

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### The Iron-Palladium System

V. V. KUPRINA and A. T. GRIGOR'EV, *Russ. J. Inorg. Chem.*, 1959, 4, (3), 297-300 (Transl. of *Zhur. Neorg. Khim.*, 1959, 4, (3), 655-661)

The constitution of the system was determined by differential thermal analysis, measurement of hardness, resistivity and its temperature coefficient and by studies of microstructure. Two maxima in the phase diagram correspond to PdFe and Pd<sub>3</sub>Fe. It was found that the solubility of Pd in  $\alpha$ -Fe did not exceed 5 at.% at 800°C, though in  $\gamma$ -Fe it is infinitely soluble. The temperature of the  $\alpha \rightleftharpoons \gamma$  transition of Fe is lowered by the presence of Pd. A eutectoid point at 40 at.% Pd is given by the intersection of the curve bounding the two-phase region,  $\alpha + \gamma$ , with that of the  $\gamma + \gamma_1$  region. The eutectoid horizontal extends at 620°C from the solid solution to the region where PdFe exists. At 57 at.% Pd the temperature maximum of the curve bounding the PdFe ( $\gamma_1$ ) region is formed at 830°C; that in the region of Pd<sub>3</sub>Fe occurs at 70 at.% Pd. The curves bounding the regions of PdFe and Pd<sub>3</sub>Fe intersect at 35 at.% Fe.

### The Palladium-Ruthenium System

A. A. RUDNITSKII and R. S. POLYAKOVA, *Russ. J. Inorg. Chem.*, 1959, 4, (6), 631-636 (Transl. of *Zhur. Neorg. Khim.*, 1959, 4, (6), 1404-1414)

The investigation was restricted to Pd-rich alloys which were examined by X-ray analysis, thermo-e.m.f. measurements, differential thermal analysis and measurements of hardness and electrical resistivity. Peritectic reactions occur at 1593°C between the liquid and  $\gamma$  solid solution based on Ru, with the formation of an intermediate  $\beta$ -phase and at 1575°C between the liquid and  $\beta$ -phase with the formation of a solid solution based on Pd. The intermediate  $\beta$ -phase occupies a narrow region 15-20 wt.% Ru and undergoes eutectoid dissociation at 724°C and 15 wt.% Ru. The solubility of Ru in Pd is <5 wt.% at room temperature and increases to ~12 wt.% at 1400°C. The solubility of Pd in Ru at room temperature is <10 wt.% and rises to ~40 wt.% at the temperature of the peritectic reaction.

### The Constitution and Properties of Zirconium-Palladium Alloys

K. ANDERKO and H. W. SCHLEICHER, *Metall.*, 1959, 13, (8), 763

The constitution of the Zr-rich side of the system

was investigated by thermal, microscopic and X-ray analysis and by conductivity and hardness testing. Because of the reactivity, the alloys were worked at high temperatures under vacuum or inert gas protection. The intermediate phases Zr<sub>3</sub>Pd and ZrPd exist; Zr<sub>2</sub>Pd melts at 1085°C and ZrPd at over 1600°C. There is a eutectic point at 1030°C with 27.5 wt.% Pd. The maximum solubility of Pd in  $\beta$ -Zr is 13 wt.%; in  $\alpha$ -Zr it is <0.1 wt.%. The  $\beta$ -Zr phase forms a eutectoid at 765°C with 8 wt.% Pd. Alloys with Pd content up to 10% were corrosion tested in a pressure bomb at temperatures between 350° and 480°C. The stability of the alloys at 700-800°C passes through a minimum value with increasing Pd content. A 0.5% alloy is as resistant as 5% or unalloyed Zr.

### The Structure of the Systems Cobalt-Gallium, Palladium-Gallium, Palladium-Tin and Related Compounds

K. SCHUBERT, H. L. LUKAS, H.-G. MEISSNER and S. BHAN, *Z. Metallkunde*, 1959, 50, (9), 534-540

The Co-Ga system was determined by thermal, microscopic and X-ray analysis. The structure of CoGa<sub>3</sub> was elucidated. The phases FeGa<sub>3</sub>, RuGa<sub>3</sub>, OsGa<sub>3</sub>, RhGa<sub>3</sub>, RhIn<sub>3</sub>, IrGa<sub>3</sub> (h) and IrIn<sub>3</sub> had the same structure analogous to CuAl<sub>2</sub> (C16). The systems Pd-Ga and Pd-Zn were determined in the same way. Pd<sub>3</sub>Ga is of the Ni<sub>3</sub>Si (C37') type as are Pd<sub>2</sub>Al, Pd<sub>2</sub>In, Rh<sub>2</sub>Sn and Pd<sub>2</sub>Sn. Pd<sub>3</sub>Ga<sub>3</sub>, Pd<sub>3</sub>Al<sub>3</sub> and Pd<sub>3</sub>In<sub>3</sub> are of the Rh<sub>3</sub>Gc<sub>3</sub> type with structures analogous to NiAs (B8). PdGa<sub>3</sub> has a structure similar to CoGa<sub>3</sub> (C16). Phase diagrams are given for the Co-Ga, Pd-Ga and Pd-Zn systems.

