

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Oxide Formation on Noble Metals in Cathodic Sputtering

T. SUZUKI, *Z. Naturforschung*, 1957, **12a**, (6), 497-499

Ag, Au and Pt were cathodically sputtered under a pressure of 5 mm air and their surfaces were examined by electron diffraction. Au does not oxidise but Ag forms Ag₂O. Pt differs from the other metals in that its surface remains bright up to 5 mm. However, at this pressure the presence of a Pt oxide was detected by additional lines in the Pt diffraction pattern. The lines were very weak but were probably due to tetragonal PtO.

X-Ray Investigation of Compounds in the Bismuth-Rhodium and Bismuth-Palladium Systems in Connection with Superconductivity Studies

N. N. ZHURAVLEV and G. S. ZHDANOV, *Bull. Acad. Sci. U.S.S.R. (Physical Series)*, 1956, **20**, (6), 645-649 (English Transl. of *Izvest. Akad. Nauk. S.S.S.R.*)

The phase diagrams of both systems were determined. The compounds BiRh, Bi₂Rh, Bi₄Rh, BiPd₃, BiPd and Bi₂Pd were isolated. Their densities, microhardness, crystal habits and superconducting transition temperatures were measured. Superconductivity is exhibited by BiRh, Bi₄Rh, BiPd and Bi₂Pd. Bi₄Rh and Bi₂Pd are polymorphic and it was possible to show that a relationship exists between the polymorphic transformations and changes in the superconducting transition temperatures in these compounds.

X-Ray Diffraction Study of the Sigma Phase in the Systems Rhenium-, Ruthenium- and Osmium-Chromium

R. M. WATERSTRAT and J. S. KASPER, *J. Metals*, 1957, **9**, (7), 872-873

An exploratory investigation of the Os-Cr system showed the presence of a σ -OsCr₂ phase and a phase of approximate composition OsCr₃ with an A-15 (β - ω -) structure. This is in agreement with recent work by Raub (*Platinum Metals Rev.*, 1957, **1**, (3), 100). X-ray studies of the σ -phases OsCr₂, RuCr₂ and Re₂Cr indicate little deviation of the observed intensities from those expected for a random distribution of the component atoms. A parallel to the ordering effects found in σ -phases containing only elements from the first long row of the periodic table does not exist in these systems.

The Electronic Structure of Palladium-Uranium Alloys

J. A. CATTERALL, *Phil. Mag.*, 1957, **2**, (Apr.), 491-498

The effect of U on the lattice parameter, paramagnetic susceptibility, electrical resistivity and thermoelectric power in the solid solution range of the alloys was determined.

Electrical Resistivity of Nickel-Palladium Alloys

A. W. OVERHAUSER and A. I. SCHINDLER, *J. Appl. Physics*, 1957, **28**, (5), 544-546

The occurrence of a maximum in the residual resistivity of Ni-Pd alloys at 70 at.% Pd is explained by the spin dependence of the electron scattering process and the fact that alloys with > 3% Ni are ferromagnetic. A quantitative fit of the data is possible if it is assumed that the density of states at the Fermi energy in the *d* band is approximately \propto to the number of holes rather than to the cube root of this number.

High Temperature Electrical Resistivity Measurements of the Nickel-Palladium Alloy System

A. I. SCHINDLER, R. J. SMITH and E. I. SALKOVITZ, *Bull. Amer. Phys. Soc.*, 1957, Ser. II, **2**, (3), 118, (abstract)

Resistivity measurements were carried out from room temperature to 460°C. With increased temperature the maximum resistivity moves from 70 at.% Pd to lower Pd contents. At 460° it occurs at the 50:50 composition as expected. Values of the temperature coefficient were found to be independent of composition over most of the alloy system at 450°C, although a slight decrease occurred at the Pd rich end.

X-Ray Investigation of the Reported High-Temperature Allotropy of Ruthenium

E. O. HALL and J. CRANGLE, *Acta Cryst.*, 1957, **10**, (3), 240-241

High purity Ru was examined up to 1300°C by measuring its lattice parameters. No evidence of allotropy was obtained. It was concluded that the transition points previously reported at 1035 and 1190°C have no structural significance. The transition point reported at 1500°C was not investigated.

