ABSTRACTS
of current literature on the platinum metals and their alloys

PROPERTIES

A Thermodynamic Study of the Heat of Ordering CuPt
G. W. Geiken, USAEC Rept UCRL-17675, 1967, (June), 20 pp
Heat of formation of Cu-Pt plotted against temperature at 360-1155 K indicates that the alloy is disordered as it is heated. Heat of formation decreases from -4010 cal/g-atom at 360°K to -4410 cal/g-atom at 800°K; increases to -3070 cal/g-atom at ≈1100°K, the critical temperature, and gives a total ordering energy of 1510±100 cal/g-atom.

Atomic Structure and Ferromagnetism of the Regular Platinum-Manganese Alloys
Studies of regular 20–50 at.% Mn-Pt alloys revealed the structures of the cubic and tetragonal phases and defined their limits of concentration more precisely. The relation of mean magnetic moment on an atom to alloy composition was caused by an antiferromagnetic reaction between neighbouring Mn atoms.

Magnetic Properties of Intermetallic Compounds between the Lanthanides and Platinum
Magnetic properties, particularly in the paramagnetic region, were measured for LnPt₄ compounds with C15(MgCu₂) structure, where Ln=Pr, Nd, Gd, Tb, Dy, Ho, or Er. Effective movement µeff for paramagnetic LnPt₄ is close to g√1/J(J+1), the value for Ln³⁺, but, in GdPt₄, µeff is 2% greater owing to conduction electron polarisation effects. Pt in LnPt₄ is nonmagnetic.

Low moments in the ferromagnetic state indicate incomplete saturation. All the LnPt₄ compounds become ferromagnetic at 4.2°K, except PrPt₄ which may be a Van Vleck paramagnet at 4.2°K.

Lorenz Number of Pure Palladium at Low Temperatures
Measurements of the ideal electrical and thermal resistivities of Pt at 2.5–19°K yield an ideal Lorenz number L₄ = 0.7 × 10⁻⁸ V²/deg², which is independent of temperature below ≈5°K. Comparison with data for Re and Ni indicates that low-temperature values of L₄ are parameters characteristic of each metal.

Magnetic Moment of Pd to 150 kG: Limits of Exchange Enhancement in Pd
S. Foner and E. J. McNiff, Ibid., (25), 1438–1441
Magnetic moment of Pd at 4.2°K is a linear function of magnetic field up to 150 kG. Experiments based on Wohlfarth’s analysis of the high-field enhanced paramagnetism of Pd showed the limits of exchange enhancement for Pd and an increase in the minimum field for field-induced ferromagnetism in Pd.

Volumetric studies of the solubility of H₂ and D₂ and of their diffusion rates in Pd and in up to 40% Ag-Pd foils at 20–100°C showed that solubility increases with Ag content at low pressure but decreases with increasing pressure and that diffusion is hindered at higher pressure. The kinetics of this hindrance were evaluated. D₂ had lower activation energy than H₂.

II. Electrochemical Methods
G. Holleck and E. Wicke, Ibid., 155–172
Electrochemical studies at 0–80°C gave similar results to the above. Sn-Pd alloys as well as Ag-Pd were considered.

Viscosity of Alloys on the Basis of Palladium and Silver
Composition diagrams were compared with composition- viscosity relationships at various temperatures for the systems Pd-Ag, Pd-Cr, Pd-Si and Ag-Si. Viscosity increases with increasing % Pd in Pd-Ag alloys at 1600 and 1650°C. Pd-Cr alloys at 1600–1700°C possess minimum viscosity at 63% Pd, corresponding to the eutectic point. Pd-Si alloys possess viscosity maxima at compositions corresponding to PdSi and Pd₂Si but, as the temperature rises from 1400 to 1600°C, these maxima are smoothed, which indicates partial dissociation.

Investigation of the Application of Spinodal Theory to the Palladium-Iridium System
G. Walter, USAEC Rept UCRL – 17470, 1967, (May), 34 pp
No classic spinodal decomposition occurred in
44 at.\% Ir-Pd despite long ageing times. Hardness, microstructure, and X-ray tests studied existing spinodal theory for the alloy, and ageing took place well below the predicted critical temperature. Modified theory is based upon effects of differing elastic moduli of Ir and Pd, for Ir has five times the modulus of Pd.

