

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

The Thermodynamic Properties of Pure Palladium and its Alloys with Hydrogen between 30 and 300°K

P. MITACEK and J. G. ASTON, *J. Am. Chem. Soc.*, 1963, **85**, (2), 137-141

Heat capacity curves of the Pd-H system over the range 30° to 290°K have been used to establish a model of the system and explain an anomaly which occurs at 55°K. A cage of Pd discs enclosed in a gold calorimeter was used as part of an adiabatic system. Measurements on H/Pd ratios from 0.25 to 1.25 showed that the 55°K transition on the curves is independent of hydrogen concentration. Warm drifts were noticed for concentrations below 0.5 H/Pd. A model of the Pd-H system is suggested in which planes of H atoms form in the Pd lattice. A calculated heat capacity curve from the model agrees well with the observed phenomena.

Superconductivity of Solid Solutions of Noble Metals

T. H. GEBALLE, B. T. MATTHIAS, V. B. COMPTON, E. CORENZWIT and G. W. HULL, *Phys. Rev.*, 1963, **129**, (1), 182-183

Os-Ir and W-Pt solid solutions possess superconducting properties at very low temperatures. The transition temperatures were determined as functions of composition and valence electron concentration. Ir f.c.c. solid solution has a transition temperature at 0.97°K and Os h.c.p. solid solution has one at 0.46°K.

Thermodynamic Properties of Binary Metallic Systems by the E.M.F. Method. IX. Solid Copper-Palladium Solutions

A. A. VECHER and YA. I. GERASIMOV, *Zhur. Fiz. Khim.*, 1963, **37**, (4), 739-745.

Alloys containing between 7 and 89 at.% Cu were investigated at 1000°K by the e.m.f. method. The thermodynamic properties of these non-ordered solid Cu-Pd solutions agreed with the presence of superstructures in them at lower temperatures. The results are discussed and comparisons are made between electron exchange in these and Cu-Pd alloys.

Low Temperature Resistivity Behaviour of Molybdenum-Iron, Niobium-Iron and Palladium-Iron Alloys

B. R. COLES, *Phil. Mag.*, 1963, **8**, (86), 335-337

Resistivity-temperature curves for Mo diluted with small amounts of Fe indicate that Fe causes

anomalies in the curves. Corresponding Nb alloys show no anomalies, which suggests that these only occur when Fe atoms carry localised moments. Pd alloys with < 0.1 at.% Fe show decreased resistivity below 2°K with no minimum above 2°K corresponding to that for the Mo alloys.

The Liquid \rightleftharpoons Solid and $\delta\rightleftharpoons\gamma$ Equilibria in Iron-rich Alloys

R. A. BUCKLEY and W. HUME-ROTHERY, *J. Iron Steel Inst.*, 1963, **201**, (3), 227-232

Liquid \rightleftharpoons solid transitions for the Pt metals and other transition elements alloyed with Fe are discussed. The solute free energy difference ΔG_Y varies systematically with periodic group number. $\Delta G_Y = \Delta F_Y + \Delta S_F \Delta T$, where ΔF_Y is the lattice disturbing effect, ΔS_F is the entropy of fusion and ΔT is the difference between the temperature T and the freezing point of the solute. Study of $\delta\rightleftharpoons\gamma$ phase transformations suggests that electronic factors are more important than size factors and a possible explanation is proposed.

Interruptions of Pressure Measurement in the Neighbourhood of a Gas Discharge

E. W. BLAUTH and B. M. U. SCHERZER, *Z. angew. Phys.*, 1963, **15**, (1), 28-31

Pressure measurement with W and Pt hot wire manometers was found to be possible when penetration of the metal by radicals was prevented. Measurements can therefore be made in ultra-high vacuum near gas discharges. A suitable apparatus incorporating the hot wire is described.

Reaction of Platinum and Boron under Pressure

E. D. WHITNEY and R. F. GIESE, *Nature*, 1963, **197**, (4874), 1293

A new phase was detected in high-temperature, high-pressure experiments and was identified as PtB, which has space group $\bar{r}3m/mmc$, $a = 3.36 \text{ \AA}$ and $c = 4.06 \text{ \AA}$.

Binary Transition Metal Phosphides. Their Structures and Relationships with Other Compounds between Transition Metals and Non-metals with Small Atomic Radii

S. RUNDQVIST, *Arkiv för Kemi*, 1963, **20**, (1/2), 67-113 (in English)

The preparation and properties of transition metal phosphides, including those of the Pt metals, are reviewed. Intermediate phases and their crystallographic constants are surveyed. Crystal structures are described and discussed for transition metal phosphides and transition

metal compounds with other non-metals of small atomic radius. Size-factors and bonding are also discussed. (112 references.)

Magnetic Susceptibility and Electronic Specific Heat of Transition Metals and Alloys.

II. Pd Metal and Pd-Ag and Pd-Rh Alloys

M. SHIMIZU, T. TAKAHASHI and A. KATSUKI, *J. Phys. Soc. Japan*, 1963, **18**, (2), 240-248

Curves depicting electronic specific heats of Pd showed good agreement between experimental results and figures computed from low temperature heat data of Pd-Ag and Pd-Rh alloys and Ru metal. A rigid band model was assumed. Calculated values of spin paramagnetic susceptibility χ of Pd were less than observed values because of molecular field effects. A modified band shape accounted for the 80°K maximum of χ . Alloys of Pd with small amounts of Ag or Rh gave similar results but, when Ag exceeded 20 at.%, orbital and core diamagnetism became appreciable.