### Palladium-Cadmium

M. ADER and J. PAVLIK, U.S. Atom. Energy Comm. Report ANL-5996, 1959, 94-97

The solubility between 397° and 500°C of Pd in Cd was investigated. Samples were taken after constant temperatures had been maintained for an hour and the Pd content was determined spectrophotometrically. Solubility data are given in a table and a least squares analysis of the data is given. The solubility of Pd was found to be lower than that expected by extrapolation of thermal analysis data obtained at higher Pd concentrations.

### Palladium-Uranium-Cadmium

M. ADER and J. PAVLIK, U.S. Atom. Energy Comm. Report ANL-5996, 1959, 97-99

The effect of U on the solubility of Pd in Cd

solutions was determined, Mg being included in the metal phase to suppress air oxidation of U. Pd and U solubility data are shown on a reciprocal temperature plot and a least squares analysis of the Pd data is given. Pd solubility is only slightly depressed by the presence of U in Cd-rich solutions. U solubility in liq. Cd is decreased up to 200 times by saturating with Pd.

### The Effect of Alpha-Activity on the Corrosion Rate of Platinum and Zirconium in HBr

D. M. ZIV and I. A. EFROS, *J. Nucl. Energy*, 1959, 9, (1-4), 189-190 (Transl. of *Atomnaya Energiya*, 1958, 4, 293)

In this investigation  $^{210}\text{Po}$  in solutions of specific activity 0.3-1 curie  $\text{ml}^{-1}$  was used as the source of radiation. Pt and Zr foils of 99.9% purity were washed with HBr, distilled  $\text{H}_2\text{O}$  and alcohol, dried and accurately weighed. Measurements of corrosion rates in HBr were made. After exposure, the samples were again washed and weighed. At room temperature the corrosion rate of Pt is not markedly increased by  $\alpha$ -activity and there is only a small rate increase at 80°C by an activity of 0.3 curie  $\text{ml}^{-1}$ . The corrosion rate of Zr was increased at least 100 times by a similar activity. The increased rates are due to the action of atomic Br,  $\text{H}_2\text{O}_2$  and other radiolysis products of the HBr.

### Hydrogen Absorption by Palladium in Aqueous Solution

T. B. FLANAGAN and F. A. LEWIS, *Trans. Faraday Soc.*, 1959, 55, (8), 1400-1408

Cold drawn and annealed Pd wire spirals were used in the investigation which was carried out in 2N  $\text{H}_2\text{SO}_4$  at 25°C and 1 atm. The course of absorption was followed by measurement of the relative electrical resistance,  $R/R_0$ , of the Pd wires. The relationship between  $[\text{H}]/[\text{Pd}]$  and  $R/R_0$  for these wires was established separately, the Pd being charged by electrolysis. Factors influencing the attainment of equilibrium were investigated. It was shown that hydrogen may be adsorbed from solution to an equilibrium concentration  $[\text{H}]/[\text{Pd}] = 0.69$  which corresponds to that found from gas-phase isothermal experiments. The mechanism of the absorption is discussed; dissociation at the Pd surface is rate-determining.

### Surface-to-Volume Considerations in the Palladium-Hydrogen-Acid System

J. P. HOARE, *J. Electrochem. Soc.*, 1959, 106, (8), 640-643

Experiments were carried out using Pd electrodes of wire and sheet of varying diameter, thickness and shape. The surface of some of the electrodes was partly covered with polythene film. The electrodes were charged with hydrogen by standing on open-circuit in a hydrogen-

stirred 2N  $\text{H}_2\text{SO}_4$  solution and open-circuit potential against a Pt/ $\text{H}_2$  electrode was measured as a function of time. In some cases, the electrical resistance was recorded as a function of time. Results show that the time required for charging is related to the surface-to-volume ratio of the electrode. It is suggested that the penetration of the surface skin of the metal is the rate-determining step. The mechanisms of three hydrogen-charging methods are discussed.

