

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Precipitation in Gold-Platinum Alloys. I. Thermodynamics

L. J. VAN DER TOORN and T. J. TIEDEMA, *Acta Met.*, 1960, 8, (10), 711-714

A formula for the increase in Gibbs' free energy resulting from the mixing of a total amount of 1 mole of Au and Pt was derived from experimental data. The six constants of the expression were calculated and the spinodal curve was determined.

II. Influence of the Spinodal Curve on the Rate and the Mechanism of the Precipitation Process

L. J. VAN DER TOORN, *Ibid.*, 715-727

Single crystals and polycrystalline specimens of Au-Pt alloys were examined by X-ray methods after annealing at temperatures between 500° and 750°C. The Pt content of the single crystals was in the range 87-91%, while that of the polycrystalline alloys ranged from 31.7 to 89.6%. Vickers' microhardness measurements were made on the polycrystalline samples. Numerous X-ray photographs are reproduced. It is shown that the theories of Borelius and Tichelaan, though roughly predicting the observed phenomena, may need modification because of the part played by lattice imperfections in the precipitation process.

Hall Effect and Resistivity of Ni-Pd Alloys

J. A. DREESEN and E. M. PUGH, *Phys. Rev.*, 1960, 120, (4), 1218-1223

Measurements were made between 4°K and room temperature on a series of alloys using fields up to 3.1 webers/m². It was found that the ordinary Hall coefficient decreases for small additions of Pd, but increases on further increasing the Pd content. Variation of the ordinary Hall coefficient and the residual resistivity may be correlated with the saturation magnetisation. The extraordinary Hall coefficient fails to obey proposed theoretical relationships.

A Thermomagnetic Study of Palladium-Chromium-Hydrogen Alloys

J.-P. BURGER and J. WUCHER, *Compt. rend.*, 1960, 251, (23), 2667-2669

Measurements were made on alloys containing 1.0, 2.0, 3.0, 6.0 and 9.75 at.% Cr in the temperature range 85°-300°K. It was found that the magnetic moment of Pd is neutralised on saturating the alloys with hydrogen. For Cr alone a

moment between the theoretical values of chromous and chromic ions was found. The paramagnetic Curie points of the hydrogenated alloys vary linearly with the Cr content. For Cr contents greater than 7%, hydrogenation gives rise to an increase in susceptibility.

New Varieties of Magnetic Materials

R. M. BOZORTH, *Research*, 1960, 13, (12), 485-491

Four kinds of magnetism—paramagnetism, ferromagnetism, antiferromagnetism, and ferrimagnetism—are discussed in terms of interatomic interaction and electronic structure. The measurement of magnetic moment and Curie point for various materials is described. Among the materials discussed are ferromagnetic garnets of the Y₃Fe₂Fe₃O₁₂ type and GdRu₃, and ferromagnetic superconductors formed by introducing 4% and 8.2% GdRu₂ into CeRu₂.

Some Solidus Temperatures in Several Metal-Carbon Systems

M. R. NADLER and C. P. KEMPTER, *J. Phys. Chem.*, 1960, 64, (10), 1468-1471

Minimum solidus temperatures were determined for various metal-graphite systems, and of some eutectic, peritectic and compound melting temperatures in carbide systems. Experimental details are given. For the systems M-C (M=Pd, Rh, Pt, Ir-50Rh, Ru, Mo, Ir, Nb, Re, W, Os and Ta), the minimum solidus temperatures are 1504±16, 1694±17, 1736±13, 1932±17, 1942±16, 2210±14, 2296±16, 2328±17, 2486±18, 2732±22, 2732±22, 2902±30°C, respectively. The Nb₂C peritectic and the NbC-C eutectic occur at 3080±35° and 3220±40°C, respectively. The Ta₂C peritectic and TaC-C eutectic are located at 3500±50° and 3710±50°C, respectively. Mo₂C, WC and NbC melt at 2410±15, 2720±20 and 3480±50°C, respectively.

Preparation and Crystal Structures of RuC and OsC

C. P. KEMPTER and M. R. NADLER, *J. Chem. Phys.*, 1960, 33, (5), 1580-1581

Hexagonal WC-type phases were obtained by heating 1:10 metal-C pellets of Ru and Os at 2600°C for 4 h. X-ray powder diffraction data for both compounds were obtained. Lattice constants are a₀=2.90785Å, c₀=2.82186Å and c₀/a₀=0.9704 for RuC and a₀=2.90769Å, c₀=2.82182Å and c₀/a₀=0.9705 for OsC. Microhardnesses (DPH) of RuC and OsC are 3480 and 2000 kg/mm², respectively.

Thermodynamic Properties of Some Copper Alloys

A. A. WETSCHER AND J. I. GERASSIMOW, *Z. Phys. Chem. (Leipzig)*, 1960, **215**, (3/4), 194-202

Thermodynamic properties of binary solid solutions of Cu with Ni and Pd were studied by e.m.f. methods at temperatures of about 700°C. The e.m.f. of the cell: Cu|NaI-KI-CuI|Cu-Pd was measured for 13 alloys in the range 8-89 at.% Cu after annealing the alloys for 200-250 h at 900° to 1000°C. The thermodynamic properties of Cu-Pd and Cu-Pt solid solutions are compared.

On the Sulphides, Selenides and Tellurides of Platinum

F. GRØNVOLD, H. HARALDSEN and A. KJEKSHUS, *Acta Chem. Scand.*, 1960, **14**, (9), 1879-1893

The compounds, prepared by heating together the constituent elements in evacuated, sealed SiO₂ tubes, were examined by X-ray methods. Density determinations and magnetic susceptibility measurements between -183° and 450°C were carried out. Two new intermediate phases identified were PtSe_{0.80}, and Pt with monoclinic and orthorhombic structures, respectively.

