

# ABSTRACTS

*of current literature on the platinum metals and their alloys*

## PROPERTIES

### An Investigation of the System Palladium-Rhodium-Silver

A. A. RUDNITSKII, A. N. KHOTINSKAYA and K. S. DUPLIK, *Zhur. Neorg. Khim.*, 1961, **6**, (7), 1622-1635

The alloys were investigated in the annealed and quenched states by a study of microstructure, hardness, tensile strength, elongation, electrical resistivity and its temperature coefficient, and integral thermo-e.m.f. Sections with fixed amounts of Pd, parallel to the Rh-Ag side, and with fixed amounts of Rh, parallel to the Pd-Ag side, were used for the construction of ternary diagrams. The position of the boundaries of the  $\alpha$ ,  $\beta$ , and  $\alpha + \beta$  phases were determined. It was found that the solid solubility of Pd in Ag is limited by the addition of  $> 1$  wt. % Rh and that the mechanical properties of the ternary alloys are superior to those of the binary alloys.

### The Constitution Diagram of the Tungsten-Osmium Binary System

A. TAYLOR, B. J. KAGLE and N. J. DOYLE, *J. Less-Common Metals*, 1961, **3**, (4), 333-347

Alloys in the system were examined by X-ray and micrographic techniques. Three single-phase fields observed were: (i) a b.c.c.  $\alpha$ -W primary solid solution, (ii) a tetragonal  $\sigma$ -phase, and (iii) a hexagonal close-packed  $\theta$ -Os terminal solid solution. The  $\alpha$ -W phase contains 18.5 at. % Os at 2945°C and 6 at. % Os at 1200°C, and the  $\theta$ -Os phase extends from 46 at. % Os at 2725°C to 68 at. % Os at 1200°C. The  $\sigma$ -phase forms peritectically at 22 at. % Os at 2945°C and at 1200°C extends from 21 to 35 at. % Os.

### Alloys of Platinum with Base Metals - A New Method for Their Preparation

W. KLEMM, Abstracts of papers presented at the XVIIIth International Congress of Pure and Applied Chemistry, Montreal, Aug. 1961, 118-119

Pt-rich alloys were prepared by heating the base metal powder with Pt powder in a stream of hydrogen at temperatures in the range 900° to 1200°C. Alloys with Al, Sc, Mg, Ca, Sr and Li up to the compositions Pt<sub>3</sub>Al, Pt<sub>3</sub>Sc, Pt<sub>3</sub>Mg, Pt<sub>2</sub>Ca, Pt<sub>2</sub>Sr and Pt<sub>1</sub>Li, respectively, were obtained. Experiments with Y, La, Be, Ba, Ti, Cr and V are in progress. Crystal structures of many of the alloys were determined.

### The Effect of Alkali Hydroxide Melts on Various Noble Metals and Oxides

H. LUX, E. RENAUER and E. BETZ, *Z. anorg. allgem. Chem.*, 1961, **310**, (4-6), 305-319

The behaviour of Au, Ag, Rh, Ir, Pd, Pt, Rh-Pt, Co, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, HfO<sub>2</sub>, and ThO<sub>2</sub> in molten NaOH and KOH was investigated. Rh is very resistant to anhydrous NaOH melts, but is attacked more strongly by molten KOH. Ir and Pd are attacked moderately by molten NaOH and very strongly by KOH melts. At 300° and 400°C, 30% Rh-Pt shows a better resistance than pure Pt to molten KOH.

### The Domain Structure of Ordered Platinum-Cobalt Alloy

D. J. CRAIK and F. NUÑEZ, *Proc. Phys. Soc.*, 1961, **78**, (2), 225-232

The structures of equiatomic Pt-Co alloys were found to be consistent with those of materials with high uniaxial anisotropy and low saturation magnetisation. Previous work on the nature of the ordering is supported by the distribution of the easy axes within each grain.

### Effect of Plastic Deformation on Resistivity of Gold-Palladium Alloys

H. J. LOGIE, J. JACKSON, J. C. ANDERSON and F. R. N. NABARRO, *Acta Met.*, 1961, **9**, (8), 707-713

Eight different alloys with compositions in the range 10-85 at. % Pd were examined at liquid nitrogen temperature. Alloys with 10-60 at. % Pd show a decrease in resistivity on plastic strain, while alloys with  $> 60$  at. % Pd show an increase. The effects on resistivity of annealing the deformed alloys at room temperature and of extending the alloys at room temperature were also studied. Theoretical explanations of the observed results are given.

### The Mechanism of the Reaction of Platinum with Oxygen at Temperatures up to 300°C

U. A. ASANOV and N. A. SHISHAKOV, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1961, (2), 225-229

Pt, vacuum-condensed on glass plates, was heated in an oxygen stream at different temperatures up to 300°C. The various oxides formed on the surface of the Pt were examined by the electron-diffraction method. It was found that chemisorption of oxygen molecules occurs even on a clean Pt surface. Changes in the structure of the metal surface, which occur during the formation

of a peroxide film, are indicated by changes in its crystal orientation.

### Work Function Measurements on the Platinum Alloys of the Alkaline-Earth Metals

H. BATEY, *Proc. Instn. Elect. Engrs., Part B.*, 1961, 108, (40), 468-469

The thermionic work function of Ba-Pt, Sr-Pt and Ca-Pt alloys was found to be comparable with published data for work functions of pure Ba, Sr and Ca. The possibility of direct thermionic measurements for volatile metals alloyed with Pt is suggested.