### High Pressure Diffusion of Hydrogen through Palladium Membranes

A. J. DE ROSSET, Paper presented before the Division of Petroleum Chemistry, A.C.S. Atlantic City Meeting, Sep. 13-18, 1959

Diffusion rates through a 0.0008 in. thick membrane were measured at 650°-850°F. Upstream and downstream pressures ranged from 1-700 psig and 0-300 psig respectively with a maximum pressure drop of 400 psi. It was found that below 25 psia diffusion rate is proportional to pressure drop. Above 25 psia, the linear relationship holds for the differences of the 0.8 powers of the pressures. The rate-determining processes are believed to take place at the surface below 25 psia upstream pressure and in the bulk of the metal above 25 psia. Hydrogen was separated from nitrogen and from  $\text{CH}_4$  at 850°F and upstream and downstream pressures of 700 psig and 300 psig respectively.

### Liquidus and Solidus Relations in Iron-Rich Iron-Platinum Alloys

R. A. BUCKLEY and W. HUME-ROTHERY, *J. Iron Steel Inst.*, 1959, 193, (1), 61-62

Liquidus and solidus curves of Fe-rich Fe-Pt alloys were determined by thermal analysis. The system is of the open  $\gamma$ -field type. At 1519° C there is a ( $\delta$  + liquid)  $\rightleftharpoons$  peritectic horizontal and with increasing Pt content the  $\gamma$ -liquidus and solidus probably sink to a very shallow minimum. Both  $\delta$ - and  $\gamma$ -solid solution alloys have a very narrow freezing range. A comparison of the Fe-Pt, Fe-Pd, and Fe-Ni systems shows that Pt has a strong effect in stabilising the  $\gamma$ -phase.

### The Diffusion of Hydrogen through Palladium-Coated Quartz Glass

H. BÖRNERT and U. VON WEBER, *Z. anorg. allgem. Chem.*, 1959, 300, (1/2), 81-83

The rate of diffusion of hydrogen through quartz glass was measured between 301° and 1032°C at hydrogen pressures of 0.50, 0.75 and 1.00 atm. An activation energy of 9.8 k cal/mole was obtained by plotting diffusion rate against  $1/T$ . Changes in the activation energy at lower temperatures are believed to be due to a change from crystalline to intercrystalline diffusion. The diffusion rate through quartz glass coated by a film of Pd in the temperature range 400°-700°C is 1.44 times greater than that through pure quartz glass.

### A Paramagnetic Investigation of Hydrogenated Pd-Fe Alloys

J. P. BURGER, E. VOGT and J. WUCHER, *Compt. rend.*, 1959, **249**, (16), 1480-1482

The investigation was carried out with four Pd-Fe alloys containing 1, 3, 5 and 7 at.% Fe respectively. It was found that by saturating alloys of Pd-Fe with hydrogen, the magnetic moment of the Pd was neutralised. A magnetic moment of  $5.9\mu_B$  was found for Fe alone; this is the theoretical value for ferric ions. The paramagnetic Curie points of the hydrogenated alloys vary linearly with the Fe content.

### A Note on Certain Properties of Osmium and of its Alloys with Molybdenum

J. D. BAIRD, G. A. GEACH and A. G. KNAPTON, *Plansee Proc.*, 1958, 371-379

The melting point of Os was determined as  $3000 \pm 200^\circ\text{C}$  by an optical pyrometer technique. Changes in surface orientation gave hardness values varying from 300 to 670 V.H.N. At  $1200^\circ\text{C}$  the mean hardness is still 300 V.H.N. Os is very brittle and fractures mainly by cleavage on basal planes. It work-hardens unevenly due to its anisotropy. The Mo-rich side of the Mo-Os system was examined. Phases of the  $\beta$ -tungsten and sigma structures are formed. The solubility of Os in Mo is less than that of Re. Additions of up to 10 at.% Os reduce the ductility, but it increases to a maximum at 14 at.% Os before again decreasing. The 14 at.% Os alloy has a room temperature hardness of 450 V.H.N. which is retained up to  $1200^\circ\text{C}$ .

## ELECTROCHEMISTRY

### Electrode Potentials of the Palladium-Hydrogen System

T. B. FLANAGAN and F. A. LEWIS, *Trans. Faraday Soc.*, 1959, **55**, (8), 1409-1420

Hydrogen was absorbed from 2N  $\text{H}_2\text{SO}_4$  and 2N HCl solutions into cold-drawn and annealed Pd wire. Electrode potentials were measured in the range  $[\text{H}]/[\text{Pd}] = 0$  to  $[\text{H}]/[\text{Pd}] = 0.69$ . Hydrogen content was determined simultaneously by measuring the relative resistance  $R/R_0$  of the Pd wire. Several methods of preactivating the wire surface were investigated. Agreement was found between the free energies of solution of hydrogen in Pd calculated from electrode potentials and from gas-phase isotherms. A free-energy difference between electrically charged and gas-phase saturated Pd hydrides cannot be supported.