Gaseous Ruthenium Oxides at High Temperature

H. SCHÄFER, *Angew. Chem.*, 1961, **73**, (1), 27

The formation of gaseous RuO₃ is discussed. The trioxide may be formed by heating RuO₂ in oxygen. Hot-wire experiments carried out with Ru wire in the temperature range 1465°-2090°C in an oxygen-nitrogen atmosphere also demonstrate the formation of volatile RuO₃.

Dissociation Pressure and Vapour Pressure of Palladium Chloride

M. A. ORANSKAYA and N. A. MIKHAILOVA, *Russ. J. Inorg. Chem.*, 1960, **5**, (1), 5-7 (Transl. of *Zhur. Neorg. Khim.*, 1960, **5**, (1), 12-15)

A flow method with dry oxygen-free argon as the carrier was used to determine vapour and dissociation pressures in the range 883°-1030°K. For vapour pressure, $\log p_{\text{PdCl}_2} = 8.86 - (7452.5/T)$ mm Hg at 883°-953°K; $\log p_{\text{PdCl}_2} = 6.32 - (5031.8/T)$ mm Hg at 953°-1030°K. For dissociation pressure, $\log p_{\text{Cl}_2} = 8.63 - (6728.5/T)$ mm Hg at 883°-953°K; $\log p_{\text{Cl}_2} = 7.26 - (5422.9/T)$ mm Hg at 953°-1030°K. ΔH and ΔS were calculated for the formation and vaporisation of solid and molten PdCl₂.

The Atomic Diffusion of Platinum in Gold

A. J. MORTLOCK, A. H. ROWE and A. D. LE CLAIRE, *Phil. Mag.*, 1960, **5**, (56), 803-814

The activation energy associated with the diffusion of tracer amounts of Pt was measured in the temperature range 800-1055°C and found to be larger than that for self-diffusion in Au. Both single and polycrystals of Au were used. Experimental results obtained above about 900°C may be fitted into the equation: $D = (7.6 \pm 4.7) \times 10^{-5} \exp [-(60900 \pm 1200)/RT] \text{ cm}^2/\text{sec}$. The diffusion observed below about 900°C was greater than that expected by extrapolation from higher temperatures. This effect may be due to short-circuiting diffusion of segregated Pt along dislocations.

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The Reaction between Lithium Hydride and Rhodium to form a Hydryl

J. D. FARR, *J. Inorg. Nuclear Chem.*, 1960, **14**, (3/4), 202-207

Li₄RhH₄ and Li₃RhH₅ were prepared by heating together LiH and Rh in an argon atmosphere and by heating Li and Rh or LiH and Rh in hydrogen, respectively. Evidence for the formulae of the compounds is given by powder X-ray diffraction patterns and by stoichiometry of the reactants. The hydryls melt in the range 565°-580°C.

The Equilibrium Diagram of the System Molybdenum-Ruthenium

E. ANDERSON and W. HUME-ROTHERY, *J. Less-Common Metals*, 1960, **2**, (6), 443-450

The determination of the equilibrium diagram above 1450°C is described. Lattice spacings of the various phases were measured and V.P. hardness numbers for the sintered alloys were determined. The freezing point of Ru was determined as 2310±20°C. The eutectic point at 1945±10°C corresponds to the reaction: liquid (41.6 at.% Ru) ⇌ Mo (30.5 at.% Ru) + Ru (49 at.% Ru). With falling temperature, the solubility of Ru in Mo decreases quickly, but the solubility of Mo in Ru diminishes slowly. The σ-phase, which is formed by a peritectoid reaction at about 1920° ± 10°C, exists in the region 37.0 ± 1 at.% Ru.

Capacity Test Data for the Adsorption of Volatile Ruthenium on Silica Gel

D. W. RHODES and D. R. ANDERSON, *U.S.A.E.C. Report IDO-14510*, June 17th, 1960, 22 pp.

A 6.6N HNO₃ solution containing approximately 0.03 mg/ml Ru as chloride was calcined at 400°C after removal of the chloride as AgCl. Up to 99% of the volatile Ru species, probably RuO₄, was absorbed on a SiO₂ gel bed at a temperature just above the dew-point of the calciner off-gas. Saturation of the SiO₂ by Ru was not achieved after four adsorption-desorption cycles. The apparent increase in the amount of Ru adsorbed per unit volume of SiO₂ gel is thought to be due to the catalytic decomposition of the volatile species by reduced Ru oxide already deposited on the gel. Water is an effective eluant for the adsorbed Ru.

Activities of Manganese in Solid Platinum

K. P. ABRAHAM, M. W. DAVIES, J. L. BARTON and F. D. RICHARDSON, *Acta Met.*, 1960, **8**, (12), 888-890

Activities were measured at 1500° and 1650°C. Values obtained for the activity coefficient of Mn at infinite dilution are 1.26×10^{-5} at 1500°C

and 3.16×10^{-5} at 1650°C , while for 25 at. % Mn they are 6.0×10^{-4} and 1.4×10^{-3} , respectively. ΔH_{Mn} is -39 ± 7 kcal.

Studies on Transition Metal Intermediate Phases

A. E. DWIGHT and M. V. NEVITT, *Argonne National Laboratory Annual Report for 1959, Metallurgy Division, U.S.A.E.C. Report ANL-6099*, 76-92

The crystal structure of 18 AB_2 Laves-type phases (A=rare earth, Sc, Y, Hf, or Th; B=Ir, Co, Ni, Ru, Rh, Pt or Al), and 27 AB_3 phases (A=Y, La, Ce, Pr, Nd, Gd, Er, Ho, or Th; B=Co, Ni, Cu, Pt, or Ir) was examined. Interrelations of atomic size, valency effects, and stacking geometry in the occurrence of the phases are discussed.

