ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Point Defects in Platinum

G. R. PIERCY, Atomic Energy of Canada Ltd., Report AECL 648, CRMet-782

An investigation was made of the mobility and type of point defect introduced into Pt by deformation in liquid nitrogen, quenching into water from 1600°C or reactor irradiation at 50°C. Isochronel anneals (annealing for 5 min at successively higher temperatures) were carried out on the deformed specimens. The resistance drop during the 5 min was plotted against the temperature. The specimen deformed in liquid nitrogen showed two recovery stages whilst the irradiated and quenched specimens showed only one. Recovery, and hence activation energy for motion of the defects, was also measured by changes in density, hardness and X-ray line broadening and, for the irradiated sample, by U.T.S. and proportional limit measurements. The mechanism of recovery is discussed. It is concluded that the principal lattice defects in Pt after irradiation and quenching are respectively, single vacancies with an activation energy for migration of 1.43 eV and divacancies with an activation energy of 1.13 eV. In cold-worked Pt there are two principal defects one of which is unknown (possibly interstitial atoms) with an activation energy for migration of 0.73 eV and the other of which is single vacancies.

The Use of Furnaces in the Measurement of the Rate of Oxidation of Platinum and other Metals forming Volatile Oxides

G. C. FRYBURG and H. M. MURPHY, *Trans. Met. Soc. Amer. Inst. Min. Met. Eng.*, 1958, **212**, (Oct.), 660-661

The use of furnaces in measuring the rate of oxidation of metals which form volatile oxides leads to low results since the oxide formed does not condense on the hot furnace walls but remains in the gas phase so that an equilibrium is set up between the metal and its oxide. The published rates of oxidation of Pt between 900° and 1400°C, all of which were carried out in furnaces, vary from 0.8 to 20 mg/sq dm/day depending on the conditions. These values are all too low. In the present investigation rate measurements were carried out on electrically heated Pt ribbon in cooled tubes which condense the oxide. At 1200°C under an oxygen pressure of 150μ a rate of oxidation of 100 mg/sq dm/day was obtained; the rate increases linearly with pressure up to

250μ. Above this pressure the rate increase is less than linear.

Determination of the Change in Poisson's Number during Elastic and Slight Plastic Stress

W. KOSTER and J. SCHERB, *Z. Metallkunde*, 1958, **49**, (10), 501-507

Measurements were carried out on Ir and Rh in the elastic region and on Pt, Pd, Cu, Ag, Au and Al in the region of transition from elastic to plastic stress. Poisson's number was obtained from the quotient decrease in cross-section of the specimens over their increase in length. For Ir and Rh with loads up to 12 kg/sq mm the stress is elastic and Poisson's number is independent of load and equal to 0.26. Measurements carried out on Pt up to a permanent extension of 0.2% give a proportional limit at 3.8 kg/sq mm and a Poisson number of 0.39 within the elastic region. After yielding has begun Poisson's number rises to 0.49 then falls again to 0.39. Similar behaviour is found on loading to final extensions of 0.39, 0.58 and 0.75%. For Pd the proportional limit is 5.6 kg/sq mm, modulus of elasticity 12,750 kg/sq mm and Poisson's number 0.39. The behaviour of Poisson's number on loading is similar to that for Pt. Measurements during unloading were carried out on Pt in the elastic and plastic regions. In the elastic region the extension returns to zero on unloading but the cross-sectional contraction does not revert to its original value resulting in a large increase in Poisson's number. In the plastic region the extension and contraction change in about the same ratio so that Poisson's number increases only slightly to 0.5. Poisson's number falls with increased deformation of Ag samples. The behaviour of Poisson's number at low stresses is investigated. The results are discussed theoretically.

The Use of Platinum for Protecting Molybdenum against Oxidation at High Temperatures

D. W. RHYS, Paper given at the Symposium on Glass Melting held by the Union Scientifique Continentale du Verre, Brussels, October 1958

Investigations were carried out on sheathing Mo directly with Pt and on sheathing Mo coated with an intermediate layer of Au or alumina. The Au layer, 0.025 mm thick, is electrodeposited on to the Mo and heat-sealed into a 0.5 mm thick Pt sheath to form a high-melting point alloy with

the Pt. The alumina, in the form of a paste diluted with acetone, is applied to the Mo, dried, fired in hydrogen at 1400°C and sealed into a Pt sheath. On heating in air at 1200°C the Pt/Mo specimen increases in weight immediately due to diffusion of oxygen through the Pt. The Pt/Au/Mo and Pt/Al$_2$O$_3$/Mo specimens maintain a constant weight for over 100 hr and over 1000 hr respectively before showing any increase. The limit of endurance of the specimens in air at 1200°, taken as the point where a sharp fall in weight occurs due to oxidation of Mo to the volatile trioxide, increases in the order Pt/Mo, 375-650 hr, Pt/Au/Mo, 930-2010 hr, Pt/Al$_2$O$_3$/Mo, 4070-5050 hr. Microscopic examination shows strong attack of Pt by Mo in the Pt/Mo specimen whereas in the Pt/Al$_2$O$_3$/Mo specimen no significant attack occurs except after heating for 4000-5000 hr.

The Absolute Scale of Thermoelectric Power at High Temperature

N. CUSACK and P. KENDALL, *Proc. Phys. Soc.*, 1958, **72**, (Nov.), 898-901

The absolute thermoelectric power, S, is calculated for the metals Cu, Ag, Au, Pt, Pd, W and Mo. Values for Pd and Pt are given between 100 and 2000°K. At 100°K S is 4.29 μV/degree for Pt and 2.00μV/degree for Pd and at 2000°K, −31.23 for Pt and −61.48 for Pd.