Superconductivity in the Pd-As System and the Effect of Ferromagnetic Additions

C. TRAUB, G. W. WEBB and R. W. FITZGERALD, *Bull. Am. Phys. Soc., Ser. II*, 1962, **7**, (7), 474 (abstract) Superconductivity has been observed in the Pd-As system near the composition of Pd₂As. The transition temperatures were also measured in alloys of either Co or Ni.

Influence of Salting-out on Ruthenium Separation by Naphthol from Nitrate Solutions

C. KONECNY, *Coll. Czech. Chem. Comm.*, 1963, **28**, (2), 340-348 (in German)

Small amounts of Ru were separated from U in dilute HNO₃ at 98°C with 1-naphthol and U remained in the aqueous phase. Ru yields were greatest for 0.2-0.5 M HNO₃. The mechanism of the reaction of nitrosylruthenium (III) ions with naphthol was studied and showed that the presence of HNO₃ and nitrate ions is important in the extraction of Ru compounds although the explanation is not yet complete.

On the Chemistry of the Platinum Metals: RuO₂, Chemical Transport, Properties, Chemical Occurrence

H. SCHAEFER, G. SCHNEIDERREIT and W. GERHARDT, *Z. Anorg. Chem.*, 1963, **319**, (5/6), 327-336

Tetragonal RuO₂ crystals were prepared by chemical transport and were found to have lattice parameters $a = 4.49 \pm 0.005$ Å, $c = 3.11 \pm 0.005$ Å. Specific conductivity at 20°C for single crystals was 2.10^4 ohm⁻¹ cm⁻¹. Equilibrium studies of RuO₂ = Ru + O₂ by glowing filament, thermobalance and static pressure methods gave lower O₂ pressure results than previous work, with 1 atmosphere obtained at 1580°C. The enthalpy of RuO₂ formation is $\Delta H(298) = -71$ kcal/mol.

Relation between Lattice Energy and Melting Point of Some Crystalline Substances. Some Transition Metals

R. GOPAL and M. M. HUSAIN, *J. Ind. Chem. Soc.*, 1962, **39**, (12), 827-830

The ratio $-U_0/T_m$ was calculated as about 0.5 for most platinum and other transition metals, where $-U_0 = I \times v + S$ and where $-U_0$ is the lattice energy in kilocalories, T_m is the absolute melting point, I is the first ionisation potential, v is the metallic valency and S is the latent heat of sublimation in kilocalories. Similar ratios were expected but 0.7 for Pd is high and 0.41 for Mo and 0.36 for W are low. Further work is in progress.

Rhodium: Properties and Electrodeposition

M. DANEMARK and Y. RUSCONI, *Galvanotechnik u. Oberflächenschutz*, 1962, **3**, (12), 287-301 (in German and French)

This summary deals with the extraction and refining of Rh, the properties of the metal, its electrodeposition, methods for its analysis, and with applications of Rh. The section on properties covers atomic and crystal structure, and mechanical, electrical, magnetic, thermal, optical and chemical properties. Dealt with under electrodeposition are types of bath, effect of NH₄ salts, wetting agents, ionic behaviour, contamination of baths, and equipment. Both qualitative and quantitative analysis are considered. Uses of Rh include decoration, optical work and electronics.

A Survey of Intermediate Phases in Transition Metal Alloys

Y. L. YAO, *Trans. Met. Soc. A.I.M.E.*, 1962, **224**, (6), 1146-1153

Binary alloy systems of transition metals, including the platinum group metals, are grouped according to their 'excess energy' ΔE , which depends on their atomic size factor and their solubility factor. Properties of alloys with positive, negative and weakly positive ΔE are tabulated and further properties are given in classifications of the alloys as solubility and anti-solubility compounds, size and anti-size compounds and equimolar compounds. Possible crystal structures are listed.

Trends in Organometallic Chemistry Research

R. E. DESSY, *Chem. Eng. News*, 1963, (7), 136-144

Recent developments in the field are reviewed. An explanation of the transition metal catalysis mechanism for hydrogenation, hydroformylation, polymerisation and hydration of organic compounds is offered. A commercial process uses olefin-Pd (II) complexes in aqueous solution to produce CH₃CHO (and Pd metal). Transition metal compounds, the theory of organometallic bonding, bond stabilisation and activation, and problems of optical activity are discussed. Synthetic catalysts are a future possibility.

Metal- π -complex with di- and oligo-Olefin Ligands

E. O. FISCHER and H. WERNHER, *Angew. Chem.*, 1963, **75**, (1), 57-70

This review is devoted exclusively to organometallic compounds formed between metals and di- and oligo-olefins. It covers their historical background, bonding theory, methods of preparation and structure, with structural diagrams for various classes. Metals forming these compounds include the Pt metals and V, Cr, Mo, W, Mn, Re, Fe, Co, Ni, Ag and Cu. (187 references.)

The Uranium-Osmium System

A. G. KNAPTON, *A.E.R.E. Report X/PR 2068*, 1962, (July).

The whole range of the system has been studied, using X-ray, metallographic, dilatometric and melting point techniques. Os has high solid solubility in γ -U, up to 18 at.% at the eutectic temperature of 970°C. There are four intermetallic compounds. UOs_2 and U_3Os_2 form congruently from the melt at 2280°C and 1030°C respectively. U_2Os and U_5Os_4 form peritectically. U has less than 1 at.% solid solubility in Os. Eutectic alloys occur at 2170°C (72 at.% Os), at 970 \pm 5°C (22 at.% Os) and at 900°C (40 at.% Os). (7 tables, 21 figures.)