Anomalies in the Modulus of Elasticity and in Internal Friction in the Alloy Fe_3Pt

G. I. KATAEV and Z. D. SIROTA, *Soviet Phys. JETP*, 1960, **11**, (4), 747-750 (Transl. of *Zhur. Eksp. Teoret. Fiz.*, 1960, **38**, (4), 1037-1041)

Measurements were made on a 42 wt. % Fe-Pt 3 mm diameter rod. An anomalous increase in Young's modulus (E) with temperature is found up to 220°C , with the greatest increase in the region of the Curie point (71°C) where a sharp internal friction peak also occurs. Two types of ΔE effect of different sign are produced on application of a magnetic field.

The Influence of a Palladium Addition to Titanium and Titanium Alloys on their Corrosion Behaviour and Passivation

U. ZWICKER, *Metalloberfläche*, 1960, **14**, (11), 334-337

Samples were exposed to 20% HCl for various periods up to 1000 h. It was found that corrosion resistance for both pure Ti and Ti alloys is improved by an addition of 0.1% Pd. The least attack in pure 20% HCl was found for the TiAl_4V_4 , TiAl_6V_4 and TiAl_9V_3 Pd-containing alloys. In HCl solutions containing 0.13% and 1.3% HNO_3 , the alloys TiAl_4V_4 and TiCr_5Al_3 showed the best corrosion resistance.

Changes in Some Optical Properties of Palladium under the Influence of Hydrogen

V. V. OSTROUMOV, *Zhur. Fiz. Khim.*, 1960, **34**, (11), 2571-2578 (English summary)

It was observed that when hydrogen is dissolved in a bright electrolytic layer of Pd, the reflecting powers of the layer are reduced by about a fourth. Darkening of the Pd occurs independently of the conditions of solution of hydrogen and disappears on exposure to air. Quantitative characteristics of the phenomenon are discussed.

Hysteresis in the Palladium-Hydrogen System

D. H. EVERETT and P. NORDON, *Proc. Roy. Soc., Series A*, 1960, **259**, (1298), 341-360

Measurements were made of the hydrogen

content of a Pd sponge sample at 120°C . A hysteresis loop and ascending and descending scanning curves were obtained by plotting the atomic ratio, H/Pd, against equilibrium hydrogen pressure. The main loop is analysed in terms of Lacher's theory of hydrogen solubility in Pd. Data obtained, combined with the previously reported value of the critical point of the α - β phase change, are used to account for the temperature dependence of the range of co-existence of α - and β -phases in both absorption and desorption.

Diffusion with a Concentration Discontinuity: The Hydrogen-Palladium System

R. ASH and R. M. BARRER, *J. Phys. Chem. Solids*, 1960, **16**, (3/4), 246-252

A mathematical treatment is given of the problem of diffusion through membranes of a material in which the solute dissolves to give two non-stoichiometric phases. The application of this treatment to the diffusion of hydrogen in Pd is discussed.

Influence of Grain-Size on the Rate of Absorption of Hydrogen by Palladium

T. J. TIEDEMA, B. C. DE JONG and W. G. BURGERS, *Proc. K. Ned. Akad. Wetensch., Series B*, 1960, **63**, (4), 422-426

Pd wires, 1 mm diameter, of different grain-size were charged at room temperature with purified hydrogen at a pressure of 35 atm for $4\frac{1}{2}$ h. It was shown by X-ray photography that under identical conditions the rate of hydrogen absorption decreases with increasing grain-size. The difference in the rate of absorption is probably caused by a difference in dissociation velocity of the hydrogen molecules at the surface of the Pd, influenced by the effect of the grain boundaries on the dissociation. Pd wires charged electrolytically with hydrogen do not show a difference of absorption rate dependent upon grain-size.

Investigation of Desorption of Hydrogen and Deuterium from Palladium with a Pulsed Mass Spectrometer

YU. N. BELYAKOV and N. I. IONOV, *Soviet Physics Tech. Physics*, 1960, **5**, (2), 195-200 (Transl. of *Zhur. Tekhn. Fiz.*, 1960, **30**, (2), 216-222)

The possible formation of positive and negative hydrogen ions in the penetration by hydrogen of a Pd membrane was investigated in the temperature range 80° - 750°C at pressures from 0-120 mm Hg. Neither positive nor negative hydrogen ions were observed. In the interaction of hydrogen with a heated Pd membrane, the number of hydrogen atoms formed in the desorption of atoms is 1% of the number of hydrogen molecules. In the diffusion through the membrane of an equimolecular mixture of H_2 and D_2 , effects due to the random formation of HD molecules are observed.

Electrical Resistivity and Thermoelectric Power of Desorbed Palladium-Hydrogen

A. I. SCHINDLER, R. J. SMITH and E. W. KAMMER, *Bull. Amer. Phys. Soc., Series II*, 1961, **6**, (1), 10-11 (Paper presented at the 1961 Annual Meeting, New York, Feb., 1961)

Measurements were made as a function of temperature. Electrical resistivity data indicate that the charging and subsequent desorbing of the hydrogen causes strains in the Pd lattice which increase the residual resistivity at 4°K by 5.3%. The same treatment decreases the value of d/dT between 4° and 300°K, and at 300°K the resistivity of the desorbed Pd is lower than that of pure annealed Pd. The results are interpreted in terms of a Debye temperature change of +15°K and a change in the electronic configuration.

ELECTROCHEMISTRY

Note on the Solution of Hydrogen in Palladium Wires

J. P. HOARE, *J. Phys. Chem.*, 1960, **64**, (11), 1780-1781

The resistance of a Pd wire mounted in a cell containing 2N H₂SO₄ solution and the potential against a Pt/H₂ electrode were recorded as a function of time while the wire absorbed hydrogen from the solution. Pt gauze was spot-welded to the centre of the Pd wire, and later at ten points along the centre, after dissolved hydrogen had been removed by annealing and the measurements were repeated. It was found that as the contact with Pt is increased, the length of the 50 mV plateau is shortened and the steady-state value for the potential-time curves is lowered.

