

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Permanent Magnet Materials

R. J. FABIAN, *Materials in Design Eng.*, 1959, 50, (1), 108-114

Metals and ceramic materials now available are described in a comprehensive survey. The magnetic, physical and mechanical properties, composition and applications of magnet steels, Alnico alloys, Fe-Pt, Co-Pt and other magnetic alloys are given, as are those of ceramic and fine particle materials. An explanation of the behaviour of ferromagnetic materials is given. (10 references)

Optical Determinations of the Structures of Coordination Compounds Formed by Divalent Palladium

G. B. BOKII and V. I. SOKOL, *Russ. J. Inorg. Chem.*, 1959, 4, (1), 29-30 (Transl. of *Zhur. Neorg. Khim.*, 1959, 4, 74-78)

The experimental and calculated values for the refractive index of 10 compounds were compared. Densities were measured by pycnometer. Molecular and coordinate refractions were calculated. The results, compared with those for divalent Pt, show that the order in which the trans-influence of the substituent falls is qualitatively the same for both cations, but that the intervals in the two series are different.

The Magnetochemistry of some Iridium Compounds

V. NORMAN, *Diss. Abs.*, 1959, 19, 2243-2244

Measurements of magnetic susceptibility were made in the temperature range 78-300°K on the compounds $(\text{NH}_4)_2\text{IrCl}_6$, K_2IrCl_6 , $(\text{NH}_4)_2\text{IrBr}_6$, $(\text{CH}_3\text{NH}_2)_2\text{IrCl}_6$, $(\text{PyH})_2\text{IrCl}_6$, $(\varphi_4\text{As})_2\text{IrCl}_6$, $\text{IrCl}_4 \cdot 3\text{H}_2\text{O}$, $\text{IrO}_2 \cdot 2\text{H}_2\text{O}$, KIrF_6 , $\text{Ir}(\text{Py})_2\text{Cl}_4$, Sr_2IrO_4 and $\text{Na}_6[\text{Ir}(\text{SO}_3)_4] \cdot 10\text{H}_2\text{O}$.

The Highest Fluoride of Osmium

G. B. HARGREAVES and R. D. PEACOCK, *Proc. Chem. Soc.*, 1959, (March), 85

Magnetic properties of the compound measured over the temperature range 80-297°K and analysis indicated the formula OsF_6 .

Palladium-Rhodium Alloys and the Allotropic States of Rhodium

E. RAUB, H. BEESKOW and D. MENZEL, *Z. Metallkunde*, 1959, 50, (7), 428-431

The alloys form a continuous solid solution series in which lattice parameters vary almost linearly

with composition. There is a wide miscibility gap at lower temperatures, the critical temperature being 845°C. Rh shows no structural change between room temperature and 1500°C; it crystallises only in the f.c.c. lattice.

Galvanomagnetic Phenomena in Platinum at Low Temperatures

E. S. BOROVIK and V. G. VOLOTSKAYA, *Fiziki Metallor i Metallovedenie*, 1958, 6, (1), 60-66 (*Metallurgical Abs.*, 1959, 26, (10), 741)

The electrical resistivity, Hall coefficient and magnetoresistance of Pt were measured at 4.2-20°K in magnetic fields of 0-27,000 Oe. Four groups of current carriers, two *n*-type (n_1, n_2) and two *p*-type (n_3, n_4) are postulated to explain the results. The numbers of these atoms (n_i/n_a) and their mobilities (τ_i/m_i^*), i.e. mean time of flight/effective mass, are given in a table. It is noted that $n_1 + n_3 = n_2 + n_4$. The ratio of the mean effective mass to the mass of the free electron (m^*/m_e) = 8. Mobilities are an order of magnitude less than in non-transition metals.

Alloys Formed on Platinum-Clad Molybdenum Wire

ANON., *GEC Journal*, 1959, 26, (1/2), 82-83

X-ray studies of the Pt coating showed that structural changes occur on heating above 900°C. Alterations are caused by the solid diffusion of Mo into the Pt. Increase in Mo concentration results in three successive structure transitions showing that there are three Mo-Pt alloys, Pt_3Mo , Pt_2Mo and PtMo . A table is given relating heat treatment, composition of each phase and crystal structure. Experiments were carried out on 0.1 mm diameter wire; single phase structures were difficult to isolate in wires of greater diameter.

Metal and Oxide Film Potentiometers

G. V. PLANER, *Inst. Radio Eng. Trans.: Component Parts*, 1959, CP-6, (2), 105-108

Recent developments in resistors and potentiometers of the noble metal and metal oxide film types are described. Considerations of electrical stability, ease of application to the substrate as well as control of the process led to the choice of a Au-Pt alloy as the resistive material in metal film potentiometers. The film is applied uniformly on flat plate substrates, usually glass, from paint solutions. Photographic methods of obtaining meandered resistance paths in both noble metal and oxide film types have been developed as has reinforcement of the track portions to

improve wear characteristics and to reduce contact resistance against the wiper in the case of oxide films. The relation between resistance, temperature coefficient and film thickness has been determined for oxide films on glass. Characteristics with respect to wear, noise, temperature coefficient and electrical load for both types of element are briefly discussed.

