C_6H_{12} was studied in the temperature range 100-150°C. For each experiment a fresh Pt film was deposited on the walls of the reaction vessel. Hydrogen and deuterium used in the investigation were purified by diffusion through heated Pd. It was found that C_6H_6 is hydrogenated to C_6H_{12} only after the decomposition of most of the $C_6H_{11}NH_2$. Allied reactions studied in order to explain the reaction mechanism were the decomposition of $C_6H_5NH_2$ and the hydrogenation, exchange and deuteration of C_6H_6 in the presence of $C_6H_{11}NH_2$. It is postulated that the rate-determining step is the fission of the C-N bond on the catalyst surface. Before the $C_6H_{11}NH_2$ decomposes, hydrogen atoms are dissociated from the adsorbed molecules, radicals of the type C_6H_5N or C_6H_5NH being formed.

The Use of Dual Function Catalysts in Isomerisation of High Molecular Weight *n*-Paraffins

J. W. GIBSON, G. M. GOOD and G. HOLZMAN, *Indust. & Eng. Chem.*, 1960, **52**, (2), 113-116

A pelleted 0.3% Pt/0.4% Cl/0.2% F/ Al_2O_3 catalyst was used in the hydroisomerisation at 420-430°C of purified *n*-C₂₀, *n*-C₂₉ and *n*-C₄₈ paraffins. Products were distilled into fractions of lower molecular weight and a concentrate of isomers and unchanged wax. Isomer oils were isolated and their physical properties studied in order to elucidate their molecular structures. The chief reactions under the specified conditions are isomerisation and cracking. At about constant conversion, cracking increases relative to isomerisation as the molecular weight of the feed is increased. With a rise in C number of the feed, solid isomer formation relative to liquid isomers increases. Lubricant base stocks of high viscosity and low pour point are produced.

Study of Properties of Metal-Oxide Catalysts for Gasoline Reforming. VI. Reforming of 89.5-126°C Gasoline Fraction of the Volga-Ural Group of Petroleum on Palladium-Alumina-Silica Catalyst

KH. M. MINACHEV, M. A. RYASHCHENTSEVA and N. I. SHUKIN, *Akad. Nauk SSSR, Izvest. Otdel. Khim. Nauk*, 1959, (10), 1813-1817.

Four 0.5% Pd/ Al_2O_3 / SiO_2 catalysts which differed in specific surface area were used in this investigation. Two of the catalysts showed considerable aromatising properties and stability. For all the catalysts there was complete desulphurisation of the first fraction. It is implied that the aromatisation process results in six- and five-membered cyclic compounds and *n*-alkanes.

New Data on the Gilsonite Process

L. P. MORRIS, *Chem. Eng. Progress*, 1960, **56**, (4), 49-53

The functions of the various units operated in the refining of the solid hydrocarbon ore are described. Ash is removed in the flotation plant and the remaining froth is converted to a slurry which is pumped to the filter-melt plant. Black oil feed from this plant is thermally cracked in the delayed coker, producing non-condensed gases, naphtha, gas oils, heavy fuel oil, and coke. In the catalytic reformer, coker gasoline is hydrogenated to remove catalyst poisons before being fed to the Platforming section. The major Pt-catalysed reactions taking place in this section result in the production of high-octane gasoline and hydrogen. A high purity electrode coke is produced in the calciner plant.

Cobalt-Moly Catalyst

E. M. BLUE and B. SPURLOCK, *Chem. Eng. Progress*, 1960, **56**, (4), 54-59

Pt catalyst poisons contained by reformer feed stocks may be removed in a one-step process by hydrogenation over Al_2O_3 -based CoO-MoO₃. Principal poisons removed are S-compounds, N-compounds, olefines, As, Pb and Si. The CoO-MoO₃ catalyst itself is only slowly poisoned under operating conditions. As a result of its use, the very clean feed stocks necessary for reforming over Pt catalysts are obtained.

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

H. HEINEMANN and P. A. LEFRANCOIS, *World Petroleum*, 1960, **31**, (3), 72-74

Fifty-nine patents are discussed in this review which is mainly concerned with catalysts used for reforming and cracking processes. The preparation, activation and regeneration of the reforming catalysts are discussed.