### Influence of Surface Preparation of Platinum Electrodes on Cathodic Processes of Hydrogen Peroxide

G. BIANCHI and G. CAPRIOGLIO, *Electrochim. Acta*, 1959, **1**, (1), 18-21

Two different methods of surface preparation

were used. Treatment in boiling  $\text{H}_2\text{O}$  resulted in "bare" electrodes, while subsequent anodic or chemical oxidation gave "oxidised" electrodes. Measurements of static tension values were made and cathodic polarisation curves were plotted for Pt electrodes in  $\text{H}_2\text{O}_2$  solutions over a range of pH values. With acid and neutral solutions, results with the "oxidised" electrode could be interpreted as an electrochemical reduction of  $\text{PtO}_2$ . Values obtained for alkaline solutions are inconclusive.

### Study of the Impedance of a Platinum Electrode in a Redox System

J. LLOPIS, J. FERNÁNDEZ-BIARGE and M. PÉREZ FERNÁNDEZ, *Electrochim. Acta*, 1959, **1**, (2/3), 130-145

The system  $\text{Fe}^{2+}/\text{Fe}^{3+}$  (HCl, aq.) was studied in order to illustrate the intervention of an adsorption process in the expression of the faradic impedance of an electrode when acting in the presence of a redox system. Experimental results are interpreted and the mechanism of the electrode reaction is discussed. Results support the theory of Gerischer that adsorption is a rate-determining step. The system  $\text{I}_2/\text{I}^-$  ( $\text{H}_2\text{SO}_4$ , aq.) was also studied using active and non-activated electrodes and the mechanism of this electrode reaction is discussed.

### The Electrochemical Behaviour of Hydrogen and Oxygen Mixtures on Platinum Electrodes

G. BIANCHI and F. MAZZA, *Electrochim. Acta*, 1959, **1**, (2/3), 198-204

Electrochemical processes accompanying the combination of hydrogen and oxygen dissolved in aqueous solutions on Pt electrodes were investigated at  $25^\circ\text{C}$ . Partial processes involved are cathodic oxygen reduction and anodic hydrogen oxidation. Mixed potentials were measured and anodic and cathodic polarisation curves were plotted for acid, neutral and alkaline solutions.  $\text{H}_2\text{O}_2$  solutions are reduced by hydrogen and the measured mixed potentials may be related to the processes of hydrogen oxidation and  $\text{H}_2\text{O}_2$  reduction. For concentrated  $\text{H}_2\text{O}_2$  solutions (0.01M), the mixed potential equals the potential for  $\text{H}_2\text{O}_2$  reduction.

### Hydrogen Overvoltage on Bright Platinum III. Effect of Hydrogen Pressure

S. SCHULDINER, *J. Electrochem. Soc.*, 1959, **106**, (10), 891-895

Experiments were conducted in 1M  $\text{H}_2\text{SO}_4$  stirred by hydrogen, 5% nitrogen/hydrogen or hydrogen/helium mixtures using a small Pt sphere at the end of a short length of Pt wire as cathode. Kinetic parameters were determined from the anodic and cathodic overvoltages. Experimental data support the theory of a mechanism controlled by slow combination of hydrogen atoms adsorbed on the Pt surface. It

is shown from the Langmuir adsorption isotherm that the surface of the active Pt electrode is sparsely covered with atomic hydrogen at equilibrium.

## LABORATORY APPARATUS AND TECHNIQUE

### The Determination of Oxygen in Titanium-Manganese Alloys

D. F. WOOD and J. A. OLIVER, *Analyst*, 1959, **84**, (1000), 436-439

A semi-micro vacuum fusion method was used for the determination in an alloy containing 4% each of Al and Mn. 30 mg sample with 10 mg of Sn were placed in a graphite crucible containing about 5 g of Pt and the crucible was heated in an evacuated system for 10 minutes at 1500°C to volatilise the Mn. On raising the temperature to 1880°C, oxygen was converted quantitatively to CO in the Pt bath. Evolved gases were collected and analysed. The method should be applicable to other metals containing alloying amounts of Mn.

### Platinum-Flux Method for Determining Oxygen in Titanium

W. R. HANSEN, M. W. MALLET and M. J. TRZECIAK, *Anal. Chem.*, 1959, **31**, (7), 1237-1241

In this modification of the Pt-bath technique, a 0.25 g sample is wrapped in at least eight times its weight of Pt and dropped into a vacuum-fusion furnace maintained at 1850°C. The evolved gas is collected in a 30 min extraction and then analysed. Blank corrections are made. The accuracy of the method is compared with that of the dry-crucible technique. By both methods it is possible to recover at least 92% of the O<sub>2</sub> in unalloyed Ti. Average recovery from a 6% Al-4% V-Ti alloy was 93% by both techniques. Reproducible results were obtained from 8% Mn-Ti, 2% Fe-2% Cr-2% Mo-Ti and 5% Al-2.5% Sn-Ti alloys.