Anodic Oxidation of Palladium

A. HICKLING and G. G. VRJOSEK, *Trans. Faraday Soc.*, 1961, **57**, (1), 123-129

Anodic and cathodic charging curves for Pd electrodes of 0.05 and 0.5 cm² area were obtained using a cathode-ray oscillograph in 1N H₂SO₄, 1N NaOH and neutral solutions. Breaks in the oscillograms obtained were compared with the experimental potentials of probable redox systems. Sections of the curves corresponding to the ionisation of hydrogen dissolved in the Pd, to the charging of a double layer, to the formation of PdO.H₂O or Pd(OH)₂, and to the growth of an oxide layer 2-4 molecules thick are found. Further oxidation results in the formation of an unstable oxide, probably PdO₂, and oxygen evolution.

The Effects of γ Radiation upon Electrode Systems

Part I. Platinum Electrodes in Pure Water and Aqueous Sulphuric Acid

F. S. FEATES, *Trans. Faraday Soc.*, 1960, **56**, (11), 1671-1679

The test and control electrode used were Pt cylinders into which γ sources could be lowered

by a magnetic tool. 0.1N H₂SO₄ solutions were used for most measurements. It was shown that changes in rest potential result from competition for adsorption sites on the Pt surface by radiolytically generated hydrogen and H₂O₂. In H₂O₂ solutions the potential-determining species is the HO₂ radical. The effect of electrode pre-treatment on the changes in the kinetics of the hydrogen evolution reaction was studied. The development of a potential difference between the irradiated and control electrodes is suggested as a method for the direct conversion of nuclear energy into electrical energy.

Part II. Aqueous Redox Systems

F. S. FEATES and B. KNIGHT, *Trans. Faraday Soc.*, 1960, **56**, (11), 1680-1688

The radiolytic oxidation of FeSO₄ was studied potentiometrically. Post-irradiation effects were shown to be due to a change in the concentration of radiolytically generated hydrogen. The equilibrium potential finally reached during the irradiation of the systems is due to the effects of H₂O₂. It is possible to measure the oxidation potentiometrically for dosimetry purposes only when a platinised Pt electrode is used in a solution rapidly swept with argon.

Double Layer Capacity of Platinum and Bismuth Electrodes in Molten Lithium Chloride-Potassium Chloride

H. A. LAITINEN and D. K. ROE, *Coll. Czech. Chem. Comm.*, 1960, **25**, (12), 3065-3069 (In English)

The indicator electrodes used in this investigation were Pt wire and a Bi-plated W micro-electrode; counter electrodes were Pt foil and a pool of liquid Bi. These were used in conjunction with a Pt reference electrode and a graphite rod as the working electrode. A voltage-step method was used for the measurement of double layer capacity. The drift in potential of the polarised indicator electrode was reduced by using switching relays with a rise time of less than 1 microsecond.

An Investigation of the Mechanism of the Electrochemical Corrosion of Titanium. II. Corrosion and Passivation of Titanium in Hydrochloric Acid in the Presence of Platinum, Copper and Iron Ions

N. D. TOMASHOV and R. M. ALTOVSKII, *Zhur. Fiz. Khim.*, 1960, **34**, (10), 2268-2274 (English summary)

The investigation was carried out in 15% HCl solution with additions of various small amounts H₂PtCl₆, CuCl₂ and FeCl₃. Results obtained show that the passivity of Ti in HCl solution in the presence of Pt⁴⁺, Cu²⁺ and Fe³⁺ cations is due to shift of the potential of the metal in the positive direction resulting from facilitation of the cathodic process. The role of the noble metal and non-noble metal cations in accelerating the cathodic reaction is discussed.

A Reference Electrode for Use in Baths of Oxygenated Salts at High Temperature

J. BESSON, C. DEPORTES and M. DARCY, *Compt. rend.*, 1960, **251**, (16), 1630-1632

The electrode consists of a Pt wire which passes through the base of and is wound round the outside of an Al_2O_3 tube. This tube, which serves as a lead-in for oxygen, is surrounded by Pt filings contained in an outer sheath of ZrO_2 . The combination, $Pt_2O_3(1 \text{ atm})|ZrO_2$ stabilised by CaO bath, is equivalent in potential to the electrode $Pt_2O_3(1 \text{ atm})|bath$. This electrode is reversible in Na_2SiO_3 at $1200^\circ C$.

A Comparative Study of Some Noble Metals and their Alloys with Regard to Exchange Current in Redox Solutions

E. LEWARTOWICZ, *Electrochim. Acta*, 1960, **3**, (1/2), 28-46

The behaviour of Pt, Au, 5% Au-Pt and 10% Pt-Au electrodes, activated by anodic polarisation, was compared in quinhydrone solutions. Effects of surface poisoning of the electrodes were eliminated by an extrapolation method. In the operating cycle used the electrodes were brought to the potential $E_H = +1.5V$, and then the potentials on open circuit and with a given current density were measured. The minimum value of the polarisation resistance, the transfer resistance at equilibrium, and the exchange current were determined.

An Investigation of the Mechanism of a Carbon-Chlorine Electrode

H. JANKOWSKA and W. TOMASSI, *Electrochim. Acta*, 1960, **3**, (3), 211-216

Measurements of potential of (i) C powder and a layer of adsorbed chlorine as a function of time, (ii) C powder during the adsorption of chlorine from aqueous KCl solution, and (iii) Pt wire surrounded by C powder in a 0.5N KCl solution were used to study a system consisting of aqueous KCl solution and chlorine adsorbed on C.