Recent Developments in Fixed Resistors

R. H. W. BURKETT, *Inst. Radio Eng. Trans.: Component Parts*, 1959, **CP-6**, (2), 105-108

Metal film and metal oxide film resistors, C film resistors, wire wound resistors and composition resistors are discussed. Pt-Au films on glass fibres wound on a cylindrical former produce stable resistors with higher resistance than the orthodox metal film. Another noble metal film resistor uses a combination of metallic Pd and PdO₂. It has a low temperature coefficient and is apparently more reliable than the pyrolytic C resistor. Improvement in the latter is foreseen as is the wider availability and use of metal and metal oxide films.

On the Superstructure of the Ordered Alloy Cu₃Pd III—High Temperature Electron Diffraction Study

D. WATANABE, *J. Phys. Soc. Japan*, 1959, **14**, (4), 436-443

Cu₃Pd alloys in thin evaporated films were investigated, using a high temperature electron diffraction camera, at temperatures above and below the critical point of order-disorder. Films of alloys containing 13, 18, 25 and 28 at.% Pd were prepared and examined at temperatures up to 750°C. Results show that in α'-phase alloys, the line-up number of anti-phase domains and the degree of order inside domains decrease with increasing temperature in the range of 20~40°C below the critical point. At the critical point, there is an abrupt decrease of the line-up number of domains. In the range 100~150°C above the critical point, short chains of one-dimensional anti-phase domains with the same period of out-of-steps as in the ordered state are present in equilibrium, being scattered in the disordered state. In the α'-phase alloy, anti-phase domains are absent both above and below the critical point.

Electrical Resistance in Acidic Solution of Palladium and Palladium Alloys Containing Hydrogen

A. W. CARSON, T. B. FLANAGAN and F. A. LEWIS, *Naturwiss.*, 1959, **46**, (11), 374-375

The investigation was carried out using Pd, Pd-Pt and Pd-Ag wires in 2N H₂SO₄ at 25°C and resistances were determined by measuring the potential drop across the specimen. Measured values of resistance increased steadily on application of the measuring current. Drifting resistances occurred only for absorption of hydrogen

both before and after the attainment of a final equilibrium concentration. Identical resistance-time curves were obtained with different measuring currents; therefore, heating effects are not responsible for the drift. Drifts were observed only in wires which readily absorbed hydrogen from solution.

Sorption of Hydrogen by Disperse Palladium-Copper Alloys

R. A. KARPOVA and I. P. TVERDOVSKII, *Zhur. Fiz. Khim.*, 1959, **33**, (6), 1393-1400 (English summary)

The solubility of H₂ in the alloys was studied at 24°C by determining the Q-φ curves. Increasing Cu content is accompanied by decreasing solubility of H₂, zero solubility being obtained at about 66 at.% Cu. The regions of the H₂ solubility isotherms which correspond to pure Pd phase-transition become shorter with increasing Cu concentration and disappear at 26 at.% Cu. Cu exhibits divalency in the region where two phases of the Pd-Cu system exist. The heats of solutions of H₂ in alloys containing up to 20 at.% Cu were determined. With increasing Cu content the differential heat of solution passes through a minimum.

The Kinetics of Chlorine Ion Oxidation on Platinum

G. A. TEDORADZE, *Zhur. Fiz. Khim.*, 1959, **33**, (1), 129-136 (English summary)

Polarographic and polarisation curve methods were used to show that the limiting stage for all processes occurring in the anodic polarisation of Pt in HCl is the discharge of the Cl ions. A possible mechanism for the oxidation of Cl is proposed and the retarding effect of oxygen adsorbed on the electrode surface is considered.

Preparation of some Ternary Oxides of the Platinum Metals

J. J. RANDALL and R. WARD, *J. Am. Chem. Soc.*, 1959, **81**, (11), 2629-2631

Oxides of the alkaline earths with Ru, Rh, Ir and Pt were prepared either by heating the alkaline earth carbonate and metal powder in air at 1000-1500°C or by heating pellets *in vacuo* in an evacuated silica capsule. The oxides were of the types ABO₃, A₂BO₄ and A₄BO₆, (A≡Ca, Sr or Ba and B≡Ru, Rh, Ir or Pt). With the exception of Sr₄RhO_(6-y), and SrRuO_(3-y), the compounds appear to be stoichiometric. A change in structure from the perovskite type with B-O-B bonds in three dimensions for ABO₃ compounds, to phases with B-O-B bonds in two dimensions for A₂BO₄ compounds, to discrete BO₆ octahedra for A₄BO₆ compounds is shown. Of all theoretically possible perovskite-type compounds, the only ones to form were CaRuO₃, SrRuO₃ and phases in the system SrRu_(1-x)Ir_xO₃. BaRuO₃ has a hexagonal structure.