Physical Properties of Ruthenium

A. A. RUDNITSKII and R. S. POLYAKOVA, *Zhur. Neorg. Khim.*, 1957, **2**, 2758-2761 (*Chem. Abs.*, 1958, **52**, 15182g)

The physical properties of metallic Ru were studied. The specific gravity is 11.90 g/cc. The microstructure was studied by etching the polished surface by electrolysis in 10% oxalic acid. The lattice parameters are a−=2.7015, c−4.2760Å. The Brinell hardness is 193.6 kg/sq mm and does not change on heating at 1200°C in a vacuum for 15 hr. The specific electrical resistance and its temperature coefficient were determined for tempered and quenched samples. At 25° the values for electrical resistance are 7.427 and 7.657 respectively and at 100°, 9.262 and 9.574 microhm-cm. The values of temperature coefficient between 25 and 100°C are 0.003589 and 0.003643 for the tempered and quenched samples respectively. The thermoelectric properties of Ru are determined.

Electrical Resistance of some Noble-Metal Alloys at Liquid Helium Temperatures

N. BÄCKLUND, *J. Phys. Chem. Solids*, 1958, **7**, (Oct.), 94-95

The resistivities of alloys in the systems Cu-Pd, Ag-Pd, Au-Pd, Cu-Si, Cu-P, Cu-Cd, Cu-Co, Au-Co, Cu-Cr, Cu-Mn and Au-Ti were measured at temperatures up to 4.2°K. Most alloys had a negative temperature coefficient, indicating a resistivity minimum at some higher temperature.

Studies in the Platinum-Aluminium System

W. KLEMM, F. DORN and R. HUCH, *Naturwiss.*, 1958, **45**, (20), 490

The Pt-rich region of the system was studied. Two previously unknown compounds Pt$_5$Al$_3$ and Pt$_3$Al were found. A eutectic between Pt$_5$Al$_3$ and PtAl occurs at about 53 at.% Pt. The two compounds are hard and brittle and Pt$_5$Al$_3$ is resistant to attack by air, water and dilute acids. Above 1200°C a solid-solution region exists between 75 and 100 at.% Pt.

Processing and Properties of Cobalt-Platinum Permanent Magnet Alloys

D. L. MARTIN, *Trans. Met. Soc. Amer. Inst. Min. Met. Eng.*, 1958, **212**, (Aug.), 478-485

The results of processing and heat-treatment studies on alloys containing 30-72.5 at.% Co and their effect on magnetic properties are given. One alloy was prepared by sintering the metal powders and the rest by melting and casting; both methods gave satisfactory material. The alloys possess good ductility and can be fabricated by hot or cold deformation. The general treatment consists of heating to high temperature (900-1000°C) to disorder and cooling to room temperature followed by isothermal ordering at about 600°C. Magnetic properties of the alloys are compared by a single open-circuit induction measurement. The variation in magnetic properties with ordering treatment, cooling rate, disordering temperature and composition were studied. An ordering temperature of 600°C appears to be best; coercive force (H$_c$) and (BH)$_{max}$ increase to a maximum on ageing and then decrease with further ageing time. The maximum H$_c$ is obtained when the alloys are about half ordered; this is confirmed by their microstructure. The rate of cooling from disordering temperature prior to ageing influences the magnetic properties; the optimum cooling rate is 100°C/min for most of the alloys. The effect of disordering temperature was slight except for the 56.7% alloy. Alloys with composition around 50 at.% have the best magnetic properties; any deviations from this rule are attributed to differences in grain size. The highest coercive force, 4700 oersted and (BH)$_{max}$, 9 × 10^6 gauss-oersted, are obtained for the 49.3 at.% Co alloy by controlled cooling (100°C/min) from disordering treatment prior to ageing at 600°C.

Investigations on an Ordered Phase in Iron-Nickel-(Platinum) Alloys with Low Thermal Expansion

A. KUSSMANN and K. JESSEN, *Arch. Eisenhüttenwesen*, 1958, **29**, (9), 585-594

Studies were made of the ordered phase Fe$_3$Pt in Fe-Pt invars and of the Fe-Ni-Pt system in order to try and establish the reason for the change in properties—increase in expansion coefficient and displacement of magnetic transition point—which

occurs in Fe-Ni alloys containing 30-40% Ni on heat-treatment. The ternary alloys were studied by X-ray investigation and dilatometric and magnetic measurements. X-ray investigation showed Fe_3Pt to be still present in the ternary alloy 10 at.%Pt-22 at.%Ni-Fe after annealing at 500°C. The expansion coefficients and Curie-points were found to be about the same for a series of alloys including the Fe-Ni invars, i.e. alloys with and without detectable superstructure. On the basis of these results it is concluded that the characteristic properties of Fe-rich Fe-Ni alloys is due to the formation of an ordered phase, Fe_3Ni, on heat treatment.

Constitution of Uranium and Thorium Alloys

F. A. ROUGH and A. A. BAUER, U.S. Atomic Energy Comm. Report BMI-1300

A collection of data on the binary and ternary alloys of U and Th from the literature and from private sources. The systems U with each of the Pt metals, U-Mo-Ru, Th-Os and Th-Ir are mentioned.

Magnetic Investigations on the Palladium-Chromium System

D. GERSTENBERG, Z. Metallkunde, 1958, 49, (9), 476-480

Alloys containing between 1 and 60 at.% Cr were studied in the temperature range 80-1100°K. Heat treatment indicates a strong temperature dependence of magnetic properties from 10 at.% Cr with maximum values at 40 and 50%. The formation temperature of the ordered phase is about 500°C. From the change in temperature dependence of the magnetic susceptibility with increasing Cr content, it can be concluded that in the ordered phase a strong partly positive, partly negative, exchange-coupling takes place between the Cr ions. In solid-solution in the range 30-36 at.% Cr, positive exchange coupling predominates whilst in the tetragonal phase (PdCr) negative exchange coupling is the more preponderant.