Antiferromagnetism of the Antiphase Domain Structure of Pd_3Mn

J. W. CABLE, E. O. WOLLAN, W. C. KOEHLER and H. R. CHILD, *Phys. Rev.*, 1962, **128**, (5), 2118-2120

Polycrystalline samples of the alloy were prepared and their neutron diffraction patterns were obtained. Long-range positional order, of the one-dimensional antiphase domain type based on Cu_3Au , was obtained by cooling from 1000°C to room temperature over 2 weeks. Antiferromagnetism developed in the ordered alloy below 170°K. A proposed magnetic structure accounts for the experimental results.

Constitution Diagram of the Palladium-Osmium System

M. A. TYLKINA, V. P. POLYAKOVA and O. CH. CHAMIDOV, *Zh. Neorg. Khim.*, 1963, **8**, (3), 776-778

The system possesses a peritectic temperature of 1640 \pm 25°C with no intermediate phase. α -Os exists for alloys containing <2 wt.%, β -Os for those with > 97 wt.%. Measurements were made on cast and annealed samples of melting point, hardness, microstructure, resistivity and of thermal e.m.f. with Cu. (7 photomicrographs.)

Chemical and Magnetic Order in Platinum-rich Pt-Fe Alloys

G. E. BACON and J. CRANGLE, *Proc. Roy. Soc.*, 1963, **272**, (1350 A), 387-405

The magnetic properties of alloys approximating to Pt_3Fe depend on their chemical structure. Neutron diffraction and magnetic studies were

made on alloys with compositions of between 24% and 38% Fe down to cryogenic temperatures. Stoichiometric alloys with perfect chemical order showed simple antiferromagnetism but as the amount of Fe increased there was a tendency towards ferromagnetism and with more than 34% Fe there was bulk ferromagnetism. The magnetic moment of the Fe atoms was about 3.3 μ_B throughout and the Pt atoms showed very little alignment.

Electronic Configuration and Formation of Complexes of Transition Metals

R. S. NYUKHOL'M, *Uspekhi Khim.*, 1963, **32**, (3), 354-387

This review studies metals with isoelectronic configuration which form similar complexes. The nature of transition metal-ligand bonding is discussed with the aid of thermodynamic, magnetic and spectral data. X-ray spectra are studied with special attention to carbonyl bonding. Atoms and ions with electronic configurations d_{10} , d_9 , d_8 , d_7 , d_6 and d_5 are considered in detail for the platinum metals and other transition metal complexes. (93 references.)

Titanium-Iridium Phase Diagram

J. G. GROENI, C. E. ARMANTROUT and H. KATO, *U.S. Bur. Mines, Rept. Invest. 6079*, 1962

The Ti-Ir system over the 500° to 2400°C range was investigated. Alloys with <10 at.% Ir or 45 to 55 at.% Ir have possibilities as control rod materials in nuclear reactors. The phase diagram was plotted from results obtained from melting point determinations, thermal analyses, dilatometry, resistivity measurements, X-ray diffraction analyses and metallographic examinations (10 figs.). The compounds Ti_3Ir and $TiIr_3$ were observed in some of the alloys and a new compound $TiIr$ was identified. Alloys containing intermetallic compounds tended to be brittle. Ir acted as a beta stabiliser in Ti-rich alloys.

The Crystal Structure of Th_3Pd_5 and Th_3Pt_5

J. R. THOMSON, *Acta Cryst.*, 1963, **16**, (4), 320-321

Examination of Th_3Pd_5 and Th_3Pt_5 suggested that they were isostructural and hexagonal. Th_3Pd_5 has $a=7.149\pm 0.003$, $c=3.899\pm 0.002$ Å; Th_3Pt_5 has $a=7.162\pm 0.003$, $c=3.908\pm 0.002$ Å. Interatomic distances for Th_3Pd_5 were calculated.

The High Temperature Specific Heat of Palladium

N. K. HINDLEY and P. RHODES, *Proc. Phys. Soc.*, 1963, **81**, (4), 717-725

Reasonable agreement was shown between values of the electronic contribution C_e to the specific heat of Pd obtained from measurements of the specific heat of Pd, and from calculations based on an electronic density of states curve for Pd derived from low temperature specific heat coefficients γ of Ag-Pd and Rh-Pd alloys. A rigid

band model was assumed for these alloys. Over the range 0° to 1500°K both sets of data differ widely from the approximation $C_e = \gamma T$. A maximum occurs on the density of states curve near the Fermi limit.

New Compounds of Cobaltite Structure

F. HULLIGER, *Nature*, 1963, **198**, (4878), 382-383

A range of ternary semiconducting compounds was prepared by substitution in cobaltite CoAsS of Rh or Ir for Co; of P, Sb or Bi for As; of Se or Te for S. Structure and valency are similar to FeS₂. Another range was prepared by substitution in NiAsS and NiSbS, but this time Pd and Pt were substituted for Ni. In a series containing one element, where this element is changed for another of the same group, the lattice constant changes are almost identical. The compounds so far prepared are tabulated with their lattice constants a.

LABORATORY APPARATUS AND TECHNIQUE

The Determination of Hydrogen, Oxygen and Nitrogen in Metals and Compounds by the Micro-Platinum Bath Vacuum Fusion Method

U.K.A.E.A. Production Group, 1962, Report PG 381 (S)

Small samples of metals and compounds were reacted in vacuo in a degassed bath of molten Pt held in a small graphite crucible and the H₂, O₂ and N₂ evolved were estimated in a low pressure gas analysis apparatus. The operating temperature of 1900°C was attained by radio-frequency heating. Samples required relatively low vapour pressures at this temperature. 3.5 g of Pt were used in each trial. Limits of detection were about 1 p.p.m. H₂, 5 p.p.m. O₂ and 2 p.p.m. N₂ with a precision of $\pm 5\%$. Pt beads and sample capsules were used because of the very low vapour pressure of Pt.