**Equiatomic Transition Metal Alloys of Properties of Pd-Mn Phases**

Studies of 40-66 at.\% Pd-Mn alloys show that effects of differing elastic moduli of Ir and Pd, temperature. Modified theory is based upon effects of differing elastic moduli of Ir and Pd, for Ir has five times the modulus of Pd.

**Striction Susceptibility of an Alloy near the Fe-Pd Composition in Weak Magnetic Fields**


Following annealing for 1 h at 600-800°C and slow cooling to room temperature, the magnetic striction susceptibility of 60 wt.\% Fe-Pd and of Ni was determined and showed maxima of 200 and 80 units respectively, 60 wt.\% Fe-Pd has advantages over Permendur-type alloys.

**On the Mechanism of the Antiferromagnetic Transition in the System of Ordered Fe(Pd,Pt)\(_{1-x}\) Alloys**


Tests confirmed that the antiferromagnetic-ferromagnetic transition in Fe(Pd\(_{1-x}\)Pt\(_x\)) alloys occurs by a complex magnetic structural change involving noncollinear orientation of atomic magnetic moments. The cases of FePt\(_8\) and FePd\(_8\) are discussed. Pd and Pt have opposite tendencies in the ternary alloys. 0-37 at.\% Pd alloys show antiferromagnetic FePt\(_8\) structure, 55-75 at.\% Pd alloys show ferromagnetic FePd\(_8\) structure, and 37-55 at.\% Pd alloys have the complex structure with noncollinear orientation of the moments of the alloy components.

**Neutron-diffraction Study of Antiferro-ferromagnetic Transition in a System of Ordered Fe(Pd,Pt)\(_{1-x}\) Alloys**


Studies of the antiferro-ferromagnetic transition in ordered Fe(Pd\(_{1-x}\)Pt\(_x\)) alloys by analysis of the dependence of the intensity of the (100) ferromagnetic reflection on the average magnetic moment per atom of the alloys showed that it occurs by a set of complex magnetic structures with a noncollinear orientation of the atomic magnetic moment of the components.

**Equiatomic Transition Metal Alloys of Manganese. VI. Structural and Magnetic Properties of Pd-Mn Phases**


Studies of 40-66 at.\% Pd-Mn alloys show that CsCl-type cubic PdMn is stable only at high temperatures, is homogeneous at \(\sim 40-\sim 50\) at.\% Pd at 685°C, and is paramagnetic, whereas CuAuI-type tetragonal PdMn is homogeneous at \(45\pm 1\) to 65.5 at.\% Pd according to temperature, is paramagnetic above \(825 \pm 10\)K for \(\sim 50\) at.\% Pd to \(290 \pm 10\)K for 66 at.\% Pd, and is antiferromagnetic below these temperatures. The magnetic cell structure is discussed.

**Metallurgical Problems with the Hot Working of Rhodium and Iridium**


The low ductility of Rh and Ir compared to other f.c.c. noble metals makes working of them difficult but a review of theory and experiments to elucidate their brittle behaviour suggests that purification to 99.999\%, and transformation of the normal polygonal structure to fibrous or single crystal structure leads to enhanced ductility. However, this enhancement is limited by the high shear modulus of Rh and Ir.

**Superconductivity and Specific Heat of Titanium-Rhodium Alloys**


Specific heats of 0-10 at.\% Rh-Ti alloys were measured at 0.9-8\,K and transition temperatures of hexagonal 0-2 at.\% Rh-Ti and cubic 3-10 at.\% Rh-Ti were determined by calorimetry. Both transition temperature and electronic specific heat increase with \% Rh. Influence of cooling rate on transition temperature was studied. Unlike Hf,Rh and Zr,Rh, Ti,Rh is not superconducting down to 1.2\,K.

**Thermodynamic Properties of Hexagonal Close-packed (hep) Iron and Iron-Ruthenium Alloys**


Results of measurements on h.c.p. Fe-Ru alloys of specific heat at 60-300\,K, and of vapour pressure of Fe over f.c.c. and h.c.p. Fe-Ru alloys at 1600\,K, were used to describe the lattice stability of h.c.p. Fe and the thermodynamic properties of the Fe-Ru system. Earlier theory is supported by the vibrational entropy of h.c.p. Fe exceeding that of the b.c.c. form.