Superconducting Properties of Rhenium, Ruthenium and Osmium

J. K. HULM and B. B. GOODMAN, *Phys. Rev.*, 1957, **106**, (4), 659-671

Magnetic measurements were carried out on Re, Ru and Os in the region of 1°K. The influence of various methods of specimen preparation and treatment was studied, particularly for Re. The transition temperatures were found to be: Re 1.699°K, Ru 0.47°K and Os 0.71°K. The results support the conclusion of previous workers that non-ideal superconducting behaviour frequently found in the transition metals is not a fundamental property of this group of elements but a consequence of the metallurgical history of the specimens.

Alloys of Platinum and Gold with Alkaline and Alkaline-Earth Metals

I. L. SOKOL'SKAYA, *Zhur. Tekhn. Fiz.*, 1957, **27**, (Jan.), 127-129

The conductivity and other electrical properties of the systems were determined. Na-Au is semi-conducting and also probably Na-Pt and Ba-Pt.

Precipitation in Gold-Platinum Alloys

T. J. TIEDEMA, J. BOUMAN and W. G. BURGERS, *Acta Met.*, 1957, **5**, (6), 310-321

Tests were carried out on alloys containing 10, 40 and 80 wt. % Pt, all initially in a homogeneous state. The two-phase boundary was determined and agreed well with previous results. Specimens of the 40 and 80% alloys were annealed for up to 100 hours at 510°C and Debye-Scherrer photographs were taken. In the state known as "pre-precipitation" diffuse side-bands developed on either side of the original reflections, the intensity being greater on one side than the other. After annealing for 24 hours or more the reflections are those of the Au and Pt rich phases existing at 510°C. Micro-photographs were also taken and showed that precipitation occurs first at grain boundaries. The microvickers hardness varies with annealing time, reaching a maximum in the early stages of precipitation. The appearance of side-bands is due to a periodic variation of the lattice parameter. A modification of the model by Hargreaves accounts for all observed features by adjustment of the undefined parameters.

Results of Low Temperature Research. XVIII The Atomic and Electronic Heat of Platinum between 10 and 273°K

K. CLUSIUS, C. G. LOSA and P. FRANZOSINI, *Z. Naturforschung*, 1957, **12a**, (1), 34-38

The atomic heat reaches the theoretical value of 6 at about 235°K and at 273°K it is 6.119 cal./°. The characteristic Debye temperature, θ , falls steeply with increasing temperature. The electronic heat $C_e = \gamma T$ where $\gamma = 15.81 \times 10^{-4}$ below

16°K. However this value of γ gave incorrect values for θ_D , the Debye temperature of the lattice, at 90°K and the correct value at high temperatures was found to be 10×10^{-4} . This temperature dependence of γ is also found in Pd.

A₅B-Phases of the Type Cu₅Ca and Laves Phases in the Systems of Strontium with Palladium, Platinum, Rhodium and Iridium

T. HEUMANN and M. KNIEPMEYER, *Z. anorg. allgem. Chem.*, 1957, **290**, (3/4), 191-204

The alloys were studied in the Pt metal rich region up to the composition A₂Sr where A=Pt metal. All the systems form Laves phases with compositions A₂Sr and structures analogous to Cu₂Mg. Pd forms a congruently melting compound Pd₅Sr of the hexagonal Cu₅Ca type, Pt₅Sr was also detected but was incongruently melting. Hexagonal Rh₅Sr and Ir₅Sr were not formed although unstable f.c.c. phases occurred between Rh and Ir and the phases Rh₂Sr and Ir₂Sr. The atomic radius ratios of the Pt metals to Sr should be about 1.6 which makes the formation of Laves phases surprising. However, a contraction in atomic volume is found for both series of compounds which is larger for the A₂B type phases and results in a radius ratio of 1.2. The forces causing this contraction, which also occurs in other Group VIII metal alloys, are not known for certain.

Structural Investigations of Metallic Phases II

K. SCHUBERT *et al*, *Naturwiss.*, 1957, **44**, (7), 229-230

The system Pd-Se was among those studied. The following phases were found: Pd₉Se₈, PdSe, and PdSe₂.