### High Temperature Chemistry of the Chlorides of the Palladium-Group Metals

W. E. BELL, U. MERTEN, K. TAGAMI and M. C. GARRISON, Abstracts of papers presented at the XVIIIth International Congress of Pure and Applied Chemistry, Montreal, Aug. 1961, 108

The chlorides of Ru, Rh and Pd were studied in the temperature range 500°-1500°C and in the chlorine pressure range 0.1-1 atm. Dissociation pressures and vapour pressures were measured, and vapour species and condensed phases were identified. Thermodynamic properties of the various species were calculated. Under the experimental conditions, RuCl<sub>3</sub> and RhCl<sub>3</sub> are the only stable condensed chlorides of Ru and Rh. PdCl<sub>2</sub> is the only stable solid chloride of Pd. The important gaseous species are RuCl<sub>3</sub>, RuCl<sub>4</sub>, RhCl<sub>3</sub>, PdCl<sub>2</sub> and Pd<sub>5</sub>Cl<sub>10</sub>, a gaseous polymer.

### Vapour Pressures of the Platinum Metals

R. F. HAMPSON and R. F. WALKER, Abstracts of papers presented at the XVIIIth International Congress of Pure and Applied Chemistry, Montreal, Aug. 1961, 101-102. (Also *J. Res. Nat. Bur. Stds., Part A.*, 1961, 65A, (4), 289-295)

The rate of vaporisation of samples of Pt, Ir, Rh, and Pd, which were suspended from a micro-balance and heated inductively, was measured. Results obtained were: Pt,  $\log P_{\text{atm}} = 6.776 - (27,575/T)$  at 1916-2042°K,  $\Delta H^{\circ}_{\text{v}}(298) = 134.8 \pm 1.0$  kcal/mole; Ir,  $\log P_{\text{atm}} = 7.153 - (33,337/T)$  at 1986-2260°K,  $\Delta H^{\circ}_{\text{v}}(298) = 159.8 \pm 2.0$  kcal/mole; Rh,  $\log P_{\text{atm}} = 6.911 - (27,276/T)$  at 1709-2075°K,  $\Delta H^{\circ}_{\text{v}}(298) = 132.4 \pm 2.0$  kcal/mole. The heat of vaporisation,  $\Delta H^{\circ}_{\text{v}}(298)$ , for Pd was provisionally estimated to be  $90 \pm 2.0$  kcal/mole.

### Ruthenium and Rhodium Hexafluorides

H. H. CLAASSEN, H. SELIG, J. G. MALM and C. L. CHERNICK, *Abstracts of Papers*, 50 N, Div. of Inorganic Chem., 140th Meeting, A.C.S., Chicago, Sept. 1961

RuF<sub>6</sub> and RhF<sub>6</sub> were prepared by heating the metals in a fluorine atmosphere in a liquid nitrogen cooled quartz reactor. The compounds were identified by chemical analyses, vapour

density determinations, infrared spectral measurements, and X-ray powder photographs. Some physical and chemical properties of the compounds are discussed.

### The Adsorption of Hydrogen by Metals

N. N. KAVTARADZE, *Z. Phys. Chem. (Frankfurt)*, 1961, 28, (5/6), 376-392

The results of experimental work on the adsorption of hydrogen by vacuum-deposited Ni films are used to interpret the mechanism of the adsorption of hydrogen by Fe, Cr, and Pt. It was found that both reversible and irreversible adsorption occur, the former being molecular in character, while the latter is atomic.

### The Phase Diagram of Palladium Hydride and Deuteride at Lower Temperatures

E. WICKE, *Österr. Chem.-Ztg.*, 1961, 62, (10), 324-325 (Abstract of paper presented at Chemikertreffen, Vienna, Oct. 1961)

It has been established that the hydrides of U, Ti, Th, Ce catalyse the gas phase absorption of hydrogen by Pd and the evolution of hydrogen by Pd hydride at temperatures as low as -100°C. Using UH<sub>3</sub> as catalyst the phase diagrams for the systems Pd-hydrogen and Pd-deuterium were completed for the temperature region +50° to -78°C. A thermodynamic interpretation explains the difference in behaviour of hydrogen and deuterium.

### Adsorption of Carbon Monoxide on Palladium and Properties of Carbon Monoxide Surface Compounds

N. N. KAVTARADZE, E. G. BORESKOVA and V. I. LYGIN, *Kinetika i Kataliz*, 1961, 2, (3), 378-385

Volumetric methods and infrared spectroscopy were used in the investigation of CO adsorption on Pd films and on 10% Pd/SiO<sub>2</sub>. The simultaneous occurrence of both strong and weak adsorption is indicated by the data obtained. Strongly chemisorbed molecules of CO in the bridge form are found on the Pd surface. Variations of the spectra of CO surface compounds on reaction with oxygen were investigated.

## ELECTROCHEMISTRY

### A Method for Prevention of Hydrogen Embrittlement of Tantalum in Aqueous Media

C. R. BISHOP and M. STERN, *Corrosion*, 1961, 17, (8), 85-91

Further details of work reported previously (*J. Metals*, 1961, 13, (2), 144-145) are given. Ta in contact with small areas of Pt, Pd, Au, Ir, Rh, Os, Ru, Re, and Ag was exposed to concentrated HCl at 190°C. Pt and Pd were also used as contact materials in concentrated HCl at 250°C and in boiling 85% H<sub>2</sub>SO<sub>4</sub>. In all the tests Pt was

found to be the most effective in preventing hydrogen embrittlement of the Ta. The corrosion rates of both Pt and Ta in contact are reduced.