### Laboratory Equipment Made of High-Stability Platinum

G. REINACHER, *Werkstoffe u. Korrosion*, 1959, **10**, (9), 564-572

A Au-Pt alloy containing a small amount of Au has been developed in an attempt to improve the mechanical strength and dimensional stability of Pt laboratory apparatus without detriment to its chemical resistance. The alloy, which melts at 1740°C, in the annealed state has twice the tensile strength of normal crucible-Pt at temperatures up to 1000°C. Comparison of crucibles and dishes of the Au-Pt alloy with those of normal Pt in analytical laboratories has shown that they have excellent shape stability and that their chemical resistance is as good. The weight constancy of both materials is compared after use for ignition,

fusion with various materials and after contact with acids.

### The Palladium Electrode in Aqueous and Non-Aqueous Titrimetry

J. T. STOCK, W. C. PURDY and T. R. WILLIAMS, *Anal. Chim. Acta*, 1959, **20**, (1), 73-78

Two types of electrode are described, one with a horizontal Pd diaphragm and the other, a generating electrode, with a vertical diaphragm and fast constant speed circulation. The latter type was found to be the more reliable; it responds rapidly and gives reproducible results. This electrode has been used in a variety of acid-base titrations in aqueous and non-aqueous systems.

## CATALYSIS

### Selective Hydrogenation of Olefines in Olefine-Aromatic Mixtures

R. M. SOEMANTRI and H. I. WATERMAN, *Chim. et Ind.*, 1959, **82**, (2), 181-188

Selective hydrogenation of olefines in the presence of Pt/SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, Pt/Al<sub>2</sub>O<sub>3</sub>/Cl, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and WS<sub>2</sub> was investigated. A 1:1 mixture of hexenes and xylenes (o-, m- and p-) and hydrogen was passed over the catalyst after preheating. The gases and liquids were separated and the reaction products were analysed by the fluorescent indicator adsorption method. A study was made of the influence of varying temperatures, pressures, space velocities and H<sub>2</sub>:organic mixture ratios. Pt/SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, Pt/Al<sub>2</sub>O<sub>3</sub>/Cl and WS<sub>2</sub> showed good selectivity under the experimental conditions.

### The Reactions of Palladium Chloride with Olefinic C=C Double Bonds

J. SMIDT and R. SIEBER, *Angew. Chem.*, 1959, **71**, (19), 626

Experiments were carried out to ascertain the action of aqueous PdCl<sub>2</sub> solution on olefinic compounds containing nitrogen. The compounds chosen were unsaturated amines, unsaturated nitro-compounds, an unsaturated nitrile and unsaturated amides. From the unsaturated amines the N was split off and mono- and dicarbonyl compounds were obtained. The nitro group was retained by the unsaturated nitro-compounds, with the higher nitro-olefines giving a mixture of several carbonyl compounds. Unsaturated amides reacted as free carbonic acids.

### Decomposition of Hydrogen Peroxide Catalysed by Ruthenium Complexes

F. P. DWYER, N. NELSON KING and M. E. WINFIELD, *Austral. J. Chem.*, 1959, **12**, (2), 138-146

Kinetic measurements and experiments such as electrolytic oxidation of Ru complexes followed by reduction with H<sub>2</sub>O<sub>2</sub> were used to obtain evidence for the mechanism of the decomposition. The four selected octahedral Ru<sup>II</sup> complexes

[Ru<sup>II</sup> dipy<sub>2</sub> gly](ClO<sub>4</sub>), [Ru<sup>II</sup> acac dipy<sub>2</sub>](ClO<sub>4</sub>), [Ru<sup>II</sup> gly py<sub>4</sub>](ClO<sub>4</sub>), and [Ru<sup>II</sup> acac py<sub>4</sub>](ClO<sub>4</sub>), (where dipy, gly, acac and py represent dipyridyl, glycinato, acetylacetonato and pyridine groups respectively), were all oxidisable at least in part to the Ru<sup>IV</sup> state by H<sub>2</sub>O<sub>2</sub>. Oxidation of Ru<sup>II</sup> to Ru<sup>IV</sup> accompanied by reduction of H<sub>2</sub>O<sub>2</sub> to hydroxyl ions, followed by a 2-electron reduction of Ru<sup>IV</sup> to Ru<sup>II</sup> with oxidation of H<sub>2</sub>O<sub>2</sub> to O<sub>2</sub> and hydrogen ions appears to be the basis of the catalysis.