**A New Structure Type with Octahedral Pairs for Rh\(_{2}S\)\(_{3}\), Rh\(_{2}Se\)\(_{3}\) and Ir\(_{2}S\)\(_{3}\)**


Rh\(_{2}S\)\(_{3}\) has a space group Pbcm(D\(_{4h}\)\(^{1}\)) and lattice constants \(a = 8.452\,\text{Å}, b = 5.985\,\text{Å}, c = 6.138\,\text{Å}\). The Rh atoms possess octahedral coordination. Four Rh atoms surround each S atom at the vertices of a distorted tetrahedron. Rh\(_{2}S\)\(_{3}\) is isotypical with...
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Rh$_2$Se$_3$ and Ir$_2$S$_2$. A complete range of solid solubility exists between Rh$_2$S$_3$ and Rh$_2$Se$_3$.

Decomposition Pressures and Enthalpies of Formation of Some Transition Metal Diarsenides and Diselenides


Studies of the decomposition pressures of PtAs$_3$, OsAs$_3$, RuSe$_3$, and OsSe$_3$ as a function of temperature by the torsion effusion technique, and of the heats and entropies of decomposition gave as heats of formation, at 298°C, $-42.0 \pm 3.5$, $-32.5 \pm 5.0$, and $-42.9 \pm 3.5$ kcal/mole respectively. Phase relationships of Pt-As, Os-As, Ru-Se, and Os-Se at 850-1250°C were studied.

Constitution Diagrams of Plutonium with Metals of Groups IIIA, IVA, VIII and IB


Sixteen constitution diagrams of Pu alloys are collected in this article and include those of Pu-Ir, Pu-Pd, Pu-Pt, Pu-Rh, and Pu-Ru.

CHEMICAL COMPOUNDS

Semiconducting d$^9$ Metal Complexes Found


Studies of transition metal complexes in which the metal has planar d$^9$ configuration showed that single crystals of the groups of compounds [Ir(CO)$_2$acac] and [Rh(CO)$_2$acac], [Pt(NH$_3$)$_2$]$^{3+}$ [PtCl$_2$]$^{4-}$ and [Pt(NH$_3$)$_2$]$^{3+}$[PdCl$_2$]$^{5-}$ are particularly suitable for electrical measurements. Workers at Research Triangle Institute, University of North Carolina and Manchester University have studied the structures and physical properties of these compounds, which appear to be intrinsic semiconductors, leading to intermetallic polymers capable of being tailored to specific physical and electrical requirements.

Mass Spectrometric-Knudsen Cell Study of the Gaseous Oxides of Platinum


These studies confirmed the species PtO$_2$(g) and established the existence of PtO(g). Thermodynamic data for their formation are recorded and enthalpy data for the vapourisation of Pt.

Preliminary Investigations in the Systems Au-O, Rh-O and Pt-O at High Oxygen Pressures


Studies on the systems at up to 900°C, 3000 atm. O$_2$ showed that whereas Rh$_2$O$_3$ is stable at 1 atm. O$_2$, RhO$_2$ is the stable phase at slightly higher pressures. RhO$_2$ has rutile structure with $a=4.489$, $c=3.909$ Å. In the Pt-O system, hexagonal $\alpha$-PtO$_2$ appears stable at lower temperatures and higher O$_2$ pressures while $\beta$-PtO$_2$ is formed at 650-750°C, 2000 atm. O$_2$. PtO$_2$ is formed at 680-780°C, 200-500 atm. and has cubic NaPt$_4$O$_9$ structure with $a=5.585$ Å and Na positions vacant. An intermediate phase of stoichiometry between PtO$_2$ and Pt$_2$O$_3$ has also been detected. The $\alpha$-PtO$_2$ to $\beta$-PtO$_2$ transition is unusual in involving the break up of peroxide-type O-O bonds.

Synthesis of Thallium Platinate at High Pressure


Ti$_2$PtO$_2$, prepared by reacting Ti$_2$O$_3$ with Pt or PtO$_2$ at 1000°C, 40 kbar, is a brown solid insoluble in aqua regia and thermally stable to 750°C at 1 atm. The f.c.c. lattice has $a=10.132 \pm 0.004$ Å. Measured density is $11.12$ g/cm$^3$. Pt-O and Ti-O bond lengths and structure are discussed. The infrared spectrum has maxima at 684, 562, 449 and 363 cm$^{-1}$.