### **The Influence of Alloying Additions on the Corrosion Behaviour of Titanium**

W. R. FISCHER, C. ILSCHNER-GENSCH and W. KNORR, *Werkstoffe u. Korrosion*, 1961, **12**, (10), 597-607

The corrosion properties of welded Ti and of Ti-O and Ti-N alloys in 2.5% H<sub>2</sub>SO<sub>4</sub> were investigated. Improvements in the corrosion resistance in non-oxidising media of Ti alloyed with 0.2% or more Pd, observed by other workers, were confirmed. The corrosion behaviour of Ti-Pd alloys is explained by means of potential measurements and current/potential curves.

### **Electrochemical Aspects of Catalytic Hydrogenation at Platinum Contacts in Buffered Solutions**

F. BECK and H. GERISCHER, *Z. Elektrochem.*, 1961, **65**, (6), 504-517

The hydrogenation rate for a series of unsaturated compounds having olefinic double bonds was measured in an aqueous-alcoholic buffer solution using a platinised Pt gauze contact. The influence on the reaction rate of pH value, concentration of unsaturated compound and of Cl ions, and of polarisation of the catalyst was studied. It was found that the hydrogenation rate decreases with increasing pH, that the potential of the catalyst is an indirect measure of the hydrogenation rate, and that adsorbed Cl ions reduce the active surface.

### **The Behaviour of a Platinum Electrode in Silicate Melts**

V. I. MINENKO, S. M. PETROV and N. S. IVANOVA, *Zhur. Fiz. Khim.*, 1961, **35**, (7), 1534-1537 (English summary)

An investigation of the dependence of the potential of a Pt electrode upon the activity of oxygen ions in the melt, the partial pressure of oxygen in the gaseous phase, and the temperature showed that, in silicate melts, the electrode is reversible with respect to oxygen ions. A mechanism for the electrode processes is proposed.

## **METAL WORKING**

### **Influence of Some Platinum Metals on the Wettability of Silver**

J. B. ADAMEC and R. N. RHODA, *Welding J.*, 1961, **40**, (7), 330S-336S

Wetting tests were made in argon, hydrogen, and air at 1200°C with Ag alloys containing up to 20 wt.% Pt and/or Pd, or Ru. A 5% Ru-Ag alloy has wetting properties similar to those of pure Ag. Addition of Pd and Pt to Ag generally increases the wetting of Ni-base alloys in both argon and hydrogen. A Pd- or Pd-rich phase immiscible

with the Ag alloy is formed between the filler and base. The presence of oxide films on the base may hinder the wetting process. The greater oxidation resistance of the Pt alloys compared with Pd alloys results in better wettability.

### **The Evolution of Ductile High-Temperature Brazing Alloys**

D. C. HERRSCHAFT, *Metal Progress*, 1961, **80**, (3), 97-100

Cu-Ag brazing alloys have been modified for use in brazing stainless steel honeycomb material by the addition of small amounts of Li, In, and Pd. Pd-Ag and Pd-Au alloys have been used successfully in the brazing of components of jet engines, as have Pd-Cu and Pd-Ni alloys to a lesser extent. The possible use for brazing of other ternary Pd-containing alloys is mentioned. Liquidus and solidus temperatures for many of the alloys discussed are given in a table.

## **CATALYSIS**

### **Removing Carbon Monoxide from Ammonia Synthesis Gas**

H. C. ANDERSEN and W. J. GREEN, *Ind. Eng. Chem.*, 1961, **53**, (8), 645-646

A supported Pt catalyst is used in a two-stage adiabatic oxidation process which is operated at pressures in the range 100 to 200 p.s.i.g. In the first stage, in which steam is introduced, 1 to 2% CO is reduced to 0.2 to 0.4%, and in the second stage 0.3 to 0.5% CO is reduced to 5 to 10 p.p.m. Removal of CO is affected by CO<sub>2</sub> inlet concentrations >0.1%. Optimum process conditions are shown in a table.

### **Platinum-Acidic Oxide Catalysts for Hydrocracking**

H. L. COONRADT, F. G. CIAPETTA, W. E. GARWOOD, W. K. LEAMAN and J. N. MIALE, *Ind. Eng. Chem.*, 1961, **53**, (9), 727-732

Pt/Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> catalysts were used in the hydrocracking of light and heavy gas oils, catalytic cycle, and thermal gas oils in a continuous flow fixed-bed system. The effects of hydrogenation activity of the Pt and the acid activity of the support on activity, selectivity and stability of the catalysts are discussed. A study of product distribution shows a small change in ratio of light products with increased conversion, together with a large change in the ratio of gasoline to fuel oil. The advantages of pretreating, recycle and multiple pass operations are mentioned.

### **Pentane and Hexane Isomerisation**

J. A. RABO, P. E. PICKERT and R. L. MAYS, *Ind. Eng. Chem.*, 1961, **53**, (9), 733-736

The performance of a Pd/zeolite catalyst in the isomerisation of C<sub>5</sub> and C<sub>6</sub> paraffins is described.

Isomerisation takes place with excellent selectivity between 608° and 662°F, at 450 p.s.i. and with a hydrogen : hydrocarbon ratio of 3. Pressure and space velocity may be varied provided contact time remains constant. The catalyst is water insensitive and coke-resistant and is unaffected by up to 10 p.p.m. S in the feed. It has a long life under normal operating conditions.