ELECTROCHEMISTRY

On the Passivation of the Platinum Electrode

E. A. AIKAZYAN, *Zhur. Fiz. Khim.*, 1959, **33**, (5), 1016-1022 (English summary)

The investigation was carried out with reference to ionisation of molecular hydrogen in HCl, HBr, H₂SO₄, HClO₄ and NaOH solutions. It is shown that the passivation is associated with a reduction in the number of sites on the electrode surface active to molecular hydrogen. This loss of activity results from specific adsorption of anions lowering the Pt-H bond energy.

Mechanisms of Hydrogen Producing Reactions on Palladium, VI—Atomic Hydrogen Overvoltage on an α Pd-H Bielectrode

S. SCHULDINER, *J. Electrochem. Soc.*, 1959, **106**, (5), 440-444

The electrochemical system used consisted of two cells, one with a Pd tube anode and the other with a similar cathode, connected by the bielectrode, a Pd diaphragm 0.004 in. thick. Reference electrodes were (Pd-H)_a/H₃O⁺. Atomic hydrogen overvoltages on the bielectrode were determined and the experimental results were found to support a kinetic analysis of the system.

Precious Metals

E. A. PARKER, *Plating*, 1959, **46**, (6), 621-627

A survey is made of processes for the electro-deposition of Au, Ag, Pt, Pd, Ru, Ir and Rh. Details of plating bath composition and operating data for Au-, Ag-, Pt-, Pd- and Rh-plating are given. Applications and various types of bath are discussed. (68 references)

A Study of the Electrochemical Behaviour of Ozone on the Platinum Electrode by the Method of Cathodic Polarography

K. I. NOSOVA, A. A. RAKOV and V. I. VESELOVSKII, *Zhur. Fiz. Khim.*, 1959, **33**, (2), 349-356 (English summary)

Experiments were carried out at temperatures between 25 and -70°C. It was shown that ozone may be determined quantitatively by means of cathodic polarography with a rotating Pt electrode. A mechanism for the cathodic reduction of ozone is discussed

Investigation of Polarisation Phenomena at Electrodes of Smooth Platinum by Using Charging Curves

J. GINER, *Z. Electrochem.*, 1959, **63**, (3), 386-397

By using resting potential measurements (ϵ), charging curves and post-polarisation curves, the behaviour of Pt electrodes in N H₂SO₄ was investigated in the absence of current, and under anodic and cathodic conditions. Measurements show that the electrode behaviour is determined by chemisorbed oxygen, not by specific oxides.

The degree of oxygen cover was determined from the charging curves. Resting potential increased with coverage which was produced by anodic charging or chemical oxidation with H₂CrO₄ and which was reduced by cathodic charging. Double steps occurred in the anodic charging curves of heavily covered electrodes. Chemisorption of atomic hydrogen occurred before the evolution of hydrogen. The reaction Pt + H⁺ + e⁻ → Pt-H had no overvoltage, but the reaction Pt-H → Pt-H₂ → Pt + H₂ was very slow. The reaction Pt + H⁺ + e⁻ → Pt-H in neutral and alkaline solution also showed an overvoltage. The effect of an oxygen atmosphere on Pt electrodes in the absence of current and when charged was investigated.

Chronopotentiometric Oxidation of Ferrocene, Ruthenocene, Osmocene, and some of their Derivatives at a Platinum Electrode

D. E. BUBLITZ, G. HOH and T. KUWANA, *Chem. & Ind.*, 1959, (20), 635-636

An investigation of the redox properties of the metallocenes has indicated the nature of the bond between the metal and *cyclo*-pentadiene rings.

LABORATORY APPARATUS AND TECHNIQUE

Machine for Preparing Phosphors for the Fluorometric Determination of Uranium

R. E. STEVENS, W. H. WOOD, K. G. GOETZ, C. A. HERR, *Anal. Chem.*, 1959, **31**, (5), 962-964

The machine consists of a metal plate which revolves above a ring gas burner with fused silica rods supporting 18 Pt dishes attached to the edge of the plate. Detailed operating instructions are given. Phosphors prepared in the Pt dishes at one time show good reproducibility.

Measuring Equipment for Polarisation Studies in Distilled Water

J. E. DRALEY, W. E. RUTHER, F. E. DE BOER and G. A. YOUNGDAHL, *J. Electrochem. Soc.*, 1959, **106**, (6), 490-494

Special equipment was designed for potential-current measurements for corroding metals in low conductivity solutions. A recording voltmeter and current interrupter are described, as is the electrolysis cell. In order to prevent contamination of the distilled water the cell was constructed of Pyrex glass and Pt. Polarisation data for high-purity Al in boiling distilled water are given.