The Dissociation Energies of the Molecules PtC and RhC


Mass spectrometric studies of the Pt-C and Rh-C systems showed that the dissociation energies of the gaseous molecules of PtC and RhC are respectively $145.3 \pm 1.5$ and $138.5 \pm 1.5$ kcal/mole.

Structural Investigations on Rhodium Halides


X-ray, magnetic and thermal studies on RhBr$_3$ and Rhl$_3$ showed that their monoclinic crystals have lattice structures: RhBr$_3$, $a=6.27 \pm 0.01$, $b=10.85 \pm 0.01$, $c=9.35 \pm 0.01$ Å, $\beta=109.0^\circ$; Rhl$_3$, $a=6.77 \pm 0.02$, $b=11.72 \pm 0.02$, $c=8.83 \pm 0.02$ Å, $\beta=109.3^\circ$. Atomic positions and distances were recorded.

The Formation of Complexes of Molecular Nitrogen with Compounds of Ruthenium and Osmium


Infrared spectral studies showed that N$_2$ is coordinated to Ru and Os atoms at the reductions of RuCl$_3$ and RuOHCl$_3$ in tetrahydrofurin by Zn amalgam, C$_2$H$_5$MgBr, or C$_2$H$_5$MgBr and of OsOHCl$_3$ in similar conditions. The N$_2$ complexes are similar to [M(NH$_3$)$_2$N$_2$]X$_n$, where M = Ru, Os; X = Br$^-$,
produced by the action of \( \text{N}_2\text{H}_4 \) hydrates on RuCl\(_3\), etc. The stability and bonding of these nitrogenyl complexes have been studied using \(^{15}\text{N}\) labelling.

**Ruthenium Complexes Containing Molecular Nitrogen**


[Ru(NH\(_3\))\(_5\)N\(_2\)]\(^{2+}\) complexes were prepared by the action of \( \text{N}_2\text{H}_4 \) hydrate on Ru(II) or Ru(IV) salts, or by the action of azide ion on aquo-pentammineruthenium (III). Various Ru(II) and Ru(III) ammine complexes could be derived. The reported properties of [Ru(NH\(_3\))\(_5\)N\(_2\)]\(^{2+}\) salts are discussed.

The Formation of [Ru(NH\(_3\))\(_5\)N\(_2\)]\(^{2+}\) in Aqueous Solution by Direct Action of Molecular Nitrogen


The preparation of [Ru(NH\(_3\))\(_5\)N\(_2\)]\(^{2+}\) between \( \text{N}_2 \) and [Ru(NH\(_3\))\(_5\)H\(_2\)O]\(^{2+}\) solution at room temperature.

**ELECTROCHEMISTRY**

The Oxygen Electrode on Noble Metals


A review of the reactions between \( \text{O}_2 \) and electrodes of Pt, Au, Pd, Rh, Ir and various alloys. (327 references.)

Investigation of the Adsorption of Hydrogen on Platinum Metals at Various Temperatures


Adsorption of \( \text{H}_2 \) on Raney Os and Ir electrodes surfaced with Rh and Ru was measured and analysed by charging curves at 20–95°C using 1N H\(_2\)SO\(_4\) and 1N NaOH electrolytes.

The Electrochemical Activation of Platinum Electrodes


A review of mechanisms for the electrochemical activation of Pt electrodes led to experiments which showed that impurity desorption is the most important result of conventional brief activation. A second type of activation may exist, produced by prolonged preoxidation and possessing very stable activity. (57 references.)

On the Mechanism of Methanol Oxidation on a Platinum-Ruthenium Electrode


CH\(_3\)OH was oxidised in both H\(_2\)SO\(_4\) and KOH solutions over Pt-Ru and platinised Pt electrodes and results were plotted and compared. Graphs demonstrate the effects of the rate of electro-oxidation to the potential of the rate of oxidation to the concentration of CH\(_3\)OH, of the surface coverage of the electrodes to the potential, and also the effect of stationary polarisation.

**Comparison of the Properties of Compact and Dispersed Platinum-Ruthenium Electrodes**


Further work is recorded on 10, 20, 30 and 40\% Ru-Pt electrodes, which were tested by plotting potentiostatic anodic and cathodic curves for each in the compact and dispersed forms in H\(_2\)SO\(_4\) solutions.