ELECTROCHEMISTRY

Effects of Hydrogen Content on the Resistance and the Potential in the Palladium-Hydrogen-Acid System

J. P. HOARE and S. SCHULDINER, *J. Phys. Chem.*, 1957, **61**, (4), 399-402

The hydrogen content of the Pd was determined by relative resistance measurements or ceric sulphate reduction and the open circuit potential in hydrogen saturated H₂SO₄ solution by a Pt/H₂ reference electrode. The Pd wire spontaneously absorbed hydrogen up to a H/Pd ratio of 0.025 forming the α -phase with a potential of 0.0495 ± 0.0005 v. The Pd was then electrolytically filled with hydrogen and the potential fell to zero at a H/Pd ratio of 0.63 corresponding to the formation of the β -phase. Above H/Pd = 0.36 the wire spontaneously evolved hydrogen on open circuit. Between H/Pd = 0.025 and 0.36 the α - and β -phases coexist but the α -phase determines the potential. When hydrogen is

being evolved relative resistance measurements give correct values of H/Pd only when an oxidising agent is present.

The Cathodic Reduction of Oxygen and Hydrogen Peroxide

G. BIANCHI, *Corrosion et Anti-Corrosion*, 1957, 5, (5), 146-152

The cathodic reduction of oxygen plays a fundamental role in corrosion mechanism. It was studied using electrodes of Pt, Au, Ag, Fe₃O₄ and graphite which are not corroded in oxygen-containing solutions. The cathodic reduction of oxygen takes place in two steps: reduction to H₂O₂ followed by reduction of H₂O₂ to H₂O. Cathodic polarisation curves for these reactions and the anodic oxidation of H₂O₂ were given for each electrode. The reduction of O₂ and H₂O₂ takes place at the same potential provided the concentration of H₂O₂ is sufficiently high. The Pt electrode gives the lowest overvoltage for these three reactions.

An Electrochemical Study of Hydrogen Producing Reactions Catalysed by Gold and Gold-Palladium Cathodes

S. SCHULDINER and J. P. HOARE, *J. Phys. Chem.*, 1957, 61, (6), 705-708

The hydrogen overvoltage of Au, β -phase Pd-H and Au-Pd alloys up to an atomic ratio Au/Pd of 2.70 was determined. The rate controlling step for β -Pd-H and Au-Pd alloys up to Au/Pd = 0.6 was found to be electrochemical desorption. Above this ratio and for pure Au it was the combination of hydrogen atoms. The effect of successive additions of Au on the decrease in catalytic activity of Pd was large up to Au/Pd = 0.6 but for higher ratios there was a much smaller effect. This is due to the complete filling of the positive holes in the Pd *d*-band by Au at this ratio.

LABORATORY APPARATUS AND TECHNIQUE

A Fixed Point of Viscosity in the Working Range of Glasses. Rapid Determination of Viscosity-Temperature Curves

A. DIETZEL and R. BRÜCKNER, *Glastech. Ber.*, 1957, 30, (3), 73-79

A new fixed-point of viscosity is suggested. It is called the "penetration-point" and occurs at 10⁴ poise. It is defined as: the temperature at which a 20% Rh-Pt rod 0.5 mm. in diameter and 200 mm. in length with hemispherical ends and 0.746 g. weight sinks 2 cm. into the glass under its own weight in 2 min. A method of determination is described. Examples of the rapid determination of viscosity-temperature curves for glasses of very different composition are given, using this point and the transformation and softening points.

Design of an Apparatus for the Measurement of the Combustibility Hazard of Gases in Aircraft and other Applications

E. J. DURBIN, *Aero. Eng. Rev.*, 1957, 16, (4), 58-63

The amount of combustible gas was measured by a change in the temperature of a Pt wire due to catalytic reaction. This change is made a linear function of the percentage of combustible gas by first heating the Pt wire to 400°C or over and by keeping the temperature and pressure of the gas flow constant. The temperature change is measured by the change in resistance of the wire. The heat generated by any petroleum hydrocarbon burnt at its lower explosion limit is the same. The hot-wire indicator can therefore be calibrated for a known hydrocarbon and will give a correct reading for any other hydrocarbon or mixture of hydrocarbons and also for CO and H₂ mixtures. The indicator can be conveniently calibrated in fractions of the lower explosion limit of the gas at a certain pressure or altitude, normally sea-level. The apparatus is rendered automatic by incorporating an electrical device for stopping or starting it at a predetermined gas concentration.