The Determination of Oxygen in Uranium by Micro-Platinum Bath Vacuum Fusion

U.K.A.E.A. Production Group, 1963, Report PG411 (S)

Oxides present in U samples reacted in vacuo with C dissolved in molten Pt to form CO, which was separated from H₂ and N₂ and was measured as CO₂. For each trial 3.5 g of 0.1 in. Pt beads were degassed at the operating temperature of 1900°C and dissolved sufficient C from the graphite crucible to react with the oxides. Pt beads were superior to Fe, Ni or Sn. The accuracy was $\pm 5\%$ relative or ± 10 p.p.m. O₂.

A Sensitive Mass Flowmeter and Controller

E. ROTHWELL, *Inst. Prac.*, 1963, **17**, (2), 153-155

The alignment, calibration and operation of a new flowmeter-controller unit are described. The flowmeter consists of a Ni tube with a $\frac{1}{4}$ in. long

manganin heater element wound on it. Two 44 swg Pt resistance elements are secured on either side of the heating element and form two arms of a Wheatstone bridge circuit, all the arms of which have approximately 100 ohms resistance for maximum sensitivity. Changes in flow through the Ni tube alter the bridge balance and can be recorded or used to restore the flow by means of a feed-back circuit.

Improved Sample Holder for X-ray Diffractometer Furnace

E. M. LEVIN and F. A. MAUER, *J. Amer. Ceram. Soc.*, 1963, **46**, (1), 59-60

Radiation losses from an X-ray diffractometer furnace operating up to 1400°C were reduced by fitting Pt shields 0.005 in thick at the ends of the furnace core. A Pt sheath was fitted round the alumina sample slab. The sample adhered to petroleum jelly smeared on the Pt and did not move when melted. The Pt:10% Rh-Pt thermocouple was bonded to an area of the Pt clear of jelly. Small samples can be easily prepared, no realignment is required, temperatures gradients in the sample are limited and the X-ray pattern of the Pt acts as a check.

CATALYSIS

The Production of Acetylene in a Surface Burner

Z. SEBESTYÉN, *Internat. Chem. Eng.*, 1963, **3**, (1), 91-94

The partial oxidation of CH₄ by surface combustion to form C₂H₂ was studied in a quartz tube reactor containing a crushed chamotte bed. The reaction was started by mixing CH₄ and O₂ and retracting the flame into the bed, or by spontaneous ignition at 300°C of the gases passing over Pt wire catalyst dispersed in the bed. Partial oxidation occurred in that part of the bed below the catalyst. Preheating the feed gas minimised O₂ consumption. The Pt catalyst improved the reactor stability and throughput.

The State of Platinum in Reforming Catalysts

M. F. L. JOHNSON and C. D. KEITH, *J. Phys. Chem.*, 1963, **67**, (1), 200-201

Pt/Al₂O₃ catalyst in the oxidised state contains a Pt-Al₂O₃ complex but after reduction with H₂ the Al₂O₃ contains Pt dispersed in the metallic state. The solubility of the Pt in the catalyst was measured. CO adsorption was used to demonstrate the dispersion of Pt. Pt/Al₂O₃ catalysed H₂-D₂ exchange after high temperature reduction. Pt dispersion increased when the Pt solubility was greater but this effect was reversed above 582°C.

Catalytic Hydrogenation of Alkyl Halides

K. ISOGAI, *J. Chem. Soc. Japan.*, 1962, **83**, (11), 1238 (in Japanese, English abstr.)

Hydrogenolysis of *tert*-butyl chloride, *tert*-amyl

chloride and *tert*-butyl bromide in the presence of Raney nickel catalyst produced *iso*-butane and *iso*-pentane. C₂H₅OH solution was used and Pd/C catalyst was tested. Hydrogenolysis of *n*-isomers of the halides was less simple. An ionic mechanism is proposed to account for the differences.

Catalytic Hydrogenation of α,β -Unsaturated Ketones. III. The Effect of Quantity and Type of Catalysts

R. L. AUGUSTINE, *J. Org. Chem.*, 1963, **28**, (1), 152-155

The hydrogenation of $\Delta^1, 9$ -octalone-2 with 10% Pd/C catalyst produced *cis*- and *trans*- β -decalone in proportions which depended on the quantity of catalyst and on the pH of the medium. The decalone ratio was determined by gas chromatography. In neutral media the quantity of *cis*-isomer depends on the H availability to the catalyst surface except when very small amounts of catalyst are used and the actual surface area of the catalyst becomes important. The mechanism in acid media is similar, but a different explanation is required for basic media. Pt catalysts behaved similarly, but 5% Rh/C appeared to have lower activity.

A Criterion for Isothermal Behaviour of a Catalyst Pellet

J. B. ANDERSON, *Chem. Eng. Science*, 1963, **18**, (2), 1947-1948

Temperature gradients within a catalyst pellet are unimportant provided that $q \bar{r} \cdot \frac{1}{T_0} \cdot \frac{\rho_0^2}{\lambda} < \frac{3}{4} \frac{T_0}{\theta}$, where \bar{r} is the observed average rate of reaction, θ is the Arrhenius activation energy divided by the gas constant, T_0 is the absolute temperature at the surface of the pellet, q is the absolute value of the heat of reaction, λ is the thermal conductivity of the pellet and ρ_0 is the radial co-ordinate of the sphere. The reaction is applied to the dehydrogenation of cyclohexane over Pt/Al₂O₃ catalyst pellets and shows that the temperature gradient is needed when interpreting the rate data of the reaction.