The Purification of ¹⁸O-Water

I. LAUDER and I. R. WILSON, *Aust. J. Chem.*, 1959, **12**, (1), 29-31

A new technique for the purification of small samples of ¹⁸O-water, prior to the determination of its isotopic composition, uses CuO as oxidising

agent. A small fraction of the water is electrolysed in a Pyrex capillary cell using Pt wire electrodes and the liberated oxygen reacts with Cu gauze in a silica tube heated electrically to 750°C. Pt foil is wrapped round the gauze to prevent reaction between the CuO and SiO₂. The remainder of the water, as vapour, is pumped over the CuO seven times and traces of volatile organic compounds are quantitatively removed. Samples as small as 14 mg have been purified.

Some Equipment for Ceramic Research

F. H. ALDRED and A. E. S. WHITE, *Trans. Brit. Ceram. Soc.*, 1959, **58**, (4), 199-223

Details of several types of high-temperature furnaces and of apparatus for determination of the creep of ceramics under compressive and transverse-bending stresses are given. A hot-stage attachment for the microscope is described. Samples are heated at a 5%Rh-Pt:20%Rh-Pt junction which acts as heating element and thermocouple; temperatures approaching 1800°C can be reached. With a 20%Rh-Pt:40%Rh-Pt junction temperatures up to 1820°C may be obtained. A small quantity of material is placed at the junction of the Rh-Pt wires which are supported by Rh-Pt supports of the same composition, carried by a four-way terminal block. The stage is mounted on the platform of a petrological microscope. An accuracy of ±20°C in temperature measurement is possible. For higher temperatures, a heater wire of Rh-Ir or Rh-Pt may be used instead of the thermocouple. This may be calibrated to an accuracy of ±40°C. Furnaces for sample preparation include gas-fired, Rh-Pt and Mo wire-wound, graphite-resistor, SiC and hot-press types.

Bromoplatinic Acid as a New Reagent for the Detection of Alkaloids and Organic Bases

G. SANDRI, *Mikrochim. Acta*, 1959, (2), 214-219 (In German)

The sensitivity of H₂PtBr₆ in the microchemical detection of alkaloids and organic bases was compared with that of H₂PtCl₆ and found to be much greater. Compounds on which tests were made included C₉H₈N₂, C₆H₅N, C₄H₁₀N₂, C₈H₇N and C₁₅H₂₆N₂. The products obtained with aliphatic, aromatic and heterocyclic bases are suited to the microchemical differentiation of these compounds.

Use of a Rotating Platinum Microelectrode in Polarographic Analysis

M. B. BARDIN, YU. S. LYALIKOV and B. S. TEMYANKO, *Zhur. Anal. Khim.*, 1959, **14**, (1), 24-27 (*Chem. Abs.*, 1959, **53**, (12), 11060h)

The possibility of using rotating electrodes in polarography was investigated. Diffusion currents on such electrodes are proportional to the concentration and the square root of the

angular velocity of the electrode. Various shapes of microdisc electrodes were examined and were found to be satisfactory for polarographic analysis.

CATALYSIS

Structure and Mode of Action of the Contact γ -Aluminium Oxide/Platinum

A. KRAUSE, *Nature*, 1959, **183**, (Jun. 6), 1615-1616

The action of the contact is explained by the electron donor properties of the free radical O=Al—contained by active γ -Al₂O₃. Factors influencing the regeneration of the O—Al—radical, an important link in the chain of reactions in the hydrogenation of benzene, are discussed. An insufficiency of O=Al—radicals resulting from low Pt concentration causes rapid loss of contact activity. The transformation on heating of O—Al—radicals into (AlO)⁺ cations explains the low activity of contacts prepared above room temperature.

Fison's New Factory at Stanford-le-Hope. Ammonia from Shell Converted into Ammonium Nitrate

B. H. J. BELL, *Chem. & Ind.*, 1959, (24), 724-726

In a two-stage process, nitric acid produced by the catalytic oxidation of vaporised NH₃ over a Rh-Pt gauze pad is mixed with vaporised NH₃. Further utilisation of process heat and reduction over a noble metal catalyst of oxides of nitrogen in the tail gases are features of the nitric acid plant. In the Stengel ammonium nitrate unit, solutions over 90% NH₄NO₃ are obtainable.

An Active Platinum-Silica Gel Catalyst

P. JÍRŮ and V. JARA, *Collection Czechoslov. Chem. Commun.*, 1959, **24**, (2), 630-632 (In German)

The catalyst, prepared by mixing 10% H₂PtCl₆ solution with 3.5% SiO₂ solution and heating the resulting solidified jelly at 100°C, contained 0.18% Pt, 0.1% Cl and traces of Mg, Cu, Fe, K and Na were found. The active Pt surface is seven times greater than that of catalysts prepared by impregnation methods and the catalyst has a high activity in the reaction of O₂ with H₂.

The Kinetics of Hydrogen Chemisorption on an Iridium Catalyst

M. J. D. LOW and H. A. TAYLOR, *Canad. J. Chem.*, 1959, **37**, (5), 915-921

Rates of adsorption were calculated by measuring the change of pressure in a constant-volume system when a known amount of Pd-filtered hydrogen was admitted to a 0.5% Ir/Al₂O₃ catalyst previously evacuated. 38 experiments at 7 different temperatures are reported; readings were taken at several different initial pressures for each temperature. The data of each experiment may be precisely described by use of the Elvoich equation. Isothermal anomalies which

were observed depend on both temperature and initial pressure.