What are the Limitations of Vapour Testing?

W. A. BUSSARD, *Petroleum Processing*, 1957, 12, (5), 228-232

The importance of using Pt filament combustible gas indicators only under the correct conditions is emphasised. Where the gas may contain TEL vapour the filament temperature must be > 1500°F to avoid desensitisation. Most desensitisers are rendered inactive at this filament temperature. The exception is silicone vapour which appears to cause desensitisation at all temperatures, probably by depositing silica. Absorption of vapours by the instrument must also be avoided. Most instrument failures are due to failure of the Pt test filament or to weak batteries.

Metallographic Preparation of Noble Metal Samples by Electrolytic Lapping

G. REINACHER, *Z. Metallkunde*, 1957, 48, (4), 162-170

Electrolytic lapping, which is a combination of mechanical and anodic polishing, is described. The apparatus consists of a silver plated iron disc cathode covered by a polishing cloth and immersed in a suitable electrolyte which may contain a suspension of polishing medium. The specimen, which forms the anode, is held lightly against the slowly rotating cathode. For Pd and Pd alloys a thiosulphate electrolyte is used while for Pt and its alloys an acid halide electrolyte and alternating current give the best results. The success of this process in the preparation of heterogeneous alloy samples is particularly important since these cannot be polished by a simple anodic treatment.

CATALYSIS

Sintering Platinised Platinum by Electrochemical Methods

III Thermal Treatment in a Nitrogen Atmosphere

M. I. NICKOLAEVA and A. I. SHLYGIN, *Zhur. Fiz. Khim.*, 1956, 30, 1729-1731 (*Chem. Abs.*, 1957, 51, 7199h)

Sintering of Pt was studied at 20, 100, 200, 300, 400 and 500°C. The effect of this treatment on its catalytic activity in the decomposition of H₂O₂ was determined. The adsorption capacity decreases with increasing temperature due to a decrease in the true surface. A sharp increase is observed above 300°C due to the onset of activated adsorption.

The Magnetochemistry of Active Centres

IV The Dependence of the Magnetic Susceptibility of Platinum Adsorption Catalysts on the Temperature of Heat Treatment

A. A. LOPATKIN, Zh. V. STREL'NIKOVA and V. P. LEBEDEV, *Zhur. Fiz. Khim.*, 1957, 31, (1), 195-199
Studies were carried out on three Pt-SiO₂ catalysts. It was found that below 550°C the magnetic susceptibility and catalyst activity in H₂O₂ decomposition showed corresponding increases.

Mixed Adsorption Catalysts

III The Activity of Mixed Metallic Catalysts on Alkaline Earth Carbonates in the Decomposition of Hydrogen Peroxide

I. A. ZUBOVICH, *Zhur. Fiz. Khim.*, 1957, 31, (1), 61-71

The catalysts studied consisted of layers of Pt-Ag, Pt-Au, Pd-Cu, Pd-Ag, Pd-Au and Pd-Pt deposited on alkaline earth metal carbonates, and Pt-Cu on SrSO₄. The catalytic activity in redox processes is associated with the electronic structure of the ions, the presence of unpaired electrons and the nature of the carrier.

Mixed Adsorption Catalysts

IV The Activity of Mixed Catalysts on Alkaline Earth Metal Carbonates in the Reduction of m-Nitrophenol

I. A. ZUBOVICH, *Zhur. Fiz. Khim.*, 1957, 31, (3), 589-598

Describes the catalytic activity of Pt-Cu, Pt-Ag, Pt-Au, Pd-Cu, Pd-Ag, Pd-Au and Pt-Pd on alkaline earth carbonates and Pt-Cu and Pd-Cu on BaSO₄.

Economics of Producing High Octane Pool Gasoline

S. W. CURRY, *Petroleum Eng.*, 1957, 29, (5), C6-9
It is predicted that by 1965 a 101-leaded Research octane number pool and a 107 premium gasoline

will be required. The most economic way of achieving this level is discussed, basing the estimates on Universal Oil Products' processes. For boosting to 94 leaded Research rating reforming is best followed by isomerisation up to 101 octane number. Preliminary reforming should be done by Rexforming rather than Platforming.