The Corrosion Resistance of Titanium Alloys 3—The Equilibrium Diagram of the Titanium-Palladium System

H. NISHIMURA and T. HIRAMATSU, Nippon Kinzoku Gakkai-Si, 1958, 22, (2), 88-91 (In Japanese)

The alloys were investigated over the whole composition range by X-ray analysis, melting point determination and metallographic examination. An equilibrium diagram is constructed and photomicrographs are given. One intermediate compound, $TiPd_3$, was found having a hexagonal structure. A eutectic reaction, liquid $\rightleftharpoons$ $\beta(Ti) + TiPd_3$ occurs at 47 wt.% Pd and 1080°, a peritectic reaction, liquid $+ TiPd_3 \rightleftharpoons \gamma(Pd)$, at 89% Pd and a eutectoid reaction, $\beta(Ti) \rightleftharpoons \alpha(Ti) + TiPd_3$, at about 25% Pd and 735°. The solubility of Pd is about 45% in β-Ti at the eutectic temperature

and about 5% in α-Ti at the eutectoid temperature; the solubility of Ti in γ-Pd is 11% at 1000°. The hardness of alloys annealed at 1000° for 24 hr and then water-quenched reaches maxima of about 600 microvickers at about 40, 58 and 85 wt% Pd.

Magnetic Susceptibility of Copper-Nickel and Silver-Palladium Alloys at Low Temperatures

E. W. PUGH and F. M. RYAN, Phys. Rev., 1958, 111, (Aug. 15), 1038-1042

Magnetic susceptibilities were measured by the Gouy method on alloys with up to 39 at.% Ni and up to 10 at.% Pd at temperatures between 295°K and 2.1°K. The susceptibility is nearly temperature independent for all the Ag-Pd alloys tested and for the Cu-Ni alloys with up to 27% Ni. The simple band model of Mott adequately describes the susceptibilities of the Ag-Pd alloys but fails to predict the large temperature independent paramagnetic contribution of Ni in Cu.

Recent Advances in the Metallurgy of Zirconium and Titanium Alloys of Special Interest in Reactor Technology

G. M. ADAMSON, J. O. BETTERTON, J. H. FRYE and M. L. PICKLESHIMER, Paper No. 1993 given at the 2nd U.N. Intern. Conf. on Peaceful Uses of Atomic Energy, Geneva, September 1958

The development of a fabricating technique for producing isotropic Zircaloy-2 plate and a method of welding the alloy are described. The behaviour of Ti and Zr under irradiation is discussed. Zircaloy-2 undergoes increased corrosion in uranyl sulphate solutions when irradiated. Zr alloys containing Nb, Pd or Pt have been developed which have a lower corrosion rate under these conditions. The alloys 2%Pd-15%Nb-Zr and 2%Mo-15%Nb-Zr appear particularly promising as structural materials for use in nuclear reactors. In addition to their high corrosion resistance under irradiation they can be treated to high strength and yet remain weldable and fabricable. Fundamental studies on the properties of binary Zr and Ti alloys are discussed.

Metallographic and X-Ray Study of Alloys of the System Antimony-Iridium

R. N. KUZ'MIN, G. S. ZHDANOV and N. N. ZHURAVLEV, Kristallografiya, 1957, 2, 48-50 (In Russian)

The alloys were made by fusing or sintering the metals under a small positive pressure of argon. The melting points of the alloys were found from cooling curve measurements and by the method of drop formation. Metallographic and X-ray analyses were carried out. A tentative phase diagram for the system is given. A eutectic reaction occurs at 615°, at a composition near to pure Sb. The compounds $IrSb_3$ and $IrSb_2$ were found. $IrSb_3$ is formed by peritectic reaction at

about 900°C and has an average microhardness of 770 kg/sq mm; IrSb$_3$ is monoclinic and its average microhardness is 1130 kg/sq mm.

An X-Ray Survey of Certain Transition-Metal Systems for Sigma Phases

A. G. KNAPTON, *J. Inst. Metals*, 1958, **87**, (Sept.), 28-32

X-ray studies were carried out on binary alloys of Os and Ir with V, Cr, Nb, Mo, Ta and W to determine whether σ-phases are formed in these systems. All the systems except V-Os, V-Ir and Cr-Ir formed σ-phases, 8 of which had not previously been reported. Comparisons are drawn between the σ-phases occurring in alloys of metals of the First, Second and Third Long Periods.

Survey of Ternary and Quaternary Metastable Gamma-Phase Uranium Alloys

V. W. STORHOK, A. A. BAUER and R. F. DICKERSON, U.S. Atomic Energy Comm. Report BMI-1278

A survey is made of the effects of ternary and quaternary additions of Cr, Mo, Nb, Ru, V and Zr on the transformation kinetics, transformation temperature, hot-hardness and corrosion resistance of U-Zr, U-Nb and U-Mo γ-phase alloys. In general these additions improve the γ-stability, lower the transformation temperature and improve corrosion resistance.

ELECTROCHEMISTRY

Anaerobic Corrosion of Metals in Solutions Containing Various Metallic Cations—Inactivation and Activation

W. R. BUCK and H. LEIDHEISER, *Z. Elektrochem*, 1958, **62**, (6/7), 690-695 *(In English)*

The following metals are inactivated (corrosion reduced) by ions in solution: Fe by Sn(II) and Pb(II) ions in boiling 0.2M citric acid, Ni by Cu(II) ions in boiling 2M HCl and Ti by Pt metal ions in boiling 2M HCl. The metals Al, Cu, Fe, Ni, Ag, Zn and Sn are activated by Pt metal ions in solution. There is evidence that the metal in solution is plated on to the surface of the corroding metal and activates it or deactivates it depending on the type of intermetallic binding occurring at the surface.