Cracking of Gaseous Hydrocarbons by Partial Oxidation

E. BARTHOLOMÉ and H. NONNENMACHER, *Erdöl u. Kohle*, 1959, **12**, (5), 359-364

Partial oxidation is effective in supplying heat in endothermic cracking reactions. Three processes used as illustrations of the method are (i) homogeneous cracking with controlled quenching for the production of acetylene, (ii) heterogeneous cracking on inert solid materials for the production of olefines, and (iii) heterogeneous cracking on catalysts for the production of CO and H₂. The latter process may consist of a flame reaction followed by catalysis or a flameless, catalytic reaction. The catalyst bed consists of a layer of Pt catalyst over a layer of Ni catalyst.

One Hundred Years of Oil

N. P. HURLEY and S. J. RACITI, *World Petroleum*, 1959, **30**, (6-Section 1), 176-218

Principal developments in the petroleum industry of the U.S.A. during the past century are discussed. Production techniques and methods, refining, transportation, production areas and marketing are the topics covered. The significance in refining of catalytic processing in the last decade is emphasised.

Problems of Processing in Aromatisations Carried Out by Platinum Catalysts

R. BIRTHLER, *Acta Chim. Acad. Sci. Hung.*, 1959, **18**, (1-4), 157-165 (In German)

It has been found that yields are affected by the chemical composition of the materials used and by the operating conditions. These conditions should be varied according to whether high-octane products or pure aromatics are required. The influence of pressure, temperature, catalyst output and the catalyst itself is discussed. Pt/Al₂O₃ catalysts gave the best results in large-scale aromatisations.

Selective Hydrogenation of Olefines with Ruthenium

L. M. BERKOWITZ and P. N. RYLANDER, *J. Org. Chem.*, 1959, **24**, (5), 708-709

Monosubstituted olefines were reduced in preference to di- and tri-substituted olefines in the presence of a 5% Ru/C catalyst with water as a solvent.

Boron Exchange between Diborane and Pentaborane-9 in the Presence of Alumina Catalysts

H. G. WEISS, J. A. KNIGHT and I. SHAPIRO, *J. Am. Chem. Soc.*, 1959, **81**, (8), 1826-1827

Mixtures of pentaborane-9 vapour and diborane were heated at 90°C in the presence of a 0.3% Pt/Al₂O₃ catalyst. Boron exchange was observed;

there was no such exchange under comparable conditions in the absence of the catalyst. The mechanism of the exchange, which involves independent reactions between a catalyst-diborane complex and both diborane and pentaborane-9, was elucidated by isotopic techniques.

Isotopic Exchange between Ethers and Deuterium on Metallic Catalysts

J. M. FORREST, R. L. BURWELL, JR., and B. K. C. SHIM, *J. Phys. Chem.*, 1959, **63**, (6), 1017-1021

Mixtures of ether vapour and deuterium or hydrogen were prepared by passing the gas through a thermostated saturator containing ether. The catalysts used were 0.5% Rh/Al₂O₃, 3.3% Pd/Al₂O₃ and Ni/kieselguhr. It was found that the oxygen atom of the ether serves as a block in the exchange reaction and that the presence of an ether reduces the exchange-rate of alkanes. Ethers are adsorbed at the oxygen atom on the catalyst surface. Passage of hydrogen at reaction temperatures over the catalyst restores its activity. Ethers used in the investigation were propyl, isopropyl, ethyl butyl, methyl amyl and methyl *sec*-butyl.

First Commercial Pentane Isomerisation Unit

C. S. CRONAN, *Chem. Eng.*, 1959, **66**, (13), 80-83

A process flow-sheet for Phillips Petroleum Co.'s unit at Borger, Texas, is given. The Penex process using a Pt-containing catalyst is operated at this plant.

Polymers II—Polydimethyleneacetylene

W. J. BAILEY and E. J. FUJIWARA, *J. Org. Chem.*, 1959, **24**, (4), 545-548

Polydimethyleneacetylene was synthesised in order to study the effect of a symmetrical triple bond on the properties of a hydrocarbon. The compound was produced by condensation of 1-chloro-4-bromo-2-butyne with Mg and extraction with xylene. Its structure was determined by analysis, oxidation to succinic acid and hydrogenation in the presence of PtO₂ to polymethylene. Results show that symmetry promotes crystallinity of polymers and increases their melting points.