On the Prevention of Explosion in Apparatus for the Separation of Coal Gas by the Method of Supercooling

I. I. GEL'FERIN and A. P. DARYUSIN, *Vsesoyuznoe Khim. Obshch. im D. I. Mend.*, 1962, **7**, (6), 661-666

Nitro-compounds produced in the dry distillation of coal must be removed from coal gas before they accumulate, attack the apparatus and cause an explosion. Coal gas can be separated at low temperatures and high pressures. To remove residual amounts of NO, it is oxidised to NO₂, which is reacted with diolefins at 100°C and the products are hydrogenated over Pd, Ru and Pt catalysts. Acetylene, diolefins and other compounds are removed at the same time.

Hydrogenation of Aromatic Nitro Compounds by Ruthenium Catalyst

K. TAYA, *Sci. Papers Inst. Phys. Chem. Res. (Japan)*, 1962, **56**, (4), 285-289

The rate of hydrogenation of aromatic nitro compounds in liquid phase at ordinary pressures was raised when the quantity of Ru catalyst was increased and when the H₂O content of the solution was increased. The apparent activation energy of the hydrogenation of *p*-nitrophenol was 8 kcal/mol. Basic solutions accelerated the reaction when Ru was present in only small amounts. Various aromatic nitro compounds reacted at different rates.

A Synthesis of *L*-Proline from *L*-Glutamine

T. ITOH, *Bull. Chem. Soc. Japan*, 1963, **36**, (1), 25-29

Carbobenzoxy-*L*-glutamine esters were dehydrated to γ -cyano- α -*L*-carbobenzoxy-aminobutyric acid esters and were then catalytically hydrogenated under pressure. Hydrogenation with silk-Pd catalyst in aqueous solvent systems yielded mainly *L*-proline. Glutamic acid was the product using silk-Pd in acetic acid. Ornithine was the principal product when silk-Pt, silk-Rh or Raney Ni catalyst was used. Both proline and ornithine were produced with H₂O and CH₃OH solvent in the presence of silk-Pd.

Reactivities of Some C₆-C₈ Paraffins over Pt/Al₂O₃

J. H. SINFELT and J. C. ROHRER, *J. Chem. Eng. Data*, 1963, **8**, (1), 109-111

The rate of dehydrocyclisation increased several times but the rate of hydrocracking was not much increased when *n*-hexane, *n*-heptane, 3-methylhexane, *n*-octane and 2, 2, 4-trimethylpentane were reacted over 0.3 wt.% Pt/Al₂O₃ catalyst.

Effect of Grain Size on the Macroscopic Distribution of Platinum in Adsorption Catalysts

A. N. MAL'TSEV, N. I. KOBOZEV, A. E. AGRONOMOV and L. V. VORONOVA, *Zhur. Fiz. Khim.*, 1963, **37**, (3), 628-633

The distribution of Pt on gels of SiO₂ or Al₂O₃ remained unaffected by grinding down pellets of 2 to 4 mm to a powder with 10² to 10³ more dispersion. Given sufficient time, the amount of Pt ammoniate adsorbed on these carriers was of the initial solution strength. Adsorbed Pt did not affect the specific surface area of catalysts prepared by reduction of the ammoniate or of the powders and the catalyst activities of pellets and powders were very similar.

The Catalytic Hydrogenolysis of Small Carbon Rings

J. NEWHAM, *Chem. Rev.*, 1962, **63**, (2), 123-137

The review comprehensively covers the mechanism of hydrogenolysis of monocyclic 3-, 4-, and 5-membered C rings, with a few studies on

polycyclic rings. Hydrogenolyses studied include those of cyclopropane on metals and metal oxides, of alkyl- and arylcyclopropane, of alkenylcyclopropane and of other 3-, 4- and 5-membered C rings. Pt and Pd catalysts are particularly prominent, as well as Ni, Cu and Cr catalysts. (170 references).

Catalytic Dehydrogenation of Cyclohexane and Hydrogenation of Benzene in Alumina-Palladium Fluidised Bed

KH. M. MINACHEV and V. I. GARANIN, *Izv. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk.*, 1963, (3), 528-531

The activity and stability of a fluidised bed catalyst containing 2% Pd on fluorinated Al_2O_3 remained practically unchanged over long periods during the dehydrogenation of cyclohexane at 468-471°C and during the hydrogenation of benzene at 260°C. Both processes took place under a pressure of ten atmospheres and with various volumes of reactant.

On the Synthesis of Hydrogen Cyanide from Methane and Ammonia

E. PFEIL and P. HOFFMAN, *Ber. Bunsengesellschaft Phys. Chem.*, 1963, 67, (2), 229-235

The synthesis of HCN from NH_3 and CH_4 over a Pt catalyst was shown to be first order reaction up to 1100°C, dependent only on the partial pressure of NH_3 in the synthesis gas. NH radicals formed by the decomposition of NH_3 initiated the reaction by reacting with CH_4 and dehydrogenation to HCN followed. Pt metals were better than Fe-group catalysts, with Rh, Pd and Ir giving the best results.

A Study of the Adsorption Activity of Platinum Catalysts after Long Storage

ZH. V. STREL'NIKOVA and V. P. LEBEDEV, *Vestnik Moscov Univ., Ser II, Khim.*, 1962, (6), 75

Trials were made on Pt/SiO₂ catalyst over a period of two years and the results for the activity of decomposition of H₂O₂ were plotted on a graph. This shows little change over the period. The number of active sites on the Pt appears to be unchanged and the process remains selective.