Behaviour of Platinum Electrodes. I. Disintegration of a Platinum Anode in Acid Solutions

A. MITUYA and T. OBAYASHI, *Russ. J. Phys. Chem.*, 1960, **34**, (3), 322-325 (Transl. of *Zhur. Fiz. Khim.*, 1960, **34**, (3), 679-683)

Two discs of platinised Pt and one of polished Pt previously activated by neutron bombardment were immersed in 0.1N HCl. The activated disc was subjected in air to anodic polarisation relative to one of the other two discs. Measurement of the radioactivity of the acid solution after different stages of anodic treatment of the test electrode showed the metallic Pt used as an anode without polarisation does not disintegrate or dissolve in 0.1N HCl. It was also shown that with polarisation to about 24 mV impurities in the Pt pass into solution and that the surface layer of the electrode

dissolves or disintegrates on increasing the polarisation to 50 mV.

Preventing Hydrogen Embrittlement of Tantalum

C. R. BISHOP and M. STERN, *J. Metals*, 1961, **13**, (2), 144-145

Ta strip in contact with Pt, Pd, Au, Ir, Rh, Os, Ru, Re and Ag was exposed to concentrated HCl for over 1000 h at $190^\circ C$. Contact between the metals was made by riveting, welding, electro-deposition or by rubbing the noble metal powder on the surface of the Ta. It was found in all the tests that contact with Pt is effective in preventing embrittlement of Ta and that the corrosion rates of both metals decrease. Pd requires a larger contact area to prevent embrittlement than Pt, for which the area ratio Ta:Pt may be as low as 10,000:1.

LABORATORY APPARATUS AND TECHNIQUE

Glass Insulated Platinum Microelectrode

M. L. WOLBARSH, E. F. MACNICHOL and H. G. WAGNER, *Science*, 1960, **132**, (3436), 1309-1310

A microelectrode for electrophysiological use may be prepared by electrolytically sharpening 30% Ir-Pt wire and coating it with molten glass. Glass is removed from the electrode tip and the exposed Pt wire is coated with Pt black by passing a direct current between the electrode and a Pt wire in a $PtCl_2$ solution, the electrode being negative.

A Method for Detecting Hydrogen in Gas Mixtures

J. R. YOUNG and N. R. WHETTEN, *Rev. Sci. Instr.*, 1960, **31**, (10), 1112-1114

Nitrogen containing a known amount of hydrogen was passed through the outer jacket of a Pd diffusion leak at a rate of $200 \text{ cm}^3/\text{min}$. Hydrogen diffused through the previously evacuated Pd tube which was maintained at $500^\circ C$. The pressure of the hydrogen in the tube after equilibrium had been established, which was measured by a thermocouple gauge, indicated the partial pressure of the hydrogen in the gas mixture.

Full and Partial Particle Replication Technique for Electron Microscopy

F. LEONHARD, C. F. COOK and F. R. ANDERSON, *Rev. Sci. Instr.*, 1960, **31**, (11), 1181-1185

Improvements in coating methods are reviewed. A development is described in which the sample is preshadowed by a film of 10% Rh-Pt evaporated on to it in high vacuum. This film is strengthened by a carbon layer deposited by a residual gas scattering method and an auxiliary layer of S. A partial replication technique using polystyrene as the embedding material is described.

CATALYSIS

Purifying Olefins by Catalytic Hydrogenation

H. C. ANDERSEN, A. J. HALEY and W. EGBERT, *Ind. Eng. Chem.*, 1960, **52**, (11), 901-904

C₂H₂ may be removed from the C-2 or product stream of an C₂H₄ plant by the addition of limited hydrogen in the presence of a Pd/Al₂O₃ catalyst. In experimental work, four catalysts with Pd contents ranging from 0.001 to 0.035% were used. Pressures up to 550 p.s.i.g. were studied and temperatures were in the range 200°-400°F. The effect of poisons such as CO, H₂S, COS and CS₂ was studied. Removal to a level of < 10 p.p.m. C₂H₂ was accomplished. The removal of CH₃CCH and CH₂CCH₂ from C₃H₆ by a similar method was also studied.

The Purification of Coke Oven Gases with Platinum Metal Catalysts

H. C. ANDERSEN and D. R. STEELE, *Brit. Chem. Eng.*, 1960, **5**, (12), 864-865

A supported Pd-Ru catalyst was found to be satisfactory for the removal by hydrogenation of C₂H₂, NO and COS from a simulated coke oven gas mixture. Experiments were carried out at 180-220°C and at pressures of 1 and 14-14.7 atm. Both butadiene and cyclopentadiene were removed from another gas mixture at atmospheric pressure in experiments carried out in the range 100°-225°C using a supported Ru catalyst.

Catalysis on Metals of Group 8. Part 5. The Kinetics of the Hydrogenation of Cyclopropane and of Methylcyclopropane

G. C. BOND and J. NEWHAM, *Trans. Faraday Soc.*, 1960, **56**, (10), 1501-1514

5% M/pumice (M=Rh, Pd, Ir and Pt) catalysts were used in the study of the hydrogenation of cyclopropane which was carried out in the temperature range 0°-200°C. Orders of reaction were determined. These indicate that the rate-controlling step involves adsorbed cyclopropane and adsorbed hydrogen atoms. Activation energies and adsorption coefficients were estimated. A 5% Pt/pumice catalyst was used in the study of the hydrogenation of methylcyclopropane. Under the same conditions, methylcyclopropane is more strongly adsorbed on the catalyst surface than cyclopropane. The proportion of *n*-C₄H₁₀ in the product increases exponentially with temperature, although *iso*-C₄H₁₀ predominates at room temperature. Results are interpreted in terms of ring-fission.

Part 6. Hydrogenation of Methylene-cyclopropane and Methylene-cyclobutane over Platinum Catalysts

Ibid., 1960, **56**, (12), 1851-1860

The hydrogenations were carried out using 5% Pt/pumice catalysts in the temperature

range 0-200°C. The kinetics of the hydrogenation of the cyclic olefins and *iso*-C₄H₈ were studied by the method of initial rates. With the cyclic olefins, hydrogenation products at room temperature were paraffins and cycloparaffins, but at higher temperatures olefins also were obtained. Results of kinetic and analytical studies indicate that methylenecyclopropane is more strongly adsorbed than non-cyclic olefins. Ring-fission mechanisms for the reactions are suggested.