The Effect of Gamma Irradiation on the Potential Behaviour of Platinum and Stainless Steel Electrodes

W. E. CLARK, *J. Electrochem. Soc.*, 1958, **105**, (8), 483-485

The measurements were carried out on smooth and platinised Pt and on type 347 stainless steel electrodes in 0.1N H$_2$SO$_4$ solution at 85°C using ^{60}Co as the source of γ-radiation. Irradiation causes rapid debasement (fall in potential) of the Pt electrodes; under an atmosphere of air this is

followed by slow ennoblement which does not occur under H$_2$ or N$_2$. Removal of the source causes rapid ennoblement. The potential of steel electrodes when irradiated first falls to a value indicating corrosion and then recovers its noble value. Since the potential of smooth Pt electrodes remains debased whilst the steel is corroding these electrodes may be used as a monitor for the production of Fe(II), even in the presence of products of the radiolytic decomposition of water. The reactions occurring in γ-irradiated water and their effect on the electrodes are discussed.

Potentials of Noble Metal and Palladium Alloy Hydrogen Electrodes

J. P. HOARE, G. W. CASTELLAN and S. SCHULDINER, *J. Phys. Chem.*, 1958, **62**, (9), 1141-1142

The equilibrium potentials of Pt, Au, Rh, Ir and Ru/H$_2$ electrodes versus a Pt/H$_2$ electrode in 2N H$_2$SO$_4$ under a hydrogen pressure of 1 atm are all equal to zero. An anodic followed by a cathodic current was applied to electrodes of Pd, Au-Pd and Ag-Pd and their steady, open-circuit potentials were measured. The potential of the α-Pd-H alloy is 0.05 V and the potentials of the Au-Pd-H and Ag-Pd-H electrodes are between 0.05 V and zero. These results indicate that in both systems a 2-phase system analogous to α- and β-Pd-H can exist at room temperature.

An Electrochemical Method for the Determination of the Saturation Pressure and Heat of Solution of Hydrogen in a Two-Phase Palladium-Hydrogen Alloy

R. J. RATCHFORD and G. W. CASTELLAN, *J. Phys. Chem.*, 1958, **62**, (9), 1123-1127

The potential-temperature dependence of the saturated α-Pd-H electrode in hydrogen-stirred solution was investigated. The plot of potential, compared to a Pt/H$_2$ electrode in the same solution, versus temperature takes the form of a cooling curve with a dip before the plateau. The dip corresponds to supersaturation of the α-phase and the plateau to the slow growth of the β-phase. The potential-temperature dependence is given mathematically by E = 0.06309 −0.0005057 (T − 273.16). The standard heat of absorption of hydrogen is calculated to be 9280±100 cal/mole hydrogen and the saturation pressure of hydrogen over the saturated α-Pd electrode is expressed by log p$_8$(mm) − 7.9776 −2028.2/T. Factors affecting the stability of the α-Pd potential are discussed.

Studies on the Redoxokinetic Effect: Preparation of Reproducible Electrode Surfaces

U. H. NARAYANAN, K. SUNDARARAJAN and A. NARAYANASWAMI, *Proc. Indian Acad. Sci.*, 1958, **48A**, (Sept.), 165-174

Investigations were carried out on methods of producing a Pt electrode surface, such that values

of energy transfer coefficient, calculated from redoxokinetic potential, would be reproducible. The system studied was Pt/ferrous ammonium sulphate/ferric sulphate/sulphuric acid. The best results were obtained by immersing the Pt electrode in hot chromic acid, washing, treating with conc. HCl for 1 min, washing and immersing for 5 min in a boiling ferrous-ferric mixture of the same composition as the electrolyte.

Anodic Polarography with a Rotating Platinum Microelectrode, II—Oxidation of Various Indole Alkaloids

M. J. ALLEN and V. J. POWELL, *J. Electrochem. Soc.*, 1958, **105**, (9), 541-544

Anodic oxidation of certain indole alkaloids in acid medium results in a one electron change with probable hydroxyl introduction into the aromatic portion of the molecule. This reaction appears to be specific to those alkaloids containing a 6-methoxyindole nucleus. In a neutral medium a two electron change occurs with resultant N-oxide formation where the alkaloid contains a N atom with an unshared electron pair.

Electrolysis of Perchlorates, I—Electrolysis at Silver, Copper and Platinum Anodes in Acetonitrile

H. SCHMIDT and J. NOACK, *Z. anorg. allgem. Chem.*, 1958, **296**, (1-6), 262-272

The electrolysis of silver and copper perchlorate was studied in non-aqueous, acetonitrile, solution using attackable Ag and Cu, and non-attackable Pt anodes. The electrolysis of $AgClO_4.2C_5H_5N$ and $CuClO_4$ using Ag- and Cu-anodes respectively, gives 100% anodic and cathodic current yields for the process $Me^+ + e^- \rightleftharpoons Me$. The electrolysis of $AgClO_4$ with a Pt anode yields quantitative amounts of $HClO_4$. At the cathode, evolution of hydrogen occurs as the only side reaction in addition to deposition of Ag.

ELECTRODEPOSITION

Electrodeposition of Platinum from Chloroplatinic Acid

R. H. ATKINSON, *Trans. Inst. Metal Finishing*, 1958, **36**, (1), 7-16

The production of ductile Pt deposits from aqueous chloroplatinic acid electrolytes containing 15-25 g/l Pt and 10-390 g/l HCl is investigated. The electrodes are of Pt. The rate of deposition varies from 0.1-1.1×10^{-3} in./hr and the bath temperature from 45-75°C. Conventional stirring reduces the efficiency of plating and best results were obtained with the mixing produced by thermal convection currents with the bath at 60-70°C. A non-diaphragm cell was preferred because it was easier to operate. The deposits were tested by microexamination, hardness testing and a special rolling test to measure

ductility. There is a minimum rate of deposition for the production of ductile deposits (Knoop hardness 155-250) which varies with the acidity of the bath, i.e. from 0.7×10^{-3} in./hr at 225 g/l HCl to 0.35×10^{-3} in./hr at 290 g/l HCl. At lower deposition rates the deposits are harder and crack on plating or when rolled. For rates above about 1.0×10^{-3} in./hr, at all acidities, the deposits become rough, spongy or semi-burnt. No fully ductile deposits were obtained at acidities below about 220 g/l HCl. Blistering of the deposits on heating above 1100°F was attributed to occluded Pt compounds. The hydrolysis pH of chloroplatinic acid was determined as about pH 2.2. An explanation is proposed for the unusual relationship between rate of deposition, acidity of bath and quality of deposit. Because of its unusually high acid content the plating solution can only be used for the deposition of Pt on noble metals.