### Hydrogenation and Dehydrogenation

B. T. ALEXANDER, D. J. BATLINER, W. M. KEELY and F. J. O'HARA, *Ind. Eng. Chem.*, 1961, **53**, (9), 767-771

Papers and patents published in the period 1959-60 are reviewed. Fundamental studies of hydrogenation and dehydrogenation processes and the catalysts employed in them are included. Pt metal catalysts are used in many of the processes reviewed. (99 references)

### Catalytic Oxidation of Methane

R. B. ANDERSON, K. C. STEIN, J. J. FEENAN and L. J. E. HOFER, *Ind. Eng. Chem.*, 1961, **53**, (10), 809-812

Methods of preparing the 30 catalysts used in this investigation are described. The catalysts, which included Pd/Al<sub>2</sub>O<sub>3</sub>, Pt/Al<sub>2</sub>O<sub>3</sub>, were tested in a micro-catalytic reactor and kinetic data were obtained. It was found that the activity of the metals or metal oxides supported on Al<sub>2</sub>O<sub>3</sub> per g active metal decreases in the order: Pt, Pd, Cr, Mn, Cu, Ce, Co, Fe, Ni, Ag.

### The Hydrogenation of Cycloalkenes over Supported Palladium Catalysts

J.-F. SAUVAGE, R. H. BAKER and A. S. HUSSEY, *J. Amer. Chem. Soc.*, 1961, **83**, (18), 3874-3877

10% Pd/C and 5% Pd/BaSO<sub>4</sub> catalysts were used in the hydrogenation of several 1,4-disubstituted cyclohexenes and Δ<sup>1,9</sup>- and Δ<sup>9,10</sup>-octalin in CH<sub>3</sub>COOH. With the exception of Δ<sup>9,10</sup>-octalin, extensive isomerisation of the unhydrogenated cycloalkenes was found. Cycloalkane product mixtures in which the thermodynamically more stable isomer predominates are obtained. A reaction mechanism which includes the formation of a "stereochemically symmetrical intermediate" is postulated.

### The Temperature Dependence of the Activity of Platinum Carbon Catalysts

C. NICOLAU, P. VENKER and E. POBITSCHKA, *Z. anorg. allgem. Chem.*, 1961, **311**, (3/4), 127-133

The activity of 5% Pt/C catalysts, which had been heat treated at 50°, 200°, 300°, 400° and 500°C, was studied in the hydrogenation of crotonic acid and *p*-nitroanisole. It was established that there is a decrease in catalytic activity following heat treatment. This decrease in activity may be correlated with a decrease in the number of free electrons in the catalyst. The catalytic activity also depends on the molecular geometry of the substrates.

### Selectivity of Palladium Catalysts for the Oxidation of Carbon Monoxide in the Presence of Hydrogen

P. MARS and TH. VAN DE MOND, *Nature*, 1961, **191**, (Sept. 2), 1003

Selective oxidation of 50 p.p.m. CO present in hydrogen may be carried out at room temperature and 1 atm pressure in the presence of a 0.5% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst.

### Catalytic Combustion Installation Achieves Remarkable Results

D. S. FRASER, *Fuel Efficiency*, 1961, **9**, (8), 32-33

The installation of an automatically controlled fume burner in an enamelling plant is described. An Oxycat Pt/Al<sub>2</sub>O<sub>3</sub> catalyst bed, after 4 years' operation, is still removing by oxidation 99% of the pollutants from the baking ovens. Recovery of the heat generated in the catalyst bed has resulted in 80% fuel saving and in increased production.

### Thermal and Catalytic Decomposition of Hydrocarbons

A. J. DE ROSSET and C. V. BERGER, *Ind. Eng. Chem.*, 1961, **53**, (8), 680-683

Recent papers concerning thermal decomposition, catalytic cracking and catalytic reforming processes are reviewed. (87 references)

### Catalytic Decomposition of Acid Hydrogen Peroxide Solutions—Electrochemical Investigations with Platinum and Gold

G. BIANCHI, G. CAPRIOGGIO, F. MAZZA and T. MUSSINI, Abstracts of papers presented at the XVIIIth International Congress of Pure and Applied Chemistry, Montreal, Aug. 1961, 199

Acid solutions of H<sub>2</sub>O<sub>2</sub> are decomposed by Pt, but not by Au. The behaviour of Pt and Au electrodes during the reduction-oxidation processes of acid H<sub>2</sub>O<sub>2</sub> solutions was investigated. The formation of Pt oxides influences the behaviour of Pt.

### Liquid C-18 Saturated Acids Derived from Linseed Oil

J. P. FRIEDRICH, H. M. TEETER, J. C. COWAN and G. E. MCMANIS, *J. Amer. Oil Chem. Soc.*, 1961, **38**, (7), 329-332

The monocarboxylic acids were prepared by heating one part of linseed oil in three parts of glycol (w/v ratio) at 295°C for 1 h with 25% excess NaOH, followed by distillation, and hydrogenation of the resulting free fatty acid monomers using a 10% Pd/C catalyst. The straight-chain components were separated by low temperature crystallisation from acetone. Cyclic and straight-chain monomeric acids and polymers were obtained in proportions which varied with experimental conditions.