Processes for Synthesising Aromatic Hydrocarbons from Petroleum

C. THONON, *Rev. Inst. Franc. Petrole*, 1957, 12, (2), 218-239

Reviews the basic reactions involved in obtaining aromatics from aliphatic crude petroleum hydrocarbons by either thermal or catalytic processes. The relative merits of metallic (Pt, Pd, Ni) and oxidic (Cr, Mo, Co) catalysts are discussed. A review of the reforming processes using both types of catalysts which are in commercial operation is given.

The Treatment of Gaseous Effluents

A. AIKENS, *Metal Finishing J.*, 1957, 3, (July), 281-283

The Oxycat unit, which consists of ceramic rods coated with an activated film of Al₂O₃ and Pt alloy is used to oxidise objectionable gases such as CO or NH₃ to harmless ones. Preheating of the gas stream to at least 500°F is necessary. The installation of the unit and the method of heat recovery from the oxidation reaction is described. The catalyst is contaminated by the presence of metallic oxides or hydrocarbons in the gas but it can be easily reactivated.

Catalytic Liquid-Phase Hydrogenation

R. H. PRICE and D. B. SCHIEWETZ, *Indust. and Eng. Chem.*, 1957, 49, (5), 807-812

The hydrogenation of cyclohexene in cyclohexane solution was studied in a semi-flow system over a 5% Pt-Al₂O₃ catalyst. Hydrogen was bubbled through the solution and the catalyst was kept in suspension by stirring. The effect of all the variables was determined. The reaction rate was independent of cyclohexene concentration and of catalyst concentration, above a certain critical amount. Under most conditions investigated the rate of reaction was controlled by mass transfer of hydrogen from the bulk solution to the catalyst-liquid interface. However, no fundamental relationships useful for engineering can yet be formulated.

Aliphatic Organo-functional Siloxanes V Synthesis of Monomers by Platinum Catalysed Addition of Methylchlorosilane to Unsaturated Esters and Nitriles

L. H. SOMMER, F. P. MACKAY, O. W. STEWARD and P. G. CAMPBELL, *J. Amer. Chem. Soc.*, 1957, 79, (11), 2764-2769

A Pt/C catalyst was used in the addition of

methylchlorosilane to acrylates, methacrylates, unconjugated olefinic esters and nitriles. Methacrylate esters give stable adducts providing a simple route to synthetic polymers of organofunctional siloxanes.

On Ester Formation by Hydrogenation of Carbonic Acids in Alcoholic Solution

K. KINDLER and H.-G. HELLING, *Chem. Ber.*, 1957, **90**, (5), 750-752

Benzoic acid was hydrogenated to hexahydrobenzoic acid over Pt black or Adam's catalyst and cinnamic acid hydrogenated to hydrocinnamic acid over PdO or Pd/C. In neither case was any ester formed. Previous accounts of ester formation were probably due to traces of chlorine in the catalysts.

Hydrocarbon Ring Systems. On the Catalytic Dehydrocyclisation of cis-Cyclotetradecene

V. PRELOG and S. POLYAK, *Helv. Chim. Acta*, 1957, **40**, (3), 816-830 (In German)
Cis-cyclotetradecene in the gaseous phase over Pd-C at 400-500°C gives phenanthrene as the main product and also small amounts of anthracene. The same products are formed under similar reaction conditions on active charcoal in the absence of Pd. Radioactive tracer methods failed to indicate the mechanism involved.

The Adsorption of Anions on Metal Surfaces with the help of Radioactive Indicators

K. SCHWABE, K. WAGNER and C. WEISSMANTEL, *Z. physikal. Chem. (Leipzig)*, 1957, **206**, (5/6) 309-320

The adsorption of cyanide and iodide ions labelled with ^{14}C and ^{131}I was measured on Pt, Ni and Ag foil. The cyanide-ions formed a single, strongly adherent layer while the iodide layer was practically two ions thick and less adherent. Cyanide ions could displace iodide ions from the adsorbed layer. Greater adsorption of both ions occurred on a platinised rather than a bright Pt surface.