Effect of Some Organic Substances on the Electrodeposition of Palladium

V. V. OSTROUMOV, *Zhur. Priklad. Khim.*, 1958, **31**, (3), 402-408 (*Chem. Abs.*, 1958, **52**, 12615f)

The effect of additions of furfural and protalbinic acid (prepared from egg albumin) on the properties of electrodeposited Pd was studied. The electrolyte contains (g/l): Na_2HPO_4 100, $(NH_4)_2HPO_4$ 20, NH_4Cl 25 and Pd 1-20. The Pd was deposited on massive bronze or brass cathodes previously plated with 0.2μ Ni. The pH was varied from 9-5 by boiling off excess NH_3. The reflective capacity and mechanical stress of the deposits were measured. Addition of furfural has little effect on the reflectivity of the Pd deposits but increases the stress from 5,000 to 10,000 kg/sq cm. The addition of 0.1 g/l protalbinic acid increases the reflectivity from 40 to 67 without affecting the current efficiency or the final value of the stress. The presence of protalbinic acid retards the evolution of H during the deposition of Pd but causes a sharp rise in stress after the current is stopped and a break in the potential at -270 mV. It appears that the deposit is an unstable Pd-H system whose decomposition is retarded by the adsorbed layer of protalbinic acid at the boundaries of the crystals and on the deposit-electrolyte surface.

CATALYSIS

The Quality and Structure of Catalysts by X-Ray Low-Angle Scattering

E. L. GUNN, *J. Phys. Chem.*, 1958, **62**, (8), 928-934

The distribution in particle sizes in catalysts used in the petroleum industry can be determined by X-ray low-angle scattering. The catalysts studied were silica-alumina, $Pt-Al_2O_3$ and cobaltia-molybdena-alumina. Pilot unit test performance quality and adsorption surface can be predicted rapidly and successfully by this method using

empirical correlations. A fundamental parameter characterising these catalysts—the Debye correlation distance—was deduced from their X-ray scatter properties. The influence of plant use, heat deactivation, blending, mechanical treatment and adsorption of liquids on the fine-structure of the catalysts was interpreted in terms of the correlation distance. Characterising catalyst structure by X-ray low-angle scattering is found to be practicable.

Catalysts of the BASF (Badische Anilin-u.-Soda-Fabrik A.G.)

W. JÄCKH, *Erdöl u. Kohle*, 1958, **11**, (9), 625-629
A description of the part played by BASF in the development of industrial catalytic reactions. The development of suitable catalysts for SO_2 oxidation, NH_3 synthesis, H_2 formation, conversion of CO and H_2, organic reactions, pressure hydrogenation (i.e. of carbon, tar and oil) and petroleum refining including reforming and cracking is described.

Polyfunctional Platinum Catalyst, I—The Effect of Platinum and Hydrogen Fluoride Contents on Catalyst Activity

H.-S. KUO, A.-H. HSIE and C.-J. GOH, *Jan Liao Hsueh Pao*, 1958, **3**, 16-22 (*Chinese with English summary*) (*Chem. Abs.*, 1958, **52**, 13390c)
The principal reactions of methylcyclohexane, methylcyclopentane and pentane were investigated under the fixed conditions: temperature 472°, pressure 20 atm, space velocity 3, mol. ratio H_2 to feed 6:1, over a Pt-HF-Al_2O_3 catalyst with varying Pt and HF contents. This catalyst has two types of reaction site, the dehydrogenation (Pt) and isomerisation (HF) sites. Dehydro-isomerisation of methylcyclohexane and isomerisation of pentane can proceed effectively only on the dual site catalyst. The effect of increased HF content, up to 1%, on a catalyst containing 0.3% Pt is to increase the benzene yield from methyl-cyclohexane. A catalyst with 0.2% HF is effective for isomerising pentane. The main effect of HF above 0.2% is the acceleration of hydrocracking and the decrease in liquid yield.

West German Refinery Capacity Rose 12.4 Per Cent in 1957

A. M. STAHMER, *World Petroleum*, 1958, **29**, (Sept.), 76-79
The development in refinery construction in W. Germany in the past year is reviewed. Their cracking capacity is now over 20 million barrels and their catalytic reforming capacity nearly 14 million barrels per year.

Investigations of Hydrocarbon Transformations in a Catalytic Reforming Process

H. WELLER and W. DUVE, *Erdöl u. Kohle*, 1958, **11**, (7), 450-454
The analysis of petroleums obtained from

German crude oil is described; on the basis of these analyses the hydrocarbon transformations occurring in a reformer using a Pt catalyst can be followed. Three petroleums were studied: feed-material, clear research octane number 38, and two reformates with clear octane numbers of 74 and 91. The petroleums were separated into narrow fractions and then into paraffins, naphthenes and aromatics. The hydrocarbons were classified according to the number of C atoms in their molecules. Through differences in the analyses of feed-material and reformates the hydrocarbon transformations occurring in the reforming reaction were determined. The two reformates had increased aromatic content, decreased naphthenic content and little overall change in paraffin content—although there was an increase in C_{1-7} hydrocarbons and a decrease in $>C_8$ hydrocarbons. This change from paraffinic-naphthenic to iso-paraffinic-aromatic petroleum increases the octane rating. From reactions given in the literature these hydrocarbon transformations can be ascribed to: dehydrogenation of naphthenes to aromatics, hydrocracking of paraffins and dehydrocyclisation of paraffins by way of naphthenes to aromatics. The nature of these reactions can vary widely. In these investigations no isomerisation occurred since aromatisation took precedence over other possible changes.