#### Catalysis of Hydrogen Peroxide Decomposition by 2-Electron Oxidation and Reduction

N. NELSO KING and M. E. WINFIELD, *Austral. J. Chem.*, 1959, **12**, (2), 147-151

The decomposition of H<sub>2</sub>O<sub>2</sub> by Ru<sup>II</sup> complex catalysts is used as a basis for a thermodynamical explanation of the reaction mechanism. Support is found for the suggestion that the usual chain mechanism is not necessarily the main course of the reaction if the catalyst can readily undergo a reversible 2-electron oxidation. An ionic mechanism is thermodynamically possible and is favoured if the catalyst chosen has appropriate redox characteristics.

#### The Present State and Development Prospects of the Production of Dilute Nitric Acid

M. A. MINIOVICH, *J. Appl. Chem. U.S.S.R.*, 1958, **31**, (8), 1121-1129 (Transl. of *Zhur. Priklad. Khim.*, 1958, **31**, (8), 1129-1138)

The increase in the production of nitrogenous fertilizers in post-war years is illustrated by production figures obtained from the West. Production processes operate either at atmospheric pressure, at high pressure or by a combination of atmospheric and high pressures. An examination of the merits of the three processes shows that the combined process is the most promising of existing methods. Methods of purifying the ammonia-air mixture are described. The efficiency of Rh-Pt catalysts used in ammonia oxidation in the West is compared with that of Pd-Rh-Pt catalysts used in the U.S.S.R. Operation of a two-stage oxidation process in the U.S.S.R. makes possible a 60% reduction in precious metals used. Searches for efficient non-Pt catalysts for ammonia oxidation have not been successful. Operating techniques and plans to decrease power consumption are discussed. The problems of the development of thermal and radiation processes for the production of oxides of nitrogen and treatment of waste gases for their removal are outlined.

#### Catalytic Properties of the System Pd-Pt

A. A. ALCHUDZHIAN and M. A. INDZHIKYAN, *Zhur. Fiz. Khim.*, 1959, **33**, (7), 1467-1472 (English summary)

A study was made of co-precipitated Pd-Pt catalysts for the hydrogenation of C<sub>6</sub>H<sub>6</sub>. It was

shown that with a decreasing Pd:Pt ratio, the catalytic activity reaches a minimum where Pd:Pt has a value between 1:1 and 1:2. The paramagnetism of the solid solution decreases with increasing Pt content. Neither the paramagnetism nor catalytic activity has a zero value, whatever the ratio Pd:Pt. Similar Pd:Pt values are associated with least catalytic activity and lowest paramagnetism.

#### Kinetics of Catalytic Liquid Phase Hydrogenation. I. The Hydrogenation of Aromatic Nitrocompounds over Colloidal Rhodium and Palladium

H.-C. YAO and P. H. EMMETT, *J. Amer. Chem. Soc.*, 1959, **81**, (16), 4125-4132

Experiments were carried out by kinetic methods using *p*-nitrophenol and *p*-nitroaniline in water-ethanol and water-dioxane solutions. The reaction rate was followed by measuring (i) the change of hydrogen volume at constant pressure of 1 atm and (ii) the change of hydrogen pressure at constant volume. Results show that the catalytic behaviour of Pd towards the compounds studied is essentially the same as that of Rh. The reaction is, within the experimental conditions, first order with respect to hydrogen pressure. The reaction order with respect to substrate was found to vary with the amount of catalyst used and with the nature of the solvent. The reaction rate is affected by the nature of the substrate only when the reaction is first or fractional order with respect to it. Under conditions leading to fractional or first order with respect to the substrate, the activation energy is in the range 12-15 k cal/mole, but it is only a few k cal when the rate is limited by hydrogen diffusion through the solvent. A kinetic equation is derived which supports the kinetic characteristics of the reaction.

#### Catalytic Activation of Hydrogen in Aqueous Solution by the Chloropalladate (II) Ion

J. HALPERN, J. F. HARROD and P. E. POTTER, *Canad. J. Chem.*, 1959, **37**, (9), 1446-1450

The rate of catalytic reduction of FeCl<sub>3</sub> by molecular hydrogen in the presence of PdCl<sub>2</sub> was determined by measuring the volume of hydrogen taken up at constant pressure. The PdCl<sub>2</sub> acts as a homogeneous catalyst for the reaction. It was found that the rate law is  $-d[H_2]/dt = k[H_2][PdCl_4^{2-}]$ . The reaction mechanism is discussed.

#### Regenerative Catalytic Reforming

C. E. SLYNGSTAD, *Indust. & Eng. Chem.*, 1959, **51**, (9), 993-996

The development of Pt regenerative catalysts and the economic advantages of their use are described. Operation at lower pressures with an increased yield of high-octane fuel has become possible, while continuity of operation provides a continuous source of H<sub>2</sub> for other processes. Operating costs are reduced by lower circulating gas

rates and lower catalyst replacement costs. The essential properties of regenerative Pt catalysts are stated and a case study of a five-stage reformer is presented.