## A Contribution to the Study of Surface Phenomena Associated with Catalytic Combustion on Incandescent Platinum

F. CROUZY, University of Lyon. Thesis presented Oct. 1959, 75 pp.

The evaporation rate of Pt in nitrogen, air, oxygen, and in a combustible mixture of gases was measured in the temperature region 1400°–1500°C. It was found that maximum evaporation occurs in oxygen (0.2 to 0.5 mg/cm<sup>2</sup>/h). In air the rate is 4 to 6 times less and is hardly increased in the presence of CH<sub>4</sub>. Evaporation in nitrogen is insignificant. Changes in surface crystal structure of the Pt resulting from heat treatment were studied.

## Reaction Processes in Catalytic Reforming Using a Special Platinum Catalyst

### Part I

R. BIRTHLER and P. STEINGASZNER, *Chem. Techn.*, 1961, **13**, (7/8), 412–417

The construction of the reforming plant at Böhlen is outlined. A study was made of the output of one of the five reactors in relation to operating time. A catalyst containing only 0.2% weight Pt was used. Octane numbers of the raw material and the reformat fractions were determined. The reactor products were analysed.

### Part II

P. STEINGASZNER and R. BIRTHLER, *Ibid.*, 418–423

The composition of the reformat found experimentally is compared with that obtained by thermodynamic calculations. Products resulting from isomerisation, dehydrogenation and dehydrocyclisation processes are described and their relative proportions analysed.

## Kinetics of the Catalytic Dehydrocyclisation of *n*-Heptane

J. C. ROHRER, H. HURWITZ and J. H. SINFELT, *J. Phys. Chem.*, 1961, **65**, (8), 1458–1460

*n*-Heptane was passed over a 0.3% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst in the presence of hydrogen. Relative rates of dehydrocyclisation and isomerisation of *n*-heptane were plotted as a function of hydrogen partial pressure. The dehydrocyclisation rate increases to a maximum with increasing hydrogen pressure at 471°C and 527°C and a maximum was also found for isomerisation at 471°C. It is suggested that ring closure is preceded by a dehydrogenation step and that the rate of removal of hydrogen-deficient residues from the Pt by hydrogen is the limiting factor in the reaction.

## The State of Platinum in Reforming Catalysts

H. E. KLUKSDAHL and R. J. HOUSTON, *J. Phys. Chem.*, 1961, **65**, (8), 1469–1470

Various supported Pt catalysts were analysed for soluble Pt and the variables considered were: (1) the ratio of chloride to Pt, (2) the type of

support, and (3) the effect of exposure to oxygen. Results provide no evidence for a specific soluble Pt complex. It is suggested that the soluble species may be Pt upon which oxygen is chemisorbed.

## The Kinetics of the Catalytic Synthesis of Hydrocyanic Acid and Formaldehyde According to the Theory of Rapid Processes in Gas Streams

L. ANDRUSSOW, *Génie chim.*, 1961, **86**, (2), 39–44

Similarities in the oxidising processes for the synthesis of HCN and CH<sub>2</sub>O are noted. The process kinetics are calculated and side-reactions are mentioned. The mechanism of diffusion through the platinised ceramic tubes or Rh-Pt or Ir-Pt gauzes used as catalysts in HCN synthesis is discussed.

## Unsaturated Lactams. II. The Catalytic Dehydrogenation of $\alpha$ , $\beta$ -Unsaturated Valerolactams to Pyridones

M. SHAMMA and P. D. ROSENSTOCK, *J. Org. Chem.*, 1961, **26**, (7), 2586–2587

A route to a variety of substituted pyridones is provided by the dehydrogenation of  $\alpha$ ,  $\beta$ -unsaturated lactams in the presence of a 5% Pd/C catalyst. Experimental details are given.

## Inhibition of Catalytic Reduction with Rhodium by Compounds Leading to Strong Nitrogen Bases. I. Hydrogenation of the C=N Linkage and the Promoter Effect of Certain Organic Acids

M. FREIFELDER, *J. Org. Chem.*, 1961, **26**, (6), 1835–1837

The hydrogenation of *N*-benzylidenebutylamine to benzylbutylamine was carried out using a 5% Rh/Al<sub>2</sub>O<sub>3</sub> or 5% Rh/C catalyst. Acids within the pK<sub>a</sub> range 2.88 (tartaric acid) to 4.64 (CH<sub>3</sub>COOH) act as promoters for the reduction, but CH<sub>3</sub>CH<sub>2</sub>COOH (4.70) and (CH<sub>3</sub>)<sub>3</sub>CCOOH (5.05) are less effective. Acids stronger than tartaric acid are ineffective.

## The Catalytic Synthesis of Hydrogen Peroxide from the Elements on Palladium

### III. The Active Centres of Hydrogen Peroxide Decomposition on Palladium

T. A. POSPELOVA and N. I. KOBOZEV, *Zhur. Fiz. Khim.*, 1961, **35**, (6), 1192–1197 (English summary)

Pd/SiO<sub>2</sub> gel catalysts were used in the investigation which showed that the active centres of the Pd in the decomposition reaction differed from those for the synthesis of H<sub>2</sub>O<sub>2</sub>. With Pt, the catalytic centres for both synthesis and decomposition of H<sub>2</sub>O<sub>2</sub> coincide. Specific activity curves for H<sub>2</sub>O<sub>2</sub> decomposition and for hydrogenation on Pd are similar in shape and indicate that the decomposition mechanism involves the removal of hydrogen atoms by occlusion in the Pd lattice.