Catalytic Reforming and other Processes and their Importance in Improving Motor Fuel

F. SCHMELING, *Erdöl u. Kohle*, 1958, **11**, (8), 569-573
A review of the applicability of thermal and catalytic reforming and isomerisation processes in the upgrading of motor fuel. Flow-sheets are given for Powerforming, Rexforming, Isomate and Penex processes. The effect of addition of additives such as TEL is described. (6 references)

Chemisorption of Hydrogen on Thin Evaporated Platinum Films

R. SUHRMANN, G. WEDLER and H. GENTSCH, *Z. physikal. Chem., Neue Folge*, 1958, **17**, (5/6), 350-367
The chemisorption of hydrogen on Pt films evaporated in high vacuum was investigated at 77, 90, 195 and 295°K. Concurrent measurements were made of the change in electrical resistivity and photo-electric emission of the films together with the amount of hydrogen adsorbed. The hydrogen coverage varied from 0.1 molecular to monomolecular. Assuming that a part of the adsorbed hydrogen polarises to H_2^+, the results show clearly that a further part dissociates into atoms. These atoms either dissociate further into protons and electrons or polarise to H^+. The dissociation equilibrium is displaced in favour of proton and electron formation as the temperature increases.

The Catalytic Hydrogen Reduction and Deuterium Exchange of Cyclopentanone on Evaporated Metal Films and some Observations on Cyclohexanone

C. KEMBALL and C. T. H. STODDART, *Proc. Roy. Soc.*, 1958, **246A**, (Aug. 26), 521-538

The investigations were carried out on evaporated films of Rh, Pd, Pt, W, and Ni and the reaction products examined mass spectrometrically. The hydrogenation of cyclopentanone to cyclopentanol predominates at low temperatures on Rh, Ni and W but hydrogenolysis to cyclopentane is of equal importance on Pt and Pd. The hydrogenation of cyclopentanone is similar to that of acetone. The same order of activity of the metals applies, i.e. Pt>Ni>Fe>W>Pd. Hydrogenolysis occurs to a greater extent than with acetone; the activity of the metals is Pt≫Fe>Pd>Rh>W>Ni, which does not follow the order of percentage *d*-character of the metal bonds. The catalytic exchange of H and D atoms in cyclopentanone was studied on Ni, W and Pd films and the exchange in cyclohexanone on Pd. The order of activity, Pd>Ni>W, is the same as that for acetone exchange but the distribution of isotopic species on Pd is quite different.

Platinum Catalysed Exchange of Aromatic Compounds with Deuterium Oxide

W. G. BROWN and J. L. GARNETT, *J. Amer. Chem. Soc.*, 1958, **80**, (Oct. 5), 5272-5274

The compounds were deuterated by an exchange reaction with D_2O catalysed by active Pt. Substantially complete deuteration occurs with benzoic acid, its sodium salt, aniline and *iso*propyl benzoate; bromobenzene and nitrobenzene have a low degree of exchange and no exchange was observed with *p*-nitrobenzoic and trimesic acids.

Exchange Reactions between Hydrogen Gas and Hydroxyl Groups. A Convenient Preparation of Tritium-Labelled Water

C. G. SWAIN and A. J. KRESGE, *J. Amer. Chem. Soc.*, 1958, **80**, (Oct. 5), 5281-5283

The exchange reactions between D_2 gas and methanol or water catalysed by Pt proceed at a convenient rate at room temperature and are limited to exchange of hydroxylic hydrogen. The adaptation of this reaction to the preparation of tritiated water is described.

The Selective Hydrogenation of Acetylene

G. C. BOND, D. A. DOWDEN and N. MACKENZIE, *Trans. Faraday Soc.*, 1958, **54**, (10), 1537-1546

A study was made of the basic reasons for selectivity in the catalytic hydrogenation of acetylene to ethylene, which is already in use industrially with Pd as catalyst. The catalysts studied were Rh, Pd, Pt and some Pd-Ag mixtures all supported on α-Al_2O_3. The ethylene/ethane ratio in the product was estimated by gas-liquid chromatography. The selectivity before the onset of the generally more rapid ethylene hydrogenation falls in the order Pd>Rh>Pt. The Pd-Ag catalysts containing 10-30% Ag show notably higher initial selectivities than pure Pd and are also highly active. The contributions of thermodynamic and mechanistic factors to the catalyst selectivity are discussed. A Pd catalyst exposed to 100 mm hydrogen for 11 days prior to use is selectively poisoned; it is no longer able to hydrogenate ethylene to ethane although its initial activity for acetylene hydrogenation is only slightly reduced. This is due to the absorption of H by Pd reducing the number of holes in the *d*-band so that ethylene can no longer be adsorbed. The high activities of the Pd-Ag catalysts may also be due to reduction in holes in the *d*-band by a certain degree of solid-solution formation.

Industrial Synthesis of Papaverine

B. C. PAL, *J. Sci. Indust. Res.*, 1958, **17A**, (7), 270-276

Methods of synthesising papaverine are critically reviewed with special reference to their commercial application. A method is proposed which should be industrially feasible. This method depends on the economic production of homoveratric acid and homoveratrylamine and an improved method for the synthesis of these compounds from vanillin is described. Homoveratrylhomoveratramide is prepared by heating homoveratric acid and homoveratrylamine in tetralin medium. The amide on treatment with phosphorus oxychloride, cyclises to 3:4-dihydropapaverine which, on dehydrogenation in the presence of 10% Pd-C, gives papaverine in quantitative yield. Experimental details are given.