Platforming the Gasolines Obtained from Saharan Crude Oil

V. E. HENNY, *Bull. Assoc. Franc. Techn. Pétrole*, 1960, (144), 989-1004

The treatment of Saharan crude oil is compared with that of the Middle East. Saharan naphthas may be catalytically reformed by Platforming, without Unifining and gas recycling, to give a reformat with an octane number up to 95. Higher yields of gasoline and lower yields of liquefied and dry gases are obtained from Saharan crude oils. Reforming is carried out at a lower temperature and higher space velocity, with longer catalyst life. Saharan naphthas give twice as much C₆H₆, C₆H₅CH₃ and xylenes as the Middle East crude oils, with a greater quantity of hydrogen as a by-product.

Infra-Red Spectra of Chemisorbed Molecules. I. Acetylene and Ethylene on Silica-Supported Metals

L. H. LITTLE, N. SHEPPARD and D. J. C. YATES, *Proc. Roy. Soc., Series A*, 1960, **259**, (1297), 242-256

Finely-divided samples of Pd, Cu and Ni supported on high area porous SiO₂ glass were used in this investigation. Metal content of the samples was about 2% of the metal oxide. Spectra were obtained in the C-H bond-stretching region for C₂H₂ chemisorbed on Pd, Cu, and Ni, and of C₂H₄ chemisorbed on Pd and Ni. After initial adsorption of C₂H₂ on Pd and Cu, the surface species obtained are olefinic. With C₂H₄, a mixture of olefinic and saturated species is obtained. A species of the type M.(CH₂)_n.CH₃ was detected after hydrogenation of the initial surface species. For C₂H₂ on Pd and Cu, n>5; for C₂H₄ on Pd, n~3.

Decomposition of Nitrous Oxide

J. H. ZUFALL and H. S. MILLER, *U.S.A.E.C. Report IDO-14513*, July 1960, 19 pp.

The investigation was carried out using a reactor tube surrounded by a constant temperature bath of fluidised Al₂O₃. Gas mixtures contained some or all of N₂O, CH₄, hydrogen and oxygen with a balance of nitrogen. The catalysts used were 0.5% Rh/Al₂O₃, 0.5% Pd/Al₂O₃ and 0.5% Pt/Al₂O₃. NO₂ is formed with all the catalysts, the amount increasing as residual N₂O decreases. Satisfactory results are obtained with Rh/Al₂O₃ at a bath temperature of 500°C.

Hydrogenation of Benzene on Platinum Catalysts. I. Activity of Platinum on Silica Gel

J. E. GERMAIN and Y. BOURGEOIS, *Bull. Soc. Chim. France*, 1960, (11/12), 2127-2130

Catalysts containing 4-14% Pt were used in the hydrogenation experiments which were carried out at 20°C and atmospheric pressure. It was found that the reduction conditions have a considerable influence on the initial activity of the catalyst which undergoes an irreversible ageing. A more active and reproducible catalyst is obtained by reduction in the presence of CH₃COOH. The velocity of hydrogen absorption is proportional to the weight of Pt and independent, to a large degree, of the concentrations of C₆H₆ and C₆H₁₂. The energy of activation was estimated as 6 kcal/mole between 15° and 40°C.

The Atomisation of Hydrogen on Platinum, Gold and Carbon, and of Oxygen on Platinum

D. BRENNAN and P. C. FLETCHER, *Trans. Faraday Soc.*, 1960, 56, (11), 1662-1670

The dissociation of hydrogen on Pt and Au filaments, and of oxygen on Pt filaments was studied in the temperature range 1200°-1800°K and in the pressure range 10⁻²-10⁻⁶ mm. Mo oxide was used to trap hydrogen atoms. It was found that the rate of atomisation is proportional to \sqrt{P} at lower temperatures and to P at high temperatures. The atomisation of hydrogen on C was studied in the first-order region.

Stereochemistry and the Mechanism of Hydrogenation of Cycloolefins on a Platinum Catalyst

S. SIEGEL and G. V. SMITH, *J. Amer. Chem. Soc.*, 1960, 82, (23), 6082-6087

1,2-dimethylcyclohexene(I), 2,3-dimethylcyclohexene(II) and 2-methylmethylenecyclohexane(III) were hydrogenated in the liquid phase at 40-500 atm, 2-4 atm, and 0.25-1 atm at 25°C, using a PtO₂ catalyst. It was shown that the *cis/trans* ratio of the 1,2-dimethylcyclohexanes obtained is a function of the hydrogen pressure. With increasing pressure, the ratio increases for I, but decreases for II or III. In the range 0.25-1 atm, isomers of the initial olefins are found when the hydrogenation of II and III are interrupted. The reaction rates decrease in the order III > II > I in competitive experiments. The results are discussed in terms of the Horiuti-Polanyi theory, with the rate-determining reaction a function of hydrogen pressure.

The Stereochemistry of the Hydrogenation of Cycloolefins on Supported Palladium Catalysts

S. SIEGEL and G. V. SMITH, *J. Amer. Chem. Soc.*, 1960, 82, (23), 6087-6090

The liquid-phase hydrogenation of 1,2-dimethylcyclohexene(I), 2,3-dimethylcyclohexene(II), and

2-methylmethylenecyclohexane(III) was studied at 1 atm and 25°C in the presence of Pd/Al₂O₃ or Pd/C catalysts. The main hydrogenation product is *trans*-1,2-dimethylcyclohexane(IV). Isomerisation of the olefins occurs during hydrogenation but not in the absence of hydrogen. During the hydrogenation of III on Pd/C, there is competition for the effective surface of the catalyst between III, and I and II which are formed. Results are interpreted in terms of the Horiuti-Polanyi mechanism with the conversion of the "half-hydrogenated states" to products as the rate-limiting reaction.