## Chemistry of Allene. IV. Carbonylation Reactions of Allene

T. J. KEALY and R. E. BENSON, *J. Org. Chem.*, 1961, **26**, (9), 3126-3130

$\text{Ru}_2(\text{CO})_9$  or  $\text{RuCl}_3$  catalysts were used in the carbonylation of allene in  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$  or amines. Methacrylic acid is obtained by carbonylation in  $\text{H}_2\text{O}$  in the presence of a  $\text{RuCl}_3/\text{C}_6\text{H}_5\text{N}$  catalyst at  $120^\circ\text{C}$  and 700-1000 atm. Derivatives of methacrylic acid are obtained in the presence of  $\text{CH}_3\text{OH}$  or amines. Under certain conditions a lactone or an ester may be obtained in  $\text{H}_2\text{O}$  or  $\text{CH}_3\text{OH}$ , respectively.

## Investigation of the Mechanism of Heterogeneous Oxidation, Hydrogenation and Electrochemical Combustion on Solid Catalysts

### III. Relation between the Depolarising Oxides on Carbon and Platinum and the Catalytic Effect of the Latter in the Oxidation of $\text{SO}_2$

O. K. DAVTYAN, B. A. MANAKIN, E. G. MISYUK and YU. N. POLISHCHUK, *Zhur. Fiz. Khim.*, 1961, **35**, (6), 1186-1191 (English summary)

An electrochemical investigation showed that oxygen chemisorbed on the Pt or activated C surface at  $20-100^\circ\text{C}$  takes part in the building of the oxygen electrode potential. This chemisorbed oxygen participates in the catalytic oxidation of  $\text{SO}_2$  and is removed from the surface. The Pt becomes poisoned in an atmosphere of  $\text{SO}_2$  at  $20^\circ\text{C}$  and becomes incapable of chemisorbing oxygen.

### IV. Some Data on the Low-Temperature Oxidation of $\text{SO}_2$ over Platinum. Poisoning of the Platinum Catalyst by $\text{SO}_2$

E. N. OVCHINNIKOVA and O. K. DAVTYAN, *Zhur. Fiz. Khim.*, 1961, **35**, (9), 1907-1910 (English summary)

It was shown that in the oxidation of  $\text{SO}_2$  over a Pt black catalyst at  $20^\circ\text{C}$ , fixation of the oxidation products occurs on the catalyst surface. The catalyst is poisoned as a result of chemisorption of  $\text{SO}_2$ . The degree of  $\text{SO}_2$  poisoning increases at  $20-100^\circ\text{C}$  in the absence of oxygen. Observations support the theory that the catalytic process is interaction of  $\text{SO}_2$  with oxygen chemisorbed on the active catalytic centres.

### The Catalytic Activity of Platinum on a Cadmium Oxide Support

ZH. V. STREL'NIKOVA, E. A. TROSMAN and V. P. LEBEDEV, *Zhur. Fiz. Khim.*, 1961, **35**, (6) 1327-1330 (English summary)

The relation between the activity of Pt sorbed on CdO and the number of Pt atoms on the carrier surface was determined in the case of  $\text{H}_2\text{O}_2$  decomposition. It was found that the decomposition occurs on the active centres  $[\text{Pt}]_1$ ,  $[\text{Pt}]_2$ , and  $[\text{Pt}]_3$  through intramolecular decomposition

of the intermediate  $\text{PtO}_2$ . Kinetic equations were derived for the process.

### Activation of Metal Hydrogenation Catalysts by Irradiation

D. GRAHAM, *Abstracts of Papers*, 4-I, Div. of Colloid and Surface Chem., 140th Meeting, A.C.S., Chicago, Sept. 1961

The catalytic activities of supported Pd, Pt, and Ni catalysts have been increased by high energy irradiation. It appears that active centres are both created and destroyed by irradiation. The energy required for forming new active centres is related to the melting points of the catalyst metals.

### Crystallite Size of Platinum Particles in Supported Platinum Catalysts

C. J. PLANK, G. T. KOKOTAILO and L. C. DRAKE, *Abstracts of Papers*, 16-17-1, Div. of Colloid and Surface Chem., 140th Meeting, A.C.S., Chicago, Sept. 1961.

Pt particles from fresh  $\text{Pt}/\text{Al}_2\text{O}_3$  catalysts were found to have diameters  $<25\text{\AA}$ , while some particles from aged catalysts have diameters of 200-500 $\text{\AA}$ . A correlation exists between crystallite area and dehydrogenation activity. Factors affecting crystallite growth were studied.

### The Mechanism of Hydrocracking

#### I. Reactions of Paraffins and Olefins

H. L. COONRADT and W. E. GARWOOD, *Abstracts of Papers*, 19-1, Div. of Colloid and Surface Chem., 140th Meeting, A.C.S., Chicago, Sept. 1961.

The use of a  $\text{Pt}/\text{Al}_2\text{O}_3/\text{SiO}_2$  catalyst resulted in three major products: (i) isomerised charge stock, (ii) paraffins of moderate molecular weight, and (iii) cyclics. It is shown that the types of reactions depend largely on the relative hydrogenation activity and acid activity of the catalysts. A mechanism for hydrocracking is given.

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

M. FREIFELDER, R. M. ROBINSON and G. R. STONE, *Abstracts of Papers*, 23-O, Div. of Medicinal Chem., 140th Meeting, A.C.S., Chicago, Sept. 1961

Low pressure hydrogenations with a Rh/C catalyst are described. Partial poisoning of the catalyst by strong nitrogen bases may be overcome under certain conditions. The effect of substituents on the rate and extent of hydrogenation is discussed.