The Mechanism of Chemical Reactions XVI The Operation of Metalloids in Catalytic Hydrogenation with Palladium and Platinum

K. KINDLER, H.-G. HELLING and E. SUSSNER, *Liebig's Ann. Chem.*, 1957, **605**, 200-211

PdO and Pd black catalysts are activated by the addition of strong acids whereas the addition of a base such as morpholine reduces their activity. This is explained by the formation of catalytically active intermediates H_nPdX_n , where X is a metalloid such as O or Cl. A base will form a salt with H_nPdX which is not active in hydrogenation. Similar intermediates have been found with Pt catalysts. Pd and Pt catalysts are

also deactivated by pre-reduction. The inhibition of catalysts by controlled pre-reduction or the addition of small amounts of a base has important practical applications since it increases their specificity. Pd catalysts treated with tetrahydroquinoline will reduce acetophenone to α -phenylethylalcohol and pre-reduced catalysts will reduce 4-chlorocinnamic acid methyl ester to 4-chlorohydrocinnamic acid methyl ester. An economic catalyst with a very high activity was made by reducing PdCl_2 or H_2PdCl_4 on active C in the presence of acetophenone; the active intermediate H_nPdCl_n is deposited on the carrier.

Stepwise Reaction on Separate Catalytic Centres: Isomerisation of Saturated Hydrocarbons

P. B. WEISZ and E. W. SWEGLER, *Science*, 1957, **126**, (July 5), 31-32

Isomerisation was studied on a catalyst consisting of Pt on an acid carrier, e.g. aluminium silicate. The results confirmed the following mechanism: n-hexane \rightarrow n-hexene \rightarrow iso-hexene \rightarrow iso-hexane in which the dehydrogenation and hydrogenation take place on Pt sites and the hexene isomerisation on acidic sites. The olefinic species is desorbed and transferred in the gaseous phase from one catalytic site to another where it is readsorbed. The presence of hexenes was detected by a mass spectrometer. In order to obtain maximum efficiency in transferring intermediates from one site to another, and thus maximum isomerisation, the catalyst particle size must be $<100\mu$.

Piperidines with Motor Depressor and Anti-Inflammatory Properties

S. L. SHAPIRO, H. SOLOWAY and L. FREEDMAN, *J. Amer. Pharm. Assoc.*, 1957, **46**, (6), 333-336

Piperidines with these properties were formed by synthesising compounds having the 2-(1-methyl-2-piperidyl) ethyl and 2-(5-ethyl-1-methyl-2-piperidyl)-ethyl chain attached to the 10 and 9 positions of phenothiazine and carbazole respectively. The preparation of the precursors 5-ethyl-2-piperidine-ethanol and 5-ethyl-1-methyl-2-piperidine-ethanol was carried out by hydrogenation over PtO_2 and Pd/C respectively.

Catalytic Hydrogenation. Part I: The Hydrogenation of Unsaturated Amines over Platinic Oxide

J. M. DEVEREUX, K. R. PAYNE and E. R. A. PEELING, *J. Chem. Soc.*, 1957, (July), 2845-2851.

The kinetics of hydrogenation of NN-dimethylaniline, NN-dimethyl-m- and -p-toluidine, pyridine, pyrrole, quinoline and NN-dimethylphenethylamine and -benzylamine over PtO_2 in ethanol containing varying amounts of HCl were determined. The results show that the weakly basic aromatic amines are non-toxic to PtO_2 while the more strongly basic aromatic and hydrogenated amines are toxic. The faster

hydrogenation of amines in acid solutions is due to the formation of non-toxic ammonium ions in place of the free bases.

New Platforming Unit at Ellesmere Port
ANON., *Brit. Chem. Eng.*, 1957, **2**, (8), 432
Describes the 800 bbl./day Platforming unit recently installed by Lobitos Oilfields Ltd. at their Ellesmere Port refinery.

Catalytic Reforming at Coryton
ANON., *Petroleum*, 1957, **20**, (8), 290-291
A description of the reforming process at the Coryton refinery of Mobil Oil Co. Ltd. It uses a Pt catalyst and hydrogen-rich recycle gas, the feed-stock is desulphurised before reforming. It is designed for 6,000 bbl./day of mixed light and heavy naphtha charge and can produce 100% octane motor spirit with relatively high yields.