The Hydrogenation of Fatty Oils with Palladium Catalyst, I—Hydrogenation of Castor Oil

M. ZAJCEW, *J. Amer. Oil Chem. Soc.*, 1958, **35**, (9), 475-477

In hydrogenating castor oil for industrial purposes, all the olefinic linkages must be reduced without appreciable hydrogenolysis of the hydroxyl function. Unhydrogenated castor oil has an iodine value of 86, a hydroxyl value of 160 and an acid value of 1.7. Hydrogenations were carried out over 5%Pd-C, 1%Pd-C and a specially modified catalyst, 1% Pd-C plus 0.35% Ag and 0.20% Bi, in an agitated stainless steel hydrogenator at temperatures between 86 and 125°C and pressures 30-45 p.s.i.g. The 5% Pd-C and 1% Pd-C catalysts were not sufficiently selective; they reduced both olefinic linkages and hydroxyl groups. The modified Pd catalyst at 100°C and 45 p.s.i.g. gave a product with an iodine value of 4, a hydroxyl value of 145, an acid value of 1.8 and a melting point of 86°C. This product is entirely satisfactory for industrial purposes and was obtained under much milder conditions than in the normal industrial hydrogenation over Ni catalysts.

Catalytic Oxidations, XIII—Preparation of L-Gulose

K. HEYNS and M. BECK, *Chem. Ber.*, 1958, **91**, (8), 1720-1724

L-Gulose is formed by catalytic oxidation of an aqueous solution of D-sorbitol at 40°C using 10% Pt-C catalyst. The acids formed during the oxidation are removed on an ion-exchange resin and the L-gulose is separated from the eluent by means of benzylphenylhydrazone as gulosehydrazone.

Condensed Cyclobutane Aromatic Systems, IV—Benzocyclobutene and 1-Bromobenzocyclobutene

M. P. CAVA and D. R. NAPIER, *J. Amer. Chem. Soc.*, 1958, **80**, (May 5), 2255-2257

The hitherto unknown benzocyclobutene was obtained by catalytic hydrogenolysis of 1,2-diiodobenzocyclobutene using Pd-C in the presence of sodium ethoxide. Ziegler bromination of benzocyclobutene gave 1-bromobenzocyclobutene which was dehydrobrominated by K-t-butoxide to the dimer of benzocyclobutadiene.

Reactions of α-Ketols Derived from Tertiary Acetylenic Carbinols, 1—Preparation and Low Pressure Hydrogenation

G. F. HENNION and E. J. WATSON, *J. Org. Chem.*, 1958, **23**, (5), 656-658

A general procedure is developed for the hydration of tertiary acetylenic carbinols and is used for the preparation of six α-ketols in high yields from the corresponding commercially available carbinols. The ketols are easily converted to the *vic*-glycols by low pressure hydrogenation using a PtO₂ catalyst in the presence of alkali.

Synthesis of Unsaturated Fatty Acids : dl-Ricinoleic Acid

W. J. GENSLER and C. B. ABRAHAMS, *J. Amer. Chem. Soc.*, 1958, **80**, (Sept. 5), 4593-4596

The lithium derivative of 9-chlorononyne adds to 1,2-epoxyoctane to give 1-chloro-11-hydroxyheptadecyne-8. The corresponding iodide with KCN gives 1-cyano-11-hydroxyheptadecyne-8 which, on saponification, gives *dl*-ricinstearolic acid. On semi-hydrogenation with Pd-CaCO₃ (Lindlar) catalyst *dl*-ricinoleic acid is obtained.

Synthesis of Indoles by Catalytic Reduction of o-Nitrobenzyl Cyanides

H. R. SNYDER, E. P. MERICA, C. G. FORCE and E. G. WHITE, *J. Amer. Chem. Soc.*, 1958, **80**, (Sept. 5), 4622-4625

Many substituted indoles were synthesised by a newly developed method involving catalytic reduction of the corresponding o-nitrobenzyl cyanides over 30% Pd-C. Indole can be prepared in this way from the benzoate of o-nitromandelonitrile. The mechanism of the reaction is discussed.

Hydroxylated Codeine Derivatives

L. J. SARGENT, L. H. SCHWARTZMAN and L. F. SMALL, *J. Org. Chem.*, 1958, **23**, (9), 1247-1251

The use of OsO₄ in introducing hydroxyl groups in the codeine and neopine series is described. Amongst the reactions to which the method is applied are the preparation of 7-hydroxydihydrocodeine from desoxycodeine-C, 7,8-dihydroxydihydrocodeine from acetyl codeine and 8,14-dihydroxydihydrocodeine from acetyl neopine. The osmate esters are cleaved with sodium sulphite.

A Novel Conversion of Derivatives of Oxindoles to Indoles

E. WENKERT, B. S. BERNSTEIN and J. H. UDELHOFEN, *J. Amer. Chem. Soc.*, 1958, **80**, (Sept. 20), 4899-4903

Catalytic hydrogenation of 3-acyloxindole oximes on Pt in acetic acid or Pd-C in ethanol leads to the formation of 3-(α-aminoalkylidene)-oxindoles and 2-alkylindoles.

Catalytic Hydrogenation of Unsaturated Sulphides and Sulphones

L. BATEMAN and F. W. SHIPLEY, *J. Chem. Soc.*, 1958, (Aug.), 2888-2890

The hydrogenations were carried out using Pd-C catalyst at room temperature and atmospheric pressure with violent agitation. Simple acyclic allylic or vinylic sulphides are completely hydrogenated in 1 hr; substitution in the allylic unit greatly reduces the initial rate and extent of the reaction. Heterocyclic unsaturated sulphides react more readily than acyclic, but substitution retards the reaction. Unsaturated sulphones react more readily than the corresponding sulphides but increased alkyl-substitution at the double bond or adjacent to the sulphone group is deactivating. Concomitant hydrogenolysis with liberation of thiol inhibits the hydrogenation.