On the Catalytic Properties of the System Pt-Au

A. A. ALCHUDZHIAN and M. A. INDZHIKYAN, *Zhur. Fiz. Khim.*, 1959, **33**, (5), 983-987 (English summary)

The hydrogenation of benzene was used as a basis for the investigation of the effect of Au on the catalytic properties of Pt. The composition of the catalysts varied over the range Pt:Au from 99:1 to 1:3. For constant Pt content (0.01 g) the activity of the Pt-Au catalysts increases to a maximum at 5 at.% Au, but decreases with further increase in Au content. The catalyst containing 75 at.%

Au is completely inactive. This indicates that the fall in activity in the Pt catalyst is due to the introduction of Au. The occurrence of a maximum activity for small amounts of Au is probably due to the masking of a decrease in activity by the increase in the active surface. There is a correlation between the decrease in activity and loss of paramagnetism on the introduction of Au; both properties disappear at approximately the same composition.

Degradation of Corticosteroids III—Catalytic Hydrogenation of Cortisol

E. CASPI, *J. Org. Chem.*, 1959, **24**, (5), 669–673

The hydrogenation was undertaken in an attempt to obtain satisfactory yields of an equatorial allo isomer. PtO₂ and 5% Rh/Al₂O₃ were used separately as catalysts. In both cases, difficultly resolved mixtures were obtained instead of the single isomer.

New U.S.A. Patents on Catalysts in the Petroleum Industry

H. HEINEMANN and P. A. LEFRANCOIS, *World Petroleum*, 1959, **30**, (7), 60–65

In this review 50 patents are discussed. They refer to the preparation, regeneration and reworking of reforming catalysts.

Catalysis in Industry

J. H. DE BOER, *Chem. & Ind.*, 1959, (30), 934–941

The development of heterogeneous catalysis in the last 50 years is outlined. Four major catalytic processes in operation before the 1914–18 war are discussed – they were (i) hydrogenation of oils and fats using a Ni catalyst, (ii) the contact H₂SO₄ process using a Pt catalyst, (iii) NH₃ synthesis using an Fe catalyst, and (iv) the oxidation of NH₃ over Pt or Rh-Pt. Many catalytic oxidation and hydrogenation reactions using both metallic (Ag, Ni, Pt and Pd) and oxidic (ZnO, CuO, Al₂O₃ and Cr₂O₃) catalysts were introduced after 1918. These have led to the large-scale catalytic cracking and polymerisation processes of the present time as well as those for the conversion and purification of gases. Among the principles of catalysis discussed are catalyst surface reactions, modification and orientation of the chemisorbed species, activation entropy and activation energy. The structure and texture of catalysts, catalyst poisoning and selectivity (factors affecting rates of diffusion and reaction rates) are discussed in detail.

The Effect of Adsorbed Gases on the Catalytic Properties of Platinum

L. RIEKERT, *Z. Electrochem.*, 1959, **63**, (2), 198–206

The decomposition of HCOOH on Pt wires electrically heated to 80–110°C was investigated. In this temperature range the rate of the reaction is controlled by a diffusion process. The ratio of

dehydration (HCOOH → H₂O + CO) to dehydrogenation (HCOOH → H₂ + CO₂) depends on the pretreatment of the catalyst. Wires preheated only in H₂ give only dehydrogenation while up to 5% dehydration is obtained with wires preheated successively in H₂, O₂ and H₂O. The H₂O + CO ⇌ H₂ + CO₂ reaction is involved in neither dehydration nor dehydrogenation; however, the dependence of catalytic properties on pretreatment is also shown.

Industrial Methods of Catalyst Testing

H. RÖDER, R. BIRTHLER and C. SZKIBIK, *Chem. Technik.*, 1959, **11**, (5), 256–259

Six types of apparatus are described and illustrated. Results obtained using different types of apparatus and different catalysts with the same apparatus are given in tables. The efficiencies of Pt/Al₂O₃ and MoO₃ catalysts are compared.

The Deuterium Exchange Activities of Some Supported Platinum Catalysts

C. G. MYERS, D. J. SIBBETT and F. G. CIAPETTA, *J. Phys. Chem.*, 1959, **63**, (7), 1032–1041

Two exchange reactions, $n\text{-C}_4\text{H}_{10} + \text{D}_2 \rightleftharpoons n\text{-C}_4\text{H}_9\text{D} + \text{HD}$ and $n\text{-C}_4\text{H}_7\text{D}_3 + n\text{-C}_4\text{H}_{10} \rightleftharpoons n\text{C}_4\text{H}_8\text{D}_2 + n\text{-C}_4\text{H}_9\text{D}$, etc., were studied over Pt on 9 different supports (Al₂O₃, Al₂O₃-SiO₂, SiO₂ or activated C). The catalysts had hydrogenation-dehydrogenation and acid sites. Indicator reactions were dehydrogenation of C₆H₁₂ to C₆H₆ and 1,4-(CH₃)₂ C₆H₄ isomerisation. In either reaction, assuming that all of the H-atoms of n-C₄H₁₀ are equally replaceable by D-atoms and that there is no isotope effect on the equilibrium compositions, equilibrium product compositions matched those calculated by probability methods. In the C₄H₁₀-D₂ reaction, equilibrium was reached first among the hydrogen isotopes of the system, then for the distribution of D-atoms between H₂ molecules and C₄H₁₀ molecules, and lastly in the C₄H₁₀-C₄H₇D₃ portion of the system. Catalyst activity toward each D-exchange reaction was related first to dehydrogenation activity and secondly to "acidity". Reaction rate and apparent activation energy varied for each catalyst. Activation energies and frequency factors showed a compensation effect. The kinetics indicate that the number of D-atoms combining with a C₄H₁₀ molecule per collision of C₄H₁₀ with D is also related to catalyst "acidity". It is suggested that acid and Pt sites coact to promote this latter effect.