### Studies of Mixed Hydrogenating Adsorption Catalysts. I. An Investigation of Mixed Pd-Ag Catalysts on Silica Gel

A. A. ALCHUDZHYAN and M. A. MANTIKYAN, *Zhur. Fiz. Khim.*, 1959, **33**, (4), 780-789 (English summary)

A study has been made of the effect of Ag upon the catalytic activity of thin Pd layers on SiO<sub>2</sub> with respect to the hydrogenation of C<sub>6</sub>H<sub>6</sub>. It was shown that, in general, with increasing Ag content on the Pd/SiO<sub>2</sub> surface (at constant Pd content) the catalytic activity increases, attains a maximum and then decreases. The degree of activation or deactivation of the Pd by the Ag has been found to depend upon the extent of SiO<sub>2</sub> surface coverage by the Pd. Investigation of the kinetics of hydrogenation of C<sub>6</sub>H<sub>6</sub> has shown that the reaction is of zero order with respect to C<sub>6</sub>H<sub>6</sub> and to hydrogen, both on Pd/SiO<sub>2</sub> and Pd+Ag/SiO<sub>2</sub>, the apparent activation energy being practically the same for all the catalysts. It is concluded that on introducing Pd and Ag to the SiO<sub>2</sub> surface they interact so as to change the number of active sites without changing its energy state.

### Catalyst Applications to Continuous Strip Ovens

R. J. RUFF, *Wire & Wire Products*, 1959, **34**, (10), 1346-1348 and 1390-1391

A catalyst used for the oxidation of noxious waste gases from enamelling ovens consists of a thin coating of Pt alloys electrolytically deposited on high Ni-alloy ribbon supporting material. The design of ovens for varying requirements is illustrated and the utilisation of heat energy released by catalysis is discussed. Catalysts may be used in ovens operating at temperatures as low as 150°F although the normal operating range is 500°-600°F. Advantages of catalytic oxidation of oven exhaust gases are assessed.

### A Contribution to the Study of Catalytic Reactions on Incandescent Platinum. Determination of the Volatilisation of the Catalyst by the Use of Radioactive Platinum

P. BUSSIÈRE, University of Lyon. Thesis presented July 1959, 73 pp.

The volatilisation of a Pt ribbon catalyst during the combustion of air or an air-CH<sub>4</sub> mixture was studied. Radioactivation of the Pt prior to combustion facilitated the estimation of the amount which passed into the gaseous phase. The apparatus which was used both for the combustion reactions and for the measurement of the radioactivity of the gases is described in detail. Pt ribbons 0.02 mm thick and 2.20 mm long were heated electrically in a combustion chamber

itself enclosed in a larger Pyrex glass ampoule. Temperatures were measured by an optical micropyrometer and the radioactivity of the gaseous mixture was measured directly by a Geiger-Müller counter. The volatilised radioactive Pt was also separated by filtration of the gas mixture, chemical solution, separation by paper chromatography and was estimated by measurement of its activity. The principal activities considered in the experiments were those of Pt<sup>197</sup> and Au<sup>199</sup> (arising from the decay of Pt<sup>199</sup>), the effect of other isotopes being regarded as negligible. Measurements were made at temperatures between 1380° and 1510°C in air or a 3% CH<sub>4</sub>-air mixture. It was found that both Au and Pt volatilised more quickly in the gas mixture than in air alone and, for both metals, volatilisation increased with increasing temperature. A suggested explanation for the preferential volatilisation of Pt in the CH<sub>4</sub>-air mixture is that the interaction of CH<sub>4</sub> and the oxide (or oxides) of volatilised Pt brings about the decomposition of the latter with the production of atomic O.

### Preparation of Diamond

H. P. BOVENKERK, F. P. BUNDY, H. T. HALL, H. M. STRONG and R. H. WENTORF, *Nature*, 1959, **184**, (October 10), 1094-1098

Diamond has been synthesised in systems involving C dissolved in molten metal catalysts. Operating pressures ranged from 55,000 to 100,000 atm and temperatures were between 1200° and 2400°C. Catalysts used were Ta, Cr, Mn, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, and Pt.

## GLASS TECHNOLOGY

### Crystallisation of Sodium Disilicate Glass

J. A. PASK, *Glass Industry*, 1959, **40**, (7), 354-355 (Paper presented at the 61st Annual Meeting of the Amer. Ceram. Soc., Chicago, May 1959)

Nucleation and crystal growth from a Na<sub>2</sub>Si<sub>2</sub>O<sub>3</sub> glass were observed, using a high-temperature microscope. Both high-temperature nucleation from the glass-Pt interface and low-temperature nucleation at the glass-air interface were observed. The kinetics of the crystallisation process were studied. The crystal form produced depends upon both the temperature of growth and the nucleation catalyst on which it is grown.