Reductions with Ruthenium Catalysts, I—Preparation of some Cyclohexylalkylamines

M. FREIFELDER and G. R. STONE, *J. Amer. Chem. Soc.*, 1958, **80**, (Oct. 5), 5270-5272

Previous attempts to hydrogenate β-phenylalkylamines have not been very successful. Low pressure hydrogenation with noble metal catalysts is often slow and requires a high catalyst ratio while pressure hydrogenation using Raney Ni catalyst results in cracking. With RuO₂ catalyst (2% by wt) the hydrogenations were carried out at 90° and 70 atm and 90% yields of cyclohexylalkylamines were obtained within an hour. On hydrogenating the hydrochloride of 2-methylamino-1-phenylpropane at temperatures above 165° in aqueous solution propylcyclohexane was obtained. The effect of a branched substituent on the ring is to increase the hydrogenation time to 10-12 hrs. l-Ephedrine was hydrogenated by this method to the corresponding cyclohexyl

compound without hydrogenolysis of the -OH group and without change in rotation.

A Thermocouple Method of Studying Oxidation Reactions, Part I—Photosensitised Oxidation of Cyclohexene

J. C. ROBB and M. SHAHIN, *J. Inst. Petroleum*, 1958, **44**, (Sept.), 283-290

The non-stationary state of oxidation reactions is followed by measuring the rise in temperature of the reacting mixture using an apparatus incorporating a Pt/13%Rh-Pt thermocouple. The rate of oxidation is directly proportional to the rate of temperature rise. The method is used to study the kinetics of the photo-chemical oxidation of cyclohexene.

CATHODIC PROTECTION

The Anodic Polarisation of Lead-Platinum Bi-Electrodes

L. L. SHREIR and A. WEINRAUB, *Chem. & Ind.*, 1958, (Oct. 11), 1326-1327

Anodic polarisation of pure Pb anodes in chloride solutions results in formation of a voluminous deposit of $PbCl_2$. At 2.5 A/sq.dm the voltage increases rapidly and further electrolysis results in greater voltage increase and rapid corrosion of Pb. The insertion of a small micro-electrode of Pt into the Pb surface prior to polarisation results in the formation of an adherent coating of PbO_2 and this anode can be used for prolonged periods at high current densities. A Pb-Pt bi-electrode causes conversion of $PbCl_2$ to PbO_2 with a corresponding increase in voltage. The presence of Pt in the Pb surface is considered to increase

the lead/interface potential to a value where $PbCl_2$, Pb^{2+} and Pb are oxidised to PbO_2. Bi-electrodes of Pb and Pb alloys with Pt may have practical application as inert anodes in cathodic protection and other electrolytic processes.

TEMPERATURE MEASUREMENT

The Use of Oxygen in a Modified Tilting Furnace. Roof Temperature Measurement

J. PURDIE, *J. Iron Steel Inst.*, 1958, **190**, (Sept.), 17-19

The thermocouples 5%Rh-Pt/20%Rh-Pt and 20%Rh-Pt/40%Rh-Pt were tested for use in oxygen-blown steel furnaces. The former can be used for short periods up to 1760° and the latter up to 1850°C. The best sheath materials were found to be Al_2O_3, MgO and spinel ($MgO.Al_2O_3$). Preliminary tests carried out with a 5%Rh-Pt/20%Rh-Pt thermocouple in a tilting furnace during normal working showed that the thermocouple must protrude $\frac{1}{2}$-1 in. inside the furnace roof. The best sheath material was spinel with an inner sheath of MgO which had a life of 6.5 days. With a 20%Rh-Pt/40%Rh-Pt couple in an 'Ajax' furnace during oxygen blowing the best results were obtained using a recrystallised Al_2O_3 sheath with the thermocouple protruding $\frac{1}{2}$ in. into the furnace. MgO and spinel sheaths were less satisfactory in this furnace due to spalling and increased attack by Fe_3O_4 in the furnace atmosphere. With the degree of control now possible the roof temperature rarely exceeds 1700°C so that 5%Rh-Pt/20%Rh-Pt couples may be used.

NEW PATENTS

Production of Higher Ketones

ESSO RESEARCH AND ENGINEERING CO. *British Patent* 798,838

Ketones are synthesised by contacting 2,3-epoxybutane or a saturated epoxide containing 5-16 carbon atoms in its molecule and having its oxygen atom joined to a secondary carbon atom, at an isomerisation temperature of 200-500°C with a Group I-B or VIII metal catalyst supported on activated C. The catalyst may contain 1-20 wt% of Pt or Pd.

Hydrogenation

ENGELHARD INDUSTRIES INC. *British Patent* 799,396

An unsaturated material is contacted under hydrogenating conditions with hydrogen and a Pt-calcined Al_2O_3 catalyst. The catalyst has a large

pore, high surface area base structure composed of γ-Al_2O_3 modifications resulting from drying and calcining a mixture of precursor hydrous Al_2O_3 phases containing 65-95% of trihydrate, the amount of Pt being 0.1-1% by wt. in sufficiently divided form as to exhibit, by X-ray diffraction studies, the substantial absence of crystallites and crystals of size greater than 50Å.

Manufacture of Catalysts

UNIVERSAL OIL PRODUCTS CO. *British Patent* 799,459

An Al_2O_3 carrier is impregnated with a solution of a Pt compound and the composite is calcined, without the addition of halogen, at 250-595°C with a free oxygen-containing gas to which water has been added in amount to impart to the gas at least 15.78 g of water per kg of dry gas.