The Catalytic Deuteration and Exchange of Acetone on Evaporated Metal Films
C. KEMBALL and C. T. H. STODDART, *Proc. Roy. Soc.*, 1957, **241**, (Aug. 7), 208-222
Reduction of the carbonyl group and deuterium exchange in the methyl groups were observed on films of Rh, Pd, Pt, Ni, Fe, W, Ag and Au. The mechanisms of hydrogenation and exchange were determined.

Formation of Hydrogen Cyanide from Methane, Ammonia and Oxygen
R. MIHAIL, *Chem. Techn.*, 1957, **9**, (6), 344-349
A discussion of the equilibrium conditions and the kinetics of the reaction is given. The catalyst dimensions required for the greatest efficiency were calculated theoretically. A reaction mechanism is postulated in which NO is formed by the oxidation of NH₃ on the catalyst. The heat generated in this reaction causes the CH₄ to decompose into methyl radicals. The NO and ·CH₃ then react in the gaseous phase to form HCN. The reaction can take place without a catalyst but at a much slower rate.

GLASS TECHNOLOGY

Studies of the Wettability of Platinum by Molten Sodium Silicate
M. L. VOLPE, R. M. FULRATH and J. A. PASK, paper presented at the 59th Annual Meeting of the Amer. Ceram. Soc. (Glass Division) May 1957 (Abstract in *Glass Ind.*, 1957, June, 348)
Describes experiments carried out with Na₂O.2SiO₂ and Pt between 850 and 1000°C. The contact angle of Na₂O.2SiO₂ glass on Pt was affected by the atmosphere as follows (low angle to high angle): O₂, N₂, CO₂, A, water vapour, CO and H₂. Attempts to explain the results were based on theories of the penetration of gases into the metal surfaces. The adsorption of gases at

low pressures was determined both in the presence and absence of glass, and contact angle measurements were made simultaneously where possible.

Automatic Control of a Glassworks Feeder
M. VERBURGH, *Silicates Indust.*, 1957, **22**, (2), 95-103
Transl. *Glass*, 1957, **34**, (7), 307-311
Describes the control of temperature and glass level in the feeders of the furnaces at Momignies. Pt:13% Rh-Pt thermocouples are placed in each of the feeder zones. A Pt tube welded to the nickel thermocouple sheath is inserted into the glass melt and temperatures are measured by valve amplification of the thermal emf. The amplification and control systems are described in detail.

ELECTRICAL ENGINEERING

New Technique for Medium-Sized Internal Dialling Telephone Installations
K. ROHDE, *Siemens Z.*, 1957, **31**, (4), 175-176
The development of the new technique was outlined. It comprises high-speed relays with Pd alloy contacts connected in a cross-coupling system. This gives a small, simply constructed unit with fast switching time and high reliability.

The Noble-Metal High-Speed Relay
H. WILHELM and G. BRAUMANN, *Siemens Z.*, 1957, **31**, (4), 177-179.
For use in telephone installations five independent relays are combined in a strip giving both economical production and a sufficiently small unit for the desired flexible build-up of the cross-coupling system. The relay contacts are Pd wires, one set welded directly on to the armature and the others on to the opposite contact springs.

Medium-Sized Internal Dialling Telephone Installations using the Noble-Metal High-Speed Relay Cross-Coupling System
R. KRAUST and W. STROBELT, *Siemens Z.*, 1957, **31**, (4), 180-184
An exchange for an internal dialling telephone installation with 2-10 subscribers' lines and 10-100 extensions was described. Connections are switched through by means of relay cross-coupling.