Catalytic Activity and Sintering of Platinum Black. I. Kinetics of Propane Cracking

D. W. MCKEE, *J. Phys. Chem.*, 1963, 67, (4), 841-846

The activity of unsupported Pt black decreased as sintering proceeded. The catalyst was studied between 100° and 200°C by a static volumetric technique. Sintering of the Pt black reduced the surface area responsible for the catalytic activity. Comparison with Ni showed that with Pt black the ethane : methane product ratio was greater although the specific activity was somewhat less. The activation energy was 24 kcal/mol or less as more active sites became available. Sintering should be avoided when using Pt black as a fuel cell electrode.

The Action of Acids on Platinum Adsorption Catalysts in the Decomposition of Hydrogen Peroxide

ZH. V. STREL'NIKOVA and V. P. LEBEDEV, *Zhur. Fiz. Khim.*, 1963, 37, (4), 920-922

When the effect of acids on the decomposition of H₂O₂ over Pt/SiO₂ was tested, the deactivating action of HNO₃ and H₂SO₄ was found to be very small compared to that of HCl. Fewer than 1% of the surface atoms possessed catalytic activity but when HCl was present with Pt black, more than 32% of the catalyst atoms were active. HCl took into solution the most active surface atoms of the catalysts.

CHEMICAL TECHNOLOGY

More Hydrogen for Petrochemicals via Purification Processes

D. J. ORIOLO and D. R. MCILVAIN, *Oil and Gas J.*, 1963, 61, (5), 102-107

Catalytic reformers are a large source of H₂ in petroleum refineries. Pt-reformer offgas has high H₂ content and is well suited for purification processes. Methods for purifying H₂ which are described are low temperature purification, adsorption of impurities on molecular sieves and absorption of impurities in petroleum oils. (18 references.)

The Manufacture of Perchloric Acid by the Anodic Oxidation of Chlorine

W. MÜLLER and P. JÖNCK, *Chem.-Ing.-Techn.*, 1963, 35, (2), 78-80

Continuous production of HClO₄ used for perchlorates is now possible by the anodic oxidation of Cl₂ dissolved in dilute HClO₄. This process avoids the formation of the impurities generated in the oxidation of HCl and gives a yield of 60%. The anodes are made of Pt foil supported on Ta and the cathodes are a Ag-Sn alloy. The potential between the plates is 4.4 volts and the cell temperature remains as low as 3°C.

ELECTROCHEMISTRY

On Large Differences in the Equilibrium Solubilities of Hydrogen and Deuterium in Platinum-Palladium Alloys

T. B. FLANAGAN, *J. Phys. Chem.*, 1963, 67, (1), 203-204

Differences in the equilibrium solubilities of H₂ and D₂ with 8.80% Pt-Pd and 12.03% Pt-Pd alloys suggested a method of isotope separation. An acidic solution of 50% heavy H₂O, 0.1 N, was electrolysed at 25°C for 17 hours. The anode was Pt and the cathode 12.03% Pt-Pd. The current was 1 mA. The isotope separation factor was found to be 10.6, as predicted. The separation factor was 15.3 with 70% heavy H₂O solution.

An Investigation of the Electrochemical Behaviour of Ruthenium Catalyst Electrodes by the Method of Charging Curves

T. N. STOYANOVSKAYA, G. P. KHOMCHENKO and G. D. VOVCHEENKO, *Vest. Moskov. Univ., Ser. II, Khim.*, 1962, (5), 30-33

Charging curves were obtained for Ru-plated Pt electrodes in KOH, H₂SO₄, HCl, and HBr solutions. The influence of electrolyte composition on the capacity of Ru for adsorbing hydrogen and oxygen was shown. The effect of the degree of polarisation on the behaviour of adsorbed oxygen was determined in the various electrolytes.

Electrochemistry of Dissolved Gases. III. Oxidation of Hydrogen at Platinum Electrodes

D. T. SAWYER and E. T. SEO, *J. Electroanalyt. Chem.*, 1963, 5, (1), 23-24

Voltammetric and chronopotentiometric studies of the oxidation of H₂ at Pt electrodes showed that four mechanisms occurred, which were affected by the electrolyte, pH and electrode pre-conditioning. The most important and most reversible reaction was that of molecular H₂ at pre-activated Pt electrodes. The cyclic reaction at unconditioned electrodes of H₂ with PtO₂ and the electrolytic reformation of PtO₂ were also important. Adsorption of atomic H at pre-cathodised electrodes and absorption of H₂ by Pt after long exposure times were less important reactions. Pt electrodes aged in dissolved H₂ showed oscillating potentials in acid solutions by a combination of the important mechanisms.

A Study of the Reduction and Electroreduction of an Organic Substance on Platinised Platinum

A. D. SEMENOVA, G. P. KHOMSHENKO and G. D. VOVSHENKO, *Vest. Moskov. Univ., Ser. II, Khim.*, 1962, (6), 51-53

Alkylbenzole was catalytically reduced on platinised Pt in 0.1N electrolytes of HCl, H₂SO₄ and KOH in water and of HCl and H₂SO₄ in 50% C₂H₅OH solution. The rate of reaction was slower in the C₂H₅OH molecules substituted for H₂ molecules in the layer of H₂ adsorbed on the Pt surface.

Electrochemical Oxidation of Hydrogen on Partially Immersed Platinum Electrodes. I. Experiments and Interpretation

F. G. WILL, *J. Electrochem. Soc.*, 1963, 110, (2/1), 145-151

Experiments with cylindrical Pt electrodes showed that the current-voltage curves of immersed and partially immersed electrodes differ. Electrochemical oxidation of H₂ in the film formed on the electrode surface above the meniscus. Variations of the Pt surface, the strength of the H₂SO₄ electrolyte, temperature, and the depth of electrode immersion led to the construction of an

idealised model of the electrode-electrolyte interface. The electrolyte was saturated with H₂, which diffused into the film above the meniscus. The rate of electrochemical oxidation depended on this diffusion step.