Kinetics of the Ruthenium-Catalysed Arsenic (III)—Cerium (IV) Reaction

C. SURASITI and E. B. SANDELL, *J. Phys. Chem.*, 1959, **63**, (6), 890–892

The rate of the catalysed reaction As(III) + 2Ce(IV) → 2Ce(III) + As(V) was obtained by determining spectrophotometrically the concentration of Ce(IV) in the mixture as a function of

time. The rate was found to be independent of As(III), As(V), Ce(III) and hydrogen-ion concentrations.

"Complexforming" Process for the Catalytic Aromatisation of Gasoline and the Preparation of Cyclohexane

I. V. NICOLESCU, A. POPESCU and A. PAPIA, *Rev. Inst. Franc. Pétrole*, 1959, **14**, (7/8), 1008-1015

The principal aromatisation reactions (dehydrogenation, dehydroisomerisation and isomerisation) were studied in order to determine the most favourable conditions of temperature and pressure, contact time and choice of catalyst for the process. "Complexforming" is a variation of the process of catalytic aromatisation of gasoline (65-190°C fraction) in which C₆H₆, C₆H₅CH₃, (CH₃)₂C₆H₄, high octane number gasoline and C₆H₁₂ are produced in a single manufacturing unit. Catalysts for aromatisation reactions are Pt/Al₂O₃ for the C₆ fraction or Pt/Al₂O₃/SiO₂ for the C₇, C₈ fraction and contain 1%Pt and some HF. The catalyst for the hydrogenation of C₆H₆ is 56%Ni/SiO₂. Tables are given of operating data for the treatment of the 65-90°C and 90-190°C fractions and for the hydrogenation of C₆H₆.

CATHODIC PROTECTION

Experiments with a Trailing Platinum Anode. Cathodic Protection of s.s. "Israel" on Haifa-New York Voyage

D. SPECTOR, H. S. PREISER and D. KHOUSHY, *Corrosion Technol.*, 1959, **6**, (5), 143-148

The advantages of the use of trailing anode systems are enumerated. Details are given of the preparations for the voyage with descriptions of the Pt-clad anode, d.c. power source, bow and stern reference electrodes, recording instruments for anode current and hull potential, and propeller shaft grounding brushes. Hull potential/time graphs plotted from data obtained during dock-side tests and three underway runs are given. Methods for overcoming the mechanical difficulties encountered are described. Results indicate the feasibility of protecting cathodically large commercial ships by using inert trailing anodes.

ELECTRONICS AND COMMUNICATIONS

Pushbutton PBX with High-Speed Noble-Metal Relay Switching Array

W. FATH, *Siemens-Z.*, 1959, **33**, (4), 194-196

PBX technology has been improved with the development of a pushbutton PBX which operates with high-speed noble-metal switching relays. The layout and simplicity of operation are described.

Further Examples of the Applications of High-Speed Noble-Metal Relays

W. VILLMANN and H. VOGEL, *Siemens-Z.*, 1959, **33**, (5), 338-340

High-speed noble-metal relays are finding new applications because of their high-speed switching, superior operating reliability and adaptability in the construction of switching arrays. Examples are described of the use of the relays for load distribution, finding operations, and electronic translation in small dial offices in a nationwide dialling network.

Components for Use with Transistor Techniques

G. W. A. DUMMER, *Brit. Commun. & Electronics*, 1959, **6**, (6), 422-428

The trends of present development are reviewed. A new approach to design is necessary in order to take advantage of the characteristics of transistors. Limits on the reduction in size of components are set by the problems of soldering techniques and accessibility for servicing. The extended use of film components in which only the actual working element is used is taken to be the next logical step in development. Cracked-carbon films, fired noble metal (20% Pt-Au or 40% Pt-Au) films, sprayed metal oxide films, evaporated resistance metal films, dried anodic films and other non-metallic films are discussed.