ELECTRONICS AND TELECOMMUNICATIONS

Technological Aspects of U.H.F. Triode Design
E. G. DORGELO, *Le Vide*, 1957, **12**, (Jan./Feb.), 3-8 (In English)
The dispenser-cathode type is the most promising for U.H.F. triodes. The cathodes are normally

Ba or Th. At the high temperature of operation, 1000–2000°K, vaporisation and transfer of cathode material to the grid occurs. The grid is thus made of material having a low emission (high release function) when coated with Ba or Th. Several grid materials were tested. "K material" consisting of a Pt surface separated from the core by a layer of very fine carbide particles is used with a Th cathode. It has a high release function, high radiation constant and relatively low R.F. resistance. When working at a temperature of about 1600°K the emission remains practically unchanged after 1000 hours operation with an input of 15 W/cm² and even with 40 W/cm² the emission is still lower than the initial value for the conventional Pt clad Mo grid. For a Ba cathode the Pt is replaced by Au. A triode developed to test this material under working conditions was able to deliver 120 W at 890 Mc/s or 400 W at 500 Mc/s.

New Jobs for Ions—"Solion"

ANON., *Chem. Eng. News*, 1957, 35, (July 8), 24
The U.S. Naval Ordnance Laboratories have developed an electrolytic unit, "solion", which may replace vacuum tubes and transistors in a wide range of electronic applications. Its internal make up varies with the application but an acoustical type uses Pt electrodes in a solution of potassium iodide and iodine. Changes in conditions such as sound, temperature, pressure and acceleration alter the current and this is used to operate control devices. Among the advantages of the solion are low power needs, high sensitivity and accuracy, small size and easy maintenance.

TEMPERATURE MEASUREMENT

Inspector for Immersion Thermocouples

ANON., *Steel*, 1957, 140, (May 27), 102
A recording pyrometer and thermocouple circuit monitor, installed by the Copperweld Steel Co., work together to obtain accurate steel melting temperatures. Each time a temperature reading is taken the thermocouple is momentarily connected into the monitoring circuit. The pyrometer reading then indicates any excess

resistance due to faults in the thermocouple circuit and corrects them. The instrument can also be used to detect short circuits. The net effect is to extend the average life of each Pt couple from 25 to 35 immersions.

Temperature Controller for Steel Melting

ANON., *AEG-Mitt.*, 1957 (3/4), 117-118
A Pt:Pt-Rh thermocouple with a portable recording and regulating unit is described. The basic circuit diagram is given. The instrument enables the temperature together with the time and position of the measurement to be recorded. Temperatures of up to 1650°C can be measured with an accuracy of +5°C.

Measurement of Open Hearth Bath Temperature

Y. MITARASHI *et al*, *Tetsu to Hagane*, 1956, 42, (Sept.), 740-742 (In Japanese)
The thermocouples used in the Japanese iron and steel industry are Pt:Rh-Pt with wires 4 m. or 1 m. long. They are enclosed in a silica sheath protected by a mild steel head inserted into a steel tube with a graphite plug. Temperature measurements were carried out in four steel plants over a period of six months. Over 98% of the readings were good and the causes of failure in the remaining cases were analysed. In the good measurements standard deviations in tapping temperature of 10°C or less are frequent with a maximum deviation of 30°C.

The Error of Thermocouple Pyrometers used in the Furnaces of Steel Works

M. JINDAI *et al*, *Tetsu to Hagane*, 1956, 42, (Sept.), 751-752 (In Japanese)
Regular calibrations and a knowledge of the causes of failure have increased the reliability of measurements at the Sumitomo Metal Works. The most frequent causes of failure were due to deterioration of the Pt:Rh-Pt couples through over-heating and fire damage to the protective sheaths. In normal furnaces where a high degree of accuracy is not required, calibration once every six months is sufficient. However, in the latest heat treatment furnaces extremely accurate thermocouples are required and calibration at least every three months is necessary.

NEW PATENTS

Preparation of Pregnane Derivatives

ORGANON LABORATORIES LTD. *British Patent* 774,082

A platinum or palladium catalyst is used in a process for preparing pregnane derivatives from 11- dehydrosarmentogenin.

Preparing Derivatives of Etiocholanolic Acid

N. V. ORGANON. *British Patent* 774,083
A platinum or palladium hydrogenation catalyst

is used in the preparation of derivatives of etiocholanolic acid by oxidation of pregnane compounds.

Liquid Phase Dehydrohalogenation Process
DOMINION TAR & CHEMICAL CO. LTD. *British Patent* 774,125

Organic halogen-containing compounds of specified general formula are dehydrohalogenated by maintaining the bulk of the compound in the molten state in a receptacle and contacting part