### The Effects of Platinum Area and Surface Acidity on Hydrocracking Activity

O. A. LARSON, D. S. MACIVER, H. H. TOBIN and R. A. FLINN, *Abstracts of Papers*, 13S, Div. of Petroleum Chem., 140th Meeting, A.C.S., Chicago, Sept. 1961

Hydrogenation and acidic sites were characterised on a series of  $\text{Pt}/\text{Al}_2\text{O}_3/\text{SiO}_2$  catalysts by means

of hydrogen and  $\text{NH}_3$  chemisorption. Masking of the strongest acid sites, which results from their selective adsorption of Pt, creates a maximum in the variation of hydrocracking activity with Pt content. Charge stock poisons also cause masking of acid sites. Both Pt surface and hydrocracking activity are affected by variables of catalyst preparation.

#### Reforming and Hydroisomerisation

V. HAENSEL, *Abstracts of Papers*, 16S, Div. of Petroleum Chem., 140th Meeting, A.C.S., Chicago, Sept. 1961

Reaction mechanisms for the dehydrogenation of naphthenes, and dehydrocyclisation and hydrocracking of paraffins are discussed. The number of migrations of the intermediate species between the Pt and acid sites of the reforming catalysts is emphasised. Pt catalysts may also be used in the hydroisomerisation of  $\text{C}_4\text{H}_{10}$ ,  $\text{C}_6\text{H}_{12}$  and  $\text{C}_8\text{H}_{14}$  fractions.

#### Oxidations with Oxygen and Platinum Catalysts in Carbohydrate Chemistry

K. HEYNS, *Stärke*, 1961, 13, (6), 207-214

The syntheses of a number of compounds is described to illustrate the advantages of catalytic oxidation using a Pt catalyst in the preparation of polysaccharides. The selectivity of the oxidation reactions is emphasised. (36 references)

#### The Effect of Thermal Pretreatment on the Catalytic Properties of Platinum Films

V. M. GRYAZNOV, V. D. YAGODOVSKII and V. I. SHIMULIS, *Kinetika i Kataliz*, 1961, 2, (2), 221-227

$\text{C}_6\text{H}_6$  is obtained from cyclohexene by dehydrogenation using a Pt film catalyst which has been heated below  $500^\circ\text{C}$ , but after heating the film to  $700^\circ\text{C}$ , cyclohexadiene-1,3 is formed. On rapid cooling of the film from  $700^\circ\text{C}$ , the energy of activation of the cyclohexadiene obtained is 26 kcal/mole at  $460^\circ\text{C}$ - $520^\circ\text{C}$  and 60 kcal/mole at  $530^\circ\text{C}$ - $600^\circ\text{C}$ . After slow cooling of the film from  $700^\circ\text{C}$  or prolonged treatment above  $520^\circ\text{C}$ , the energy of activation is 60 kcal/mole in the range  $460^\circ$  to  $600^\circ\text{C}$ . The relationship between the activity of the catalyst, its thermal treatment and the experimental temperature is discussed.

#### The Catalytic Oxidation of Carbon Monoxide on Palladised $\gamma\text{-Al}_2\text{O}_3$

G. N. ALEKSEEV, Z. M. RIZOV and O. M. TODES, *Kinetika i Kataliz*, 1961, 2, (3), 400-407

Experiments were carried out using fixed and suspended beds of Pd/ $\text{Al}_2\text{O}_3$  catalysts at temperatures from  $50^\circ$  to  $340^\circ\text{C}$ , with a CO concentration of 0.2-1.0 vol.% and a space velocity of 6000-30000/h. It was found that a supported 0.5% Pd catalyst has the greatest activity. The catalyst is stable both in gas/air mixtures with up to 10%  $\text{CO}_2$  and nitric oxides. Velocity constants and energy of activation were determined for the process.

#### Reaction of Olefin-Palladium (II) Chloride Complexes with Nucleophiles: a New Vinylation

E. W. STERN and M. L. SPECTOR, *Proc. Chem. Soc.*, 1961, (Oct.), 370

Vinyl acetate was produced at room temperature by the reaction of  $(\text{C}_2\text{H}_5\text{PdCl}_2)_2$ , or  $\text{C}_2\text{H}_4$  and  $\text{PdCl}_2$ , with *iso*- $\text{C}_8\text{H}_{18}$  and  $\text{CH}_3\text{COOH}$  in the presence of  $\text{Na}_2\text{HPO}_4$ . The complex reacted in a similar way with isopropyl alcohol to yield vinyl isopropyl ether and acetaldehyde di-isopropyl acetal.

## ELECTRICAL ENGINEERING

### The Conductivity of Oxide Cathodes

#### Part 10. Spontaneous Generation of Negative Ions

G. H. METSON, *Proc. Instn. Elect. Engrs., Part C*, 1961, 108, (14), 438-449

The behaviour of S-type assemblies with a Pt core and Ba-Sr oxide matrix or single oxide (BaO or SrO) matrix, or with a Ni core and single oxide matrix was studied. The Ba-Sr oxide matrix is thermally unstable at  $1020^\circ\text{K}$  due to the evolution of negative oxygen ions by the SrO component. Factors determining the equilibrium concentration of free oxygen ions in the matrix pores were examined.

#### Part 11. Thermal Stability of the Alkaline-Earth Oxides

G. H. METSON and H. BATEY, *Ibid.*, 450-454

An experimental valve containing a Pt core having the same dimensions as in the standard S-assembly was used for the thermal stability tests. At  $1200^\circ\text{K}$ , BaO evaporates from the Pt substrate as unchanged molecules, while SrO and BaO dissociate into metal and oxygen. It is concluded that the dissociation is not related to the nature of the substrate.