A Survey of Ceramic-to-Metal Bonding

G. R. VAN HOUTEN, *Bull. Am. Ceram. Soc.*, 1959, **38**, (6), 301-305

The historical development of metal-ceramic bonding is traced and evaluated. Bonds and bonding techniques are classified; coating procedures by base and noble metals are reviewed. (142 references)

TEMPERATURE MEASUREMENT

Measurement of Rocket Exhaust-Gas Temperatures

I. WARSHAWSKY, *ISA Journal*, 1958, **5**, (11), 91-97

Techniques for measuring total and static temperatures are outlined and sources of measurement error are emphasised. The range of Pt:Rh-Pt and Ir:Ir-Rh thermocouples may be extended by deliberately operating the junction at a temperature lower than that of the gas, the heat lost by conduction and radiation being accurately calculated. In one method, bare wires transverse to the airstream are used; gas temperatures to 3200°F have been measured with a probable error of 50°F using a Pt:Rh-Pt thermocouple. It is suggested that Ir:40%Ir-Rh thermocouples used similarly may have an upper

limit of 3800°F. Cooled probes may also be calibrated against reference standards at lower temperatures and higher temperatures may be estimated by extrapolation. Aspirated thermocouples, cooled-tube probes, cooled-gas probes and pneumatic probes for the measurement of

total temperatures are described. Optical-radiation instruments for the measurement of static temperature are discussed. Accurate values are obtained only when several distinctly different instruments are operated in the same gas stream.

NEW PATENTS

Catalytic Reforming

SOCONY MOBIL OIL CO. INC. *British Patent 812,895*
A hydrocarbon mixture is reformed by contacting it under reforming conditions with a catalyst consisting of a mechanical mixture of particles of less than 100 microns diameter of (1) a porous inert carrier on which is deposited 0.05-5% by wt. of a Pt metal and (2) an acidic cracking component, the components being present in a predetermined relationship. The carrier may be Al_2O_3 , the Pt metal, Pt or Pd and the cracking component $SiO_2-Al_2O_3$.

Catalytic Cracking of Hydrocarbons

SOCONY MOBIL OIL CO. INC. *British Patent 812,896*
A hydrocarbon charge is cracked by contacting it in the presence of hydrogen with a catalyst consisting of a mechanical mixture of particles of less than 100 microns diameter of (1) a porous carrier inert to cracking activity on which is deposited 0.05-10% by wt. of a Pt metal and (2) an acidic cracking component, the components being present in a specified relationship.

Production of Hydrogen

THE BRITISH PETROLEUM CO. LTD. *British Patent 813,443*

Hydrogen is produced by contacting a petroleum distillate having an initial boiling point above 200°C, which has been hydrocatalytically desulphurised, in the presence of hydrogen, with a Pt/ Al_2O_3 catalyst at 600-850°F and a pressure of 50-500 p.s.i.g.

2-(β-Amino-Ethyl)-5-Hydroxy-Indole

J. R. GEIGY A.G. *British Patent 813,777*

Pd/charcoal is used at an intermediate stage, involving the hydrogenolysis of an amino compound, in the preparation of 2-(β-Amino-ethyl)-5-hydroxy indole.

Supported Catalysts

THE DISTILLERS CO. LTD. *British Patent 814,003*

A catalyst for use in the selective hydrogenation of unsaturated aldehydes is made by treating a solid mildly alkaline support material, e.g. Al_2O_3 , TiO_2 , Cr_2O_3 , charcoal, SiO_2 gel or pumice, with a solution of a Pt group metal compound in an organic solvent to deposit the oxide of the metal, treating the product with an aqueous solution of

an alkali metal hydroxide, carbonate or bicarbonate and reducing the oxide to the metal. The catalyst contains 0.01-5% by wt. of the Pt group metal, preferably Pd. The organic solvent used is a ketone.

Thermocouple Elements

H. NISHIMURU *British Patent 814,011*

A thermocouple has one limb formed of a Pt-13%Rh alloy and the other limb of Mo and W and balance Pt (0.5-5% Mo plus 0.5-10% W).

Production of Cyano-Benzylamines

THE DISTILLERS CO. LTD. *British Patent 814,631*

Cyano-benzylamines are prepared by hydrogenating phthalonitrile, isophthalonitrile and/or terephthalonitrile in liquid phase in the presence of a Pd or Pt catalyst. The presence of this catalyst enables selective hydrogenation of only one of the two nitrile groups. Pd or Pt/ Al_2O_3 or C is used.

Glass-to-Metal Seals

THE BRITISH THOMSON-HOUSTON CO. LTD. *British Patent 814,644*

The hermetic seal between a glass part and a ferrous alloy part sealed by fusion is protected against the effect of humidity by coating the ferrous alloy in the region of the intended seal with a layer of Rh of 0.00003-0.00005 in. thick. A layer of Ag of 0.0003-0.0005 in. thick may be first applied.

Dehydronovobiocin

THE UPJOHN CO. *British Patent 815,517*

Dehydronovobiocin is prepared by reacting novobiocin in a solvent therefor with hydrogen in the presence of a PtO_2 catalyst.

Catalyst Preparation

ENGELHARD INDUSTRIES INC. *U.S. Patent 2,885,369*

In making a Pt/ Al_2O_3 reforming catalyst by forming an alumina hydrate slurry by precipitation from a water soluble Al salt, transforming the washed slurry to a mixture of hydrate phases predominating in alumina trihydrates, drying and calcining, the Pt metal is incorporated in the mixture at a point subsequent to initial precipitation of the hydrate and prior to a transformation thereof to an over 50% alumina trihydrate composition.