The Catalytic Activity of Platinum Deposited on Cadmium

V. P. LEVEDEV and E. A. TROSMAN, *Russ. J. Phys. Chem.*, 1960, 34, (3), 327-328 (Transl. of *Zhur. Fiz. Khim.*, 1960, 34, (3), 687-690)

The catalyst was prepared by adsorption of PtCl₄ on Cd powder followed by reduction in hydrogen at 250°C. The activity of the catalyst in the decomposition of H₂O₂ at 20°, 25° and 30°C was compared with that of Pt on SiO₂ gel and C supports. Pt/Cd and Pt/SiO₂ gel have an activity of a similar order which is greater than that of Pt/C. A mechanism which explains the decomposition of H₂O₂ on active centres of odd composition, [Pt]₁, [Pt]₃, [Pt]₅, and [Pt]₇, is suggested.

The Experimental Development of Membrane Cells

E. JOACHIM and W. VIELSTICH, *Electrochim. Acta*, 1960, 3, (3), 244-252

The construction of hydrogen-oxygen fuel cells using solid ion-exchange membranes as electrolyte is described. For work in an acid medium, the catalysts selected are 10% Pt/C for both the hydrogen- and oxygen-electrodes, while in alkaline medium, Raney Ni and Ag are used for hydrogen- and oxygen-electrodes, respectively. The cells work at room temperature with gas pressures slightly above atmospheric. At 0.65V a current of 10 mA/cm² may be obtained from the most efficient type, which has an open-circuit voltage of 1.03V.

The Hydrogenation of Cyclohexenes over Platinum Oxide

J.-F. SAUVAGE, R. H. BAKER and A. S. HUSSEY, *J. Amer. Chem. Soc.*, 1960, 82, (23), 6090-6095

PtO₂ was used as a catalyst in the hydrogenation of nine 1,4-disubstituted cyclohexenes, 1,3-dimethylcyclohexene and $\Delta^9, 10$ -octalin in acetic acid at 1 atm pressure and room temperature. Isomerisation during hydrogenation is not an important side reaction under these conditions. The *cis-trans* isomer compositions of the products were determined. The results are explained in terms of steric selectivity in the adsorption of the substrates on the catalyst surface.

Kinetics of Methylcyclohexane Dehydrogenation over Pt/Al₂O₃

J. H. SINFELT, H. HURWITZ and R. A. SHULMAN, *J. Phys. Chem.*, 1960, **64**, (10), 1559-1562

The investigation was carried out using a 0.3% Pt/Al₂O₃ catalyst at three temperatures (315°, 334° and 372°) at methylcyclohexane partial pressures in the range 0.07-2.2 atm and hydrogen pressures ranging from 1.1 to 4.1 atm. It was found that the reaction is nearly zero order with respect to methylcyclohexane and hydrogen in the given conditions. The activation energy for the reaction is 33 kcal/mole. It is suggested that the active catalyst sites are heavily covered with adsorbed hydrocarbon molecules or radicals and that adsorption equilibria are not established under the experimental conditions.

Intermetallic Compounds of Alkali Metals with Platinum. A Novel Preparation of a Colloidal Platinum Hydrogenation Catalyst

C. P. NASH, F. M. BOYDEN and L. D. WHITTIG, *J. Amer. Chem. Soc.*, 1960, **82**, (23), 6203-6204

An exothermic reaction resulting in the formation of Li Pt₂, takes place at about 540°C when molten Li and Pt are heated together in a Mo crucible in an argon atmosphere. By heating Na and Pt to about 650°C in a similar manner, a Na-Pt compound, probably Na Pt₂, is obtained. Molten Li maintained at 400°C penetrates the lattice of Pt suspended in it. A Li-Pt dispersion, formed on treating this Pt with H₂O or dilute acid, is an effective catalyst for the hydrogenation of cyclohexene.

CATHODIC PROTECTION

Automatic Control of a Platinum Anode Cathodic Protection System

R. C. FRANCIS and L. S. BIRNBAUM, *Corrosion*, 1961, **17**, (1), 20-22

The components of the protection system for a U.S. Navy ship and the principles of operation are described. Six circular Pt-Pd anodes were used in conjunction with four Ag|AgCl reference electrodes, six transformer-rectifier power units, an automatic potential recorder, a shaft-propellor grounding assembly and an automatic controller. The Pt-Pd anodes were 6.5 in. diameter, 5 mils thick with a stem, originally of five Pt-Pd wires and later of Pt-Pd rod, welded on to the disc. Problems created by stray currents are discussed.

Impressed Current Anodes for Cathodic Protection

W. P. NOSER, *Corrosion*, 1960, **16**, (12), 79-84

The history of the development of impressed current anodes is traced. Protection of underground structures in various soil conditions is described in detail and the use of Pt, steel, graphite Al, and Pb alloy anodes in underwater systems is mentioned.

CHEMICAL TECHNOLOGY

Materials of Construction for Chemical Plant. Platinum

J. A. STEVENSON, *Chem. Process Eng.*, 1961, **42**, (1), 31-36

The distribution of Pt-bearing deposits and the processes for extracting and refining Pt are described. Chemical properties of Pt and the physical and mechanical properties of Pt and its alloys with Ir, Ru, Rh and Au are discussed. Among the applications described are Pt-lined pressure vessels, Pt crucibles and bushings for the glass industry, Pt alloy spinning jets for the textile industry, Pt or Pt-protected electrodes for various electrochemical processes, and bursting discs.