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

G. E. RINDONE, *Glass Industry*, 1950, **40**, (7), 354 (Paper presented at the 61st Annual Meeting of the Amer. Ceram. Soc., Chicago, May 1959)

The importance of Pt nucleation of glass was reviewed. The optimum condition of crystallisation is reached when the Pt particles are extremely small. Further studies on the crystallisation rate of a lithium silicate glass heated at constant

temperature have been carried out by X-ray diffraction analysis and electron microscopy. It was found that the amount of crystallisation occurring at a given time and temperature reaches a maximum of about 0.005% Pt when the heating time is short. With longer heating or increase of temperature, the amount of crystallisation becomes greater as the Pt content is increased to 0.025%. Electron microscopy revealed that prior to any heat treatment, the glass contained a fine structure.

## TEMPERATURE MEASUREMENT

### A Survey of Temperature Measuring Techniques

W. A. SEATHERTON, *Brit. Commun. & Electronics*, 1959, 6, (10), 700-709

The basic capabilities and limitations of various techniques for measuring temperatures encountered in industrial processes are outlined. Both

contact and non-contact methods of measurement are discussed and classified. The principles of operation and applications of electrical resistance thermometers and thermocouples made of base metals and Pt metals are given in some detail. Charts have been prepared indicating the applications of each type of instrument.

### The Vacuum Casting of Uranium

J. STEPHENSON, *J. Brit. Nucl. Energy Conf.*, 1959, 4, (4), 335-341

The design of a furnace developed by the U.K.A.E.A. for melting and casting U under vacuum is described. In experiments to establish the relationship between temperature and pressure, the casting temperature was measured by a 13% Rh-Pt:Pt thermocouple in the side wall of the crucible. A second thermocouple shielded by a mullite sheath was fitted through the sighting hole above the graphite crucible in order to measure the temperature below the metal surface. Details of the casting assemblies and techniques are given.

## NEW PATENTS

### New Dioxolane Derivatives

SOC. DES USINES CHIMIQUES RHONE POULENC  
*British Patent* 815,968

2-piperidyl-dioxolanes are prepared by reducing 2-pyridyl-dioxilanes of given general formula by means of hydrogen in the presence of an Adams' platinum catalyst.

### Saturated Aldehydes

THE DISTILLERS CO. LTD. *British Patent* 816,151

An ethylenically unsaturated aldehyde is hydrogenated in the vapour phase at elevated temperature to the corresponding saturated aldehyde by reaction with hydrogen in the presence of a platinum group metal catalyst. The catalyst is made by treating an alumina, magnesia, titania or chromia support with a solution of a compound of the platinum group metal in an organic solvent to deposit the oxide of the metal, treating the resulting product with an aqueous solution of the hydroxide, carbonate or bi-carbonate of an alkali metal and finally reducing the oxide.

### Isomerisation of Alkanes

ENGELHARD INDUSTRIES INC. *British Patent* 820,140

A normal alkane is isomerised by bringing it, in admixture with 1-5 moles of hydrogen per mole of alkane, into contact with a platinum metal-alumina catalyst at 800-900°F, a pressure of 200-500 psig and a wt. hourly space velocity of 2-20. The feed catalyst is characterised by large pore, high area base structure composed of gamma alumina modifications resulting from the drying and calcining of a mixture of precursor

hydrous alumina phases containing 65-95% of tri-hydrate. The catalyst contains 0.1-1% by wt. of a platinum metal, preferably platinum, in sufficiently finely divided form as to exhibit, by X-ray diffraction, the absence of crystallites and crystals of larger size than 50 Å.

### Reforming of Naphthas

ESSO RESEARCH & ENGINEERING CO. *British Patent* 821,210

A naphtha boiling at 170-340°F is reformed in the presence of a platinum-alumina-halogen catalyst and added hydrogen at 850-900°F, using a naphtha residence time in the reforming zone of 15-50 sec. A heart-cut fraction boiling at 175-290°F is recovered from the products and is reformed at 925-1000°F for 100-200 sec to produce a gasoline. A material containing alkyl aromatics and boiling above 290°F is recovered from at least the first reforming zone and this is thermally reformed to recover a gasoline.

### Isomerisation of Alkanes

ENGELHARD INDUSTRIES INC. *British Patent* 822,670

Alkanes are isomerised by contacting the alkane(s) and hydrogen with a catalyst composed of sulphided rhodium supported on alumina at 650-1000°F, a pressure of 200-1000 psig, a hydrogen to alkane molar ratio of 1:1 to 20:1 and a weight hourly space velocity of 0.5-20. The catalyst is prepared by contacting a calcined composition of rhodium on the support with a sulphiding agent, e.g. hydrogen sulphide, at 70-1000°F and a pressure of up to 100 psig.