#### Influence of Alloy Structure on the Transfer of Matter

W. MERL, *Brit. J. Appl. Phys.*, 1961, 12, (9), 447-449

The influence of conductivity on the transfer of matter at break (6V, 4.3A, 0.06-20 $\mu\text{H}$ ) was investigated for a 40% Cu-Pd alloy and for precipitation-hardened 16% and 10% Ni-Au and 3% Co-Au alloys.

#### Measurement of Metal Transfer in Electrical Contacts by the Radioactive Isotope Method

F. LLEWELLYN JONES, M. R. HOPKINS and C. R. JONES, *Brit. J. Appl. Phys.*, 1961, 12, (9), 485-489

Details of the experimental method and procedure are given. The relation between metal transfer and circuit inductance was established for Pt and Pd contacts operating at potential differences of about one volt. It was found that for Pt and Pd, transfer is dependent upon in-

ductance down to  $10^{-8}$  H. The total amount of Pt transferred is comparable with the volume of the molten metal bridge, while the Pd transferred is only a fraction of the bridge.

## GLASS TECHNOLOGY

### Influence of Platinum Nucleation on Constitution of and Phase Separation in Sodium Phosphate Glasses

M. K. MURTHY, *J. Amer. Ceram. Soc.*, 1961, **44**, (8), 412-417

Sodium phosphate melts containing 0.0038, 0.0076, 0.038, and 0.15% Pt were prepared in Pt crucibles. Paper chromatographic and electron-microscopic techniques were used to study the resultant glasses with  $n$ , the number average chain length, varying from 3 to 9. It appears that Pt nucleation has no effect on the distribution of

polyphosphates in the glasses, although phase separation occurs. The results are discussed in relation to immiscibility phenomena.

### Fundamentals of Glass-to-Metal Bonding VII. Wettability of Iron by Molten Sodium Silicate Containing Iron Oxide

R. B. ADAMS and J. A. PASK, *J. Amer. Ceram. Soc.*, 1961, **44**, (9), 430-433

Contact angles and adherence on Pt and Fe of  $\text{Na}_2\text{Si}_2\text{O}_7$  glasses with additions of 0.0, 2.40, 4.77, 9.10, 16.7, 28.5, and 44.4 mole% Fe were studied in vacuum at 1000°C. Fe additions have no effect on the contact angles or the adherence in the glass-Pt system. No devitrification was observed in the glass-Pt system. In the glass-Fe system, with increasing Fe content in the glass, the contact angle decreases and the adherence increases. Devitrification occurs in the glass-Fe system with glasses containing 9.10 mole% Fe and higher.

## NEW PATENTS

### Production of Hydrocyanic Acid

DEUTSCHE GOLD-UND SILBER-SCHNEIDANSTALT  
*British Patent 875,393*

Hydrocyanic acid is made by reacting a hydrocarbon with ammonia in the presence of a catalyst composed of up to 5% by wt. of platinum, palladium, iridium and/or rhodium, up to 100 at.% (based on total platinum metal content) in total of copper, nickel, aluminium and/or silicon and an oxygen, nitrogen and/or carbon compound of an alkaline earth metal, boron, aluminium or silicon.

### Oxidation-reduction Potential Measurement

DIAMOND ALKALI CO. *British Patent 875,440*

Apparatus for measuring the oxidation-reduction potential produced in reactions involving chlorine includes a unitary cell body of electrically non-conductive material in the surface of which are embedded two electrodes, one having a surface of silver and the other a surface of platinum, both surfaces being flush with the cell body surface.

### Production of Hydrogen Peroxide

FOOD MACHINERY & CHEMICAL CORP. *British Patent 875,850*

In the production of hydrogen peroxide by the alternate reduction and oxidation of an alkylated anthraquinone dissolved in a solvent, reduction is carried out by contacting the working solution with hydrogen in the presence of a fixed bed of metallic catalyst having a specific particle size of 4-100 U.S. standard mesh, the working solution being passed through the bed at a rate of 20-200

l/min/sq. ft of catalyst bed cross-section. The catalyst may be palladium, ruthenium, platinum or rhodium.

### Manufacture of Aldehydes and Ketones

CONSORTIUM FÜR ELEKTRO-CHEMISCHE INDUSTRIE  
G.m.b.H. *British Patent 876,024*

Aldehydes and ketones are made by passing an olefin, together with oxygen, over a catalyst containing a compound of a platinum group metal, preferably palladium, in the presence of steam. The catalyst may be supported on active carbon, an acidic substance being added to enhance the activity of the catalyst.

### Manufacture of Carbonyl Compounds

CONSORTIUM FÜR ELEKTRO-CHEMISCHE INDUSTRIE  
G.m.b.H. *British Patent 876,025*

Carbonyl compounds are made by contacting an olefinically unsaturated hydrocarbon with an aqueous solution containing a platinum group metal compound at 0-200°C in the presence of an oxidising agent having an oxidation potential greater than that of the platinum metal compound. Rhodium or palladium may be used.

### Production of Hydrogen Peroxide

FOOD MACHINERY & CHEMICAL CORP. *British Patent 876,459*

A fixed catalyst bed composed of 0.1-2% by wt. of palladium, supported on  $\alpha$ -alumina, magnesium oxide, calcium carbonate, silicon carbide or magnesium carbonate, is used in the production of hydrogen peroxide by alternate reduction and oxidation of an alkylated anthraquinone. The