ELECTRICAL ENGINEERING

The Conductivity of Oxide Cathodes. Part 8. Current-Dependent Matrix Dissociation

G. H. METSON and E. MACARTNEY, *Proc. Instn. Elect. Engrs., Part C*, 1960, **107**, (12), 158-162

Current was passed at 1020°K through S-type assemblies with electrode cores of Ni or Pt embedded in a matrix of co-precipitated equimolar Ba-Sr oxide. By passing the same quantity of electricity through two identical oxide systems at different rates, it was found that oxide dissociation is dependent upon the rate of application of electricity. The dissociation products are in ionic form.

The Solion, an Electrochemical Control Element

J. EULER, *Electrotech. Z., Part B*, 1960, **12**, (22), 537-540

The electrochemical principles on which the operation of the solion depends are discussed. Adaptations of solions, which consist basically of Pt electrodes in a solution of elementary I in an aqueous KI solution, for use as simple electrochemical diodes, pressure- and movement-measuring devices, integrators and amplifiers are described. The solion elements have a low limiting frequency and the current consumption of solion circuits is far less than that of the corresponding transistor circuits. Principal applications of the solion will probably be in control engineering.

TEMPERATURE MEASUREMENT

A Platinum Resistance Thermometer for Use at High Temperatures

C. R. BARBER and W. W. BLANKE, *J. Sci. Instr.*, 1961, **38**, (1), 17-19

The thermometer bulb consists of four coils, 36 mm long, of 0.3 mm diameter Pt wire loosely

mounted on recrystallised Al_2O_3 tubes 0.8 mm o.d. and 50 mm long. A sheath of recrystallised Al_2O_3 , 500 mm \times 8 mm, encloses the coil assembly which is freely exposed to dry air. The resistance of the thermometer, 1.4 Ω at 0°C and 6.4 Ω at 1063°C, allows measurements equivalent to 0.002°C. The sensitivity of the thermometer is maintained after heating for 1 h at 1063°C.

Platinum : Rhodium-Platinum Thermocouples

R. LACROIX, *Bull. Soc. Franc. Céram.*, 1960, (48), 19-30

Pt : 10% Rh-Pt or Pt : 13% Rh-Pt thermocouples are most suitable for the measurement of temperatures up to 1300°C because of the high melting points, ductility and great purity of Pt and Rh-Pt alloys. Reference tables for both combinations are given and the use of these thermocouples for precision measurements with a reproducibility better than 0.1°C, as well as for routine measurements to within $\pm 2^\circ\text{C}$, is described. The effect of contaminants such as Pb, Sn, Bi, Zr, Cd and Si and the choice of protective refractories are discussed. For temperature measurements in the range 1300°C-1850°C, combinations of Rh-Pt alloys recommended include 5% Rh-Pt : 20% Rh-Pt, 6% Rh-Pt : 30% Rh-Pt, 10% Rh-Pt :

30% Rh-Pt, 10% Rh-Pt : 40% Rh-Pt, and 20% Rh-Pt : 40% Rh-Pt. Other thermocouples which have been suggested for use above 1500°C are Rh : 8% Re-Pt, Rh : 8% Re-Rh, Ir : 10% Ru-Ir, 10% Rh-Ir : 10% Ru-Ir, Ir : 40% Ir-Rh, Ir : 40% Rh-Ir and W : Ir. (60 references).

Temperature Measurement with Platinum Metal Thermoelements

J. SAGOSCHEN, *Metall*, 1961, 15, (1), 34-40

In this review, the historical development of Pt metal thermocouples is outlined. Properties of Pt : Rh-Pt thermocouples, their construction and calibration are described in detail. The effects of various impurities and operating atmospheres on their accuracy and durability are indicated and precautions to be observed in their use are explained. Industrial uses of Pt : Rh-Pt thermocouples described include temperature measurement and control in the 1000°-1500°C range in the iron, steel, non-ferrous metal, glass, ceramic and cement industries. Other Pt combinations mentioned are 40% Pd-Au : 10% Ir-Pt, 40% Pd-Au : 10% Rh-Pt and those with a Au-Pd-Pt basis for temperatures about 1000°C. For temperatures in the range 1500°-1800°C, Rh-Pt : Rh-Pt thermocouples of various compositions are recommended. (74 references.)

NEW PATENTS

Conversion of Sulphoxides to Sulphones

THE M.W. KELLOGG CO. *British Patent* 853,623

Osmium tetroxide is used as catalyst in the preparation of organic sulphones from organic sulphoxides.

Platinum Plating

SEL-REX CORP. *British Patent* 853,939

Relatively thick layers of bright platinum are plated out by use of an electrolyte comprising an aqueous solution obtained by dissolving platinum diamino dinitrite in a mixture of sulphuric and phosphoric acids and adding water to provide a solution containing at least 6 g/l of platinum metal.

Anodes

N.V. CURACAOSCHE EXPLOITATIE MAATSHCAPPIJ UTO. *British Patent* 855,107

An anode for electrolytic or other electrochemical processes is formed of a core of titanium and a coating of a platinum group metal with a barrier layer of titanium dioxide beneath the coating where the latter is porous. The barrier layer may be formed electrolytically after the precious metal coating has been applied.

Production of New Cyclopentano-phenanthrene Derivatives

SYNTEX S.A. *British Patent* 855,801

A 5% palladium on charcoal hydrogenation catalyst is used in the production of a 19-nor-androstan-17 β -ol-3-one compound.

Low Stress Platinum Platings

SEL-REX CORP. *British Patent* 856,405

Relatively thick layers of stress-free platinum are deposited from an aqueous solution of sulphamic acid and platinum diamino dinitrite to which is added water to provide a solution containing at least 6 g/l of platinum metal. The aqueous solution is formed by heating the acid solution to dissolve the platinum salt.

Platinum or Alloy Conductors

NORTON GRINDING WHEEL CO. LTD. *British Patent* 856,309

A platinum or platinum alloy electric heating element is coated by flame spraying with a refractory oxide, e.g. alumina or zirconia, to reduce or inhibit the volatilisation of the platinum and embrittlement of the metal.