II. Theoretical Treatment

Ibid., 152-160

Current-potential relationships were derived to explain the results obtained above. The reaction is shown to take place close to the upper edge of the meniscus.

The Concentration of Molecular Hydrogen on the Platinum Cathode

S. SHIBATA, *Bull. Chem. Soc. Japan*, 1963, 36, (1), 53-57

An electrolytic cell containing a bright Pt wire cathode, a flat plate Pt reference electrode, and an auxiliary Pt foil electrode was used to determine the molecular H₂ concentration at the cathode from the potential-time curve, when the current was reversed from cathodic to anodic, and from the concentration overpotential derived from the overpotential decay curve. Results of both methods showed satisfactory agreement. The H₂ concentration approaches a limiting value of 11.6×10^{-2} mol/l for cathodic currents exceeding about 300 mA/cm².

Influence of Alternating Current on Anodic Protection

R. JUCHNIEWICZ, *Corrosion Sci.*, 1962, 2, (Oct.-Dec.), 297

Successful anodic protection requires the a.c. component of the rectified current used to be a minimum. When stainless steel was studied in 93% H₂SO₄ at 20°C, 1½ a.c. superimposed on 0.0088 mA/cm² d.c. caused the potential to fall to 340 mV from 720 mV in the passive safe range of operation. The platinised Ti wire cathode showed no evidence of corrosion.

The Electrochemical Behaviour of Hydrogen Diffusion Electrodes in a Molten Salt Medium

J. POLART, *Compt. rend.*, 1963, 256, (10), 2159-2161

The current density at Pd tube electrodes immersed in molten LiCl-KCl eutectic when H₂ circulated in the tubes at atmospheric pressure reached a limiting value dependent on the rate of diffusion of H₂ in Pd and independent of the rate of circulation. At 600°C with a thickness of 0.5 mm, the limiting current density was 265 mA/cm².

Determination of the Hydrogen Content of Palladium and Palladium Alloys from Measurements of Electrode Potential and Electrical Resistance. A Review

J. C. BARTON and F. A. LEWIS, *Talanta*, 1963, 10, (3), 237-246

Methods by which H content, electrical resistance

and electrode potential of hydrided Pd and Pd alloys have been determined are discussed with particular reference to hysteresis effects and to difficulties in measuring the electrical resistance in solutions caused by parallel conduction of the measuring current through the electrolyte. Electrode preparation, the effect of temperature and the use of the results are also discussed. (29 references.)

Hydrogen Adsorption on the Platinum Cathode

G. P. DESIDER'EV, S. I. BEREZINA and G. A. GORBACHUK, *Zhur. Fiz. Khim.*, 1963, **37**, (4), 856-861

The amount of active H adsorbed on a smooth working Pt electrode in solutions of H_2SO_4 and NaOH was measured by two methods. The results agreed with previous studies. Current densities covered the range 0.5 to 2.4 mA/cm². The electrode was cathodically polarised for times varying between 1 min and 18 hours. The potentials determined when polarisation ceased were close to the equilibrium values but the amount of H adsorbed varied within wide limits. These amounts are tabulated.

GLASS TECHNOLOGY

Polarisation of Refractories Placed at Constant Temperature in Contact with Molten Glass or Fused Salts

Y. GODRON, *Silicates ind.*, 1963, **28**, (1), 19-27,

Studies of refractory-glass or fused-salt-Pt galvanic cells at constant temperature and of the electrolysis of molten glass and fused salts at Pt electrodes showed that, except for $ZrO_2.MgO_2$, refractories act as the positive poles of cells, whatever the atmosphere or pressure. Factors affecting cell e.m.f. were studied and experimental details are given. Corrosion of the refractory occurs if the cell bath contains glass.

ELECTRICAL ENGINEERING

The Solion

Ind. Electronics, 1963, **1**, (6), 330-331

The construction and operation of solion diodes and tetrodes are described. They depend on the reversible ionic reactions of iodine at Pt electrodes. Current-potential characteristic curves for the devices have iodine concentration instead of grid volts as parameters. The solion can serve as an integrator over long periods.

ELECTRODEPOSITION

Precious Metal Coatings in Electrical Engineering

A. KEIL, *MetallOberflaeche*, 1963, **17**, (2), 33-37

The effects are reviewed of the properties and

prices of Ag, Au, Pd and Rh on their use as electrode deposits. Their general chemical resistance, resistance to S, adsorption of organic vapours, hardness, wearing characteristics, freedom from cracks and porosity, and their solderability are tabulated. Ag is most used because of its cheapness and despite its defects but improved electrolytes are encouraging the use of Au. Rh has the greatest chemical resistance, hardness and wearing properties and Pd is almost as good. The thinness of Rh and Pd coatings (< 1μ) leads to greater porosity and they tend to be more brittle.

Russian Practice in Precious Metal Plating

A. M. YAMPOLSKY, *Electroplating*, 1963, **16**, (3), 76-79

Extracts from 'Precious Metal Deposition' indicate current Russian practice in plating Ag, Au, Pt, Pd, Ir, In, and Re. The second edition of the book was published at the end of 1961.

TEMPERATURE MEASUREMENT

On the Relationship between Resistivity and Thermo-E.M.F.