ANODIC PROTECTION

Anodic Passivation Studies

J. D. SUDBURY, O. L. RIGGS and D. A. SHOCK, *Corrosion*, 1960, **16**, (2), 91-98

The present theories of passivity are reviewed and the essential conditions for its occurrence are enumerated. The basic circuit used in the study of anodic polarisation consisted of the test specimen as anode, a Pt cathode, a standard reference electrode and a potentiostat. Metals investigated included various stainless steels, mild steel, Ti, Al and bronze. Most of the results reported were obtained using stainless steel anodes in H_2SO_4 . The effects of surface preparation, H_2SO_4 concentration, surface area, temperature and agitation were studied. It was found that it is possible to establish passivity of steels in various oxidising environments which include H_2SO_4 , HNO_3 , H_3PO_4 , NH_4NO_3 , $Al_2(SO_4)_3$, NaOH and

LiOH. Cu-base metals cannot be passivated. Resistances of the passive films are very high, ranging from 26,000 ohms/cm² for mild steel to 46,000,000 ohms/cm² for Carpenter 20. The extremely good "throwing powers" of the electrochemical cell used makes possible the protection of vessels of complex geometry.

Application of Anodic Protection in the Chemical Industry

D. A. SHOCK, O. L. RIGGS and J. D. SUDBURY, *Corrosion*, 1960, **16**, (2), 99-102

The general requirements for the successful application of anodic protection in metal-electrolyte systems are discussed. Important factors are the initial current requirement, the limit of the passive range and the current necessary for the maintenance of the passive film. It has been established that there is a time relation between initial current required and attainment of passivity and that a 50 millivolt passive range is needed. An increase in temperature increases both the initial passivation current and the maintenance current, and shortens the effective passive voltage range. Anodic protection may be applied to 18/8 steels in H₂SO₄, HNO₃, H₃PO₄, NaOH, Al₂(SO₄)₃ and NH₄NO₃ solutions, but solutions containing halogens are not suitable.

Anodic Control of Corrosion in a Sulphonation Plant

O. L. RIGGS, M. HUTCHISON and N. L. CONGER, *Corrosion*, 1960, **16**, (2), 102-106

Laboratory studies were undertaken to show that anodic protection could be applied to a mild steel oleum storage tank and a 304 stainless steel NaOH-RSO₃H neutralisation tank. Severity of corrosion was determined by weight loss of the metal specimens and the total Fe, Cr and Ni content of the H₂SO₄ solution. A Pt cathode, a solid reference electrode and an automatic potential controller suitable for the operating conditions of high temperature and extreme agitation were developed. Results obtained using various stainless steel alloys show the effects of increased temperature and time of metal exposure to the 67% H₂SO₄ system. The installation of controllers on each vessel is described. Successful operation for a year has resulted in a reduction of Fe content throughout the process, improved quality of the product and increased productivity of the plant.

GLASS TECHNOLOGY

Application of Instrumentation to Glass-Melting Furnaces

N. I. WALKER, *Trans. Soc. Instr. Technol.*, 1960, **12**, (1), 38-49

Instruments used on a continuous, under-port oil-fired, regenerative-type furnace are described. Control of oil temperature and pressure and its

flow to the furnace as well as control of atomising air flow, combustion air flow, furnace pressure and furnace reversal are discussed in detail. Glass level is measured normally by using a reciprocating Pt-tipped refractory probe. Above-glass temperatures are measured by Pt:Rh-Pt thermocouples sheathed in recrystallised Al₂O₃ which project through the crown and side-walls of the furnace. Pt-sheathed thermocouples are used to measure below-glass temperatures. The various controls are co-ordinated by the operator.

Precision Temperature Control for Fibre Glass Production

ANON., *ISA Journal*, 1960, **7**, (1), 37-40 (From a paper presented by P. E. STRAIGHT and C. O. HUFFMAN at the 14th Annual ISA Instrument-Automation Conference and Exhibit, Chicago, Sep., 1959)

The control system installed by the Pittsburg Plate Glass Co. is shown in a block diagram. The functions of the input-amplifier, magnetic control chassis and magnetic summing amplifier are explained. A Pt:13%Rh-Pt thermocouple welded directly to the Pt bushing measures its temperature and actuates the control equipment.

Nucleation, Crystallisation and Glass Formation

W. A. WEYL, *Sprechaal Keram. Glas Email*, 1960, **93**, (6), 128-136 (In English)

The mechanisms of homogeneous and heterogeneous nucleation and the effect of molecular structure of glasses on their crystallisation rate are discussed in detail. The role of colloidal Pt as a nucleation catalyst is explained by the preferential adsorption by the metal particles of SiO₄ tetrahedra with the most non-bridging O²⁻ ions. (37 references)

ELECTRICAL ENGINEERING

High-Speed Noble Metal Switching Relays for Dial Offices

ANON., *Siemens Z.*, 1960, **34**, (4), 174-175

The trend of development in telephone switching technique is briefly reviewed. Special features of the relays designed for Siemens dial systems include a high percentage Pd alloy double contact.