D. SMART and E. SMART, *Phil. Mag.*, 1963, **8**, (88), 643-650

An equation derived by integration of Mott's equation relates the resistivity and thermo-e.m.f. of many thermocouples in a simple way. This was suggested by qualitative data on a number of thermocouples, several of which contained Pt.

$$AV_B = \left[\frac{2c\zeta}{e} \log \frac{\rho_2 F(T_1)}{\rho_1 F(T_2)} \right]_B^A,$$

where A and B are the metals of the couple with junctions at temperatures T_1 and T_2 . AV_B is the e.m.f., c is a constant, ζ is the Fermi energy at 0°K and e is the electronic charge. ρ is the resistivity and $F(T)$ is the effect of ionic vibrations in the lattice. Data on Pt and Cu agree with this equation if measurements are made extremely accurately.

Cryogenic Temperature Measurement with Platinum Resistance Thermometers - Is Fixed-point Calibration Adequate?

R. J. CORRUCINI, *U.S. Nat. Bur. Stds. Tech. Note*, 1962, (147), PB 161648

Similar strain-free Pt resistance thermometers of high purity show similar departures from Matthiessen's Rule, $\rho = \rho_i + \rho_o$, where ρ is the resistivity of a sample, ρ_i is the ideal resistivity and ρ_o is a residual resistivity which tends to zero as the crystalline purity of the Pt increases. Interpolation methods were used to calibrate 35 similar instruments and indicated that calibration is satisfactory in the range 14°K to 90°K if the fixed points lie in this range, with the best results from fixed points at 20°K, 30°K and 50°K or 90°K. More rugged thermometers of lower purity may be calibrated in the same way if their characteristics are sufficiently uniform.

An A.C. Double Bridge with Inductively Coupled Ratio Arms for Precision Platinum-Resistance Thermometry

J. J. HILL and A. P. MILLER, *Proc. Instn. Elect. Engrs.*, 1963, **110**, (2), 453-458

Errors in the measurement of resistance of a Pt-resistance thermometer can be reduced to a few parts in 10^7 by the use of an a.c. double

bridge circuit with inductively-coupled ratio arms which give accuracy, stability, low temperature coefficient, high input impedance and low output impedance. Details of a 400 c/s, 8 decade dial bridge are given. Errors due to the leads are reduced to 0.0001°C between -100°C and $+100^\circ\text{C}$ and are unlikely to exceed 0.0003°C over the range -183°C to $+630^\circ\text{C}$.

NEW PATENTS

Isomerisation of Paraffin Hydrocarbons

THE BRITISH PETROLEUM CO. LTD. *British Patent* 918,803

C_4 and higher paraffin hydrocarbons boiling in gasoline range are isomerised by contact, in the presence of hydrogen, with a catalyst composed of an aluminium halide and 0.01 to 5% by wt. of platinum or palladium, supported on alumina, made from an aluminium alcoholate by hydrolysis to hydrated alumina followed by calcination.

Catalyst for Selective Hydrogenation

CHEMETRON CORP. *British Patent* 920,012

A catalyst for use in the selective hydrogenation of highly unsaturated hydrocarbons contained in concentrated olefin streams is composed of palladium metal on an alumina carrier, the catalyst having a pore volume of surface pores with a threshold diameter of not over 800 \AA in the range of between 0.0 and 0.4 cc/g, the palladium being mainly concentrated on the external surface of the alumina.

Penicillins

BEECHAM RESEARCH LABORATORIES LTD. *British Patent* 920,300

A palladium or platinum on barium carbonate or carbon catalyst is used in a hydrogenating step in the preparation of new penicillins.

Thermal Radiation Sources

THE GENERAL ELECTRIC CO. LTD. *British Patent* 921,233

A thermal radiation source includes an open-fronted vessel containing a radiator and provided with a gas inlet and a screen of fine refractory wires closely spaced and extending across the open front so as to permit radiation to emerge from the vessel but to obstruct the ingress of ambient gas. The wires are made of a platinum group metal, e.g. 70% platinum and 30% iridium.

Getters

UNION CARBIDE CORP. *British Patent* 921,273

A heat-insulating system comprises a liquefied gas container having an evacuated space between an inner and outer wall and a hydrogen-selective getter in the form of palladium oxide exposed to

the space and placed adjacent the outer wall. The palladium oxide is used together with a non-hydrogen-selective getter placed near the inner wall.

Manufacture of Palladium Catalysts

LAPORTE CHEMICALS LTD. *British Patent* 922,022

A porous carrier is first treated with a palladium-containing liquor in amount such that all is taken up and in concentration to give required palladium content. Before or after such treatment, the carrier is treated with an aqueous solution of a base derived from an alkali- or an alkaline earth-metal to fix the palladium and is partially or completely dried between these treatments.

Hydrogen Permeation Cell

THE ATLANTIC REFINING CO. *British Patent* 922,103

The palladium or palladium alloy (10-50% Ag-Pd) capillary tubes of a hydrogen permeation cell are arranged in a cluster and secured at one end but unsupported against either the remainder of the outer wall or inner wall except as against one another in the cluster.

Coating of Metal

ENGELHARD INDUSTRIES INC. *British Patent* 922,105

A molten platinum group metal is sprayed on to a clean surface of molybdenum, tantalum, tungsten or titanium as a thin coat which is then plastically deformed at 600° - 1400°C and long enough to promote solid diffusion of the coating and repeating these steps until the required thickness of platinum is attained.

Isomerisation Process

ESSO RESEARCH & ENGINEERING CO. *British Patent* 922,213

The catalyst used in isomerising C_5 or C_6 paraffins is a supported platinum or palladium catalyst containing aluminium chloride. Reaction carried out at 200° - 400°F and pressure of 700-1500 p.s.i.g.

Catalysts

ENGELHARD INDUSTRIES INC. *British Patent* 922,381

A catalyst consists of a support of a glass fabric coated with alumina or other refractory and carrying platinum or palladium or an oxide thereof as