The Conductivity of Oxide Cathodes. Part 7. Solid Semiconduction

G. H. METSON and E. MACARTNEY, *Proc. Instn. Elect. Engrs.*, Part C, 1960, **107**, (11), 91-97

A standard S-type assembly consisting of Pt cores with a matrix of equimolar BaO-SrO was used in a study of the properties of the solid conductivity state below 600°K. Semiconductivity of the oxide matrix results from activation by a thermo-chemical mechanism of the form: nPt + mBaO → Pt_nO_m + mBa. This conductivity at

420°K (the low-temperature reference conductivity, σ_{420}) of a Pt-cored assembly increases almost linearly with increase of conditioning temperature. The function σ_{420} also increases with increase of chemical activity of the core metal. There is a definite relationship between the high-temperature vacuum conductivity, σ_{1020} , and σ_{420} . In the temperature range 420–300°K, the conductivity is rapidly and almost completely destroyed by oxygen. σ_{420} is constant over a wide range of applied voltage and current and shows a high degree of electrical stability with time.

TEMPERATURE MEASUREMENT

Spotting Reaction Hot Spots

J. F. LOVETT, *Instrumentation*, 1959, **12**, (4), 23

A travelling Pt:Rh-Pt thermocouple is used to detect reaction hot spots produced in a heat exchanger tube during the oxidation of naphthalene. The thermocouple, surrounded by ceramic insulating material, is sheathed with stainless steel.

High-Temperature Resistance Thermometry

ANON., *U.S. Nat. Bur. Stds. Tech. News Bull.*, 1959, **43**, (12), 233

A Pt resistance thermometer has been developed for measurement of temperatures between

630.5° and 1063°C, fixed points on the International Temperature Scale. Use of high purity Pt wire for the resistor has reduced thermometer drifts to less than 0.001 deg/hr at 1000°C. In one design, the resistor wire is supported by four synthetic sapphire discs through holes in which are threaded eight heavy lengths of Pt wire. Four leads of Pt wire are joined to the resistor. The assembly is protected by a fused Al₂O₃ tube.

Techniques of Cathode Temperature Measurements as Applied to Commercial Cathode-Ray Tubes

P. P. COPPOLA, *Rev. Sci. Instr.*, 1960, **31**, (2), 137–143

Thermocouple, optical pyrometer and retarding potential techniques of measurement were investigated and the relative merits and limitations are discussed. Corrections necessary for each method are given. The design is given of an electron-gun planar-disc cathode structure used for making thermocouple measurements. Pt:10%Rh-Pt thermocouples are used.

Radiation Effects on Thermocouples

M. J. KELLY and W. W. JOHNSTON, *U.S.A.E.C. Instrumentation and Controls Div.*, Report ORNL-2787, 1959, Nov., 77–79

Data obtained on the effect of neutron flux on Pt:Rh-Pt thermocouples are shown graphically. The percentage error at 1900°F is shown as a function of neutron exposure. A deviation curve of thermocouple error vs output for a Pt:10% Rh-Pt thermocouple is given.

NEW PATENTS

Grain-stabilising of Metals and Alloys

JOHNSON, MATTHEY & CO LIMITED *British Patent* 830,628

A grain-stabilised platinum group metal or alloy material is made by compacting and sintering a mixture of the powdered metal or metals and 0.005–5% by wt. of the total mixture of a refractory metal carbide, preferably tungsten carbide, also in powder form.

Reforming Catalysts

ENGELHARD INDUSTRIES INC. *British Patent* 830,838

In making a platinum-alumina catalyst (0.2–1.5% by wt. platinum), part of the platinum is incorporated by reaction in aqueous medium of a halogen platinum acid with hydrogen sulphide in the presence of an alumina hydrate catalyst base precursor. Another part of the platinum is incorporated by mixing the precursor with an

aqueous platinum sulphide sol. The resulting product is dried and calcined. At least 0.1% of platinum is added in each case.

Gas Analysis

H. MAIHAK A.G. *British Patent* 831,039

Carbon dioxide analysis apparatus includes an absorption chamber and an electrolytic vessel having an anode of platinum and cathode of iron or nickel separated from the anode by a diaphragm of aluminium oxide so as to prevent passage of carbon dioxide produced during electrolysis from the anode to the cathode.

Hydrogenation of Acetylene

ENGELHARD INDUSTRIES INC. *British Patent* 831,406

A catalyst for use in the selective hydrogenation of acetylene is composed of palladium on activated alumina, the weight of palladium metal