**ELECTRODEPOSITION AND SURFACE COATINGS**

Protecting Refractory Metal at High Temperature


A system is described which offers 2–5 h oxidation protection for W at 2000°C in air. The refractory metal is electroplated with Ir and sprayed with ZrO\(_2\) as a surface coating.

Electrodeposition of Iridium from Fused Sodium Cyanide and Aqueous Electrolytes. A Preliminary Study


Metals such as W and Mo, which oxidise rapidly at high temperatures, can be protected by plating adherent and coherent deposits of Ir up to 15 mils thick from a fused NaCN bath at 600°C, 10–100 mA/cm\(^2\). Pure Ir protects Mo up to 1000°C in flowing air but above this temperature the volatility of its oxide prevents its use. Coatings up to 4 mils thick of Ir-Pt, Ir-Pd and Ir-Rh alloys may offer protection above 1000°C. Aqueous electrolytes are unsuitable as they lead to low deposition rates and cracking of heavy deposits.

**LABORATORY APPARATUS AND TECHNIQUE**

How to Grow King Size Single Crystal YIGs


Single crystals of \( \text{Y}_3\text{Fe}_5\text{O}_{12} \), \( \text{Y}_3\text{Ga}_5\text{O}_{12} \) and \( \text{Y}_4\text{Al}_5\text{Fe}_{25}\text{O}_{12} \) are grown in a 3.5% Rh-Pt crucible by prolonged and carefully controlled heating at 2500°C. High purity oxides are the starting materials. The crucible is also of the highest purity to avoid chemical interaction and contamination of the crystals.
Apparatus for Making Sharp Photographic Images with X-Rays
H. F. SHERWOOD, Rev. sci. Instrum., 1967, 38, (11), 1519-1622
The jaws of the knife-edge slit for making sharp photographic images with X-rays are fabricated from 10% Ir-Pt. Their manufacture and mounting, and the operation of the apparatus, are described.

Comparison of Tips, Thin Wires and Sharp Metal Edges as Emitters for Field Ionisation Mass Spectrometry
Although tips give twice the field strength of wires, the latter are preferable for analytical purposes because of their larger emitter area and give more than ten times the field strength of a sharp metal edge. To reduce the breakages of wire by the mechanical forces exerted by the high electrical field, 2.5 μm Pt wires were strengthened by whisker growing. Uniform quality Wollaston wire of high tensile strength is necessary. A compensating electrode reduces the mechanical forces on the wire. The length of etched Wollaston wire has been reduced to 1.5-2.0 mm.

HETEROGENEOUS CATALYSIS
Noble Metal Catalysts in the Fine Chemicals Industry
A review of the uses of Pt metals in heterogeneous and homogeneous catalysis. Topics discussed include the choices of metal, support, and conditions of reaction. Other topics include evaluation of catalysts, the trickle column reactor, and the economics of using these catalysts. (17 references.)

Catalytic Conversions of Hydrocarbons
A review of the hydrodenolysis of C5-C13, C14 and C15 cyclic hydrocarbons on Pt metal and Ni catalysts, and of the dehydrocyclisation of paraffins to form aromatic and bicyclic compounds using Pt, Pd and Ni catalysts. 50 years of work by KAZANSKII and his colleagues is reported. (69 references.)

Catalytic Properties of the Pt – Cu System
The activity of Pt-Cu metallic catalysts for C6H6 hydrogenation decreases with increasing Cu content until it is zero at 75 at. % Cu because d levels in Pt are filled by electrons from Cu.

Study of the Adsorption and Energetic Properties of Metallic Catalysts. I. Specific Surface of Catalysts
Specific surfaces of Pt, Pd, Rh and Ru blacks are compared by the BET method with C6H6 and Kr adsorption, and by the electrochemical methods from the capacity of the double layer region and the amount of H2 adsorbed. The double layer region method gives higher results than the H2 adsorption method. There is a reciprocal relation between the mean size of the crystallites in the blacks and the specific surface.

The Retention of Hydrogen by Supported Metal Catalysts
He treatment of Al2O3-supported catalysts does not remove all the reactive H2 from the surface. Less remains on Pt/Al2O3 than on Pd/Al2O3 or Rh/Al2O3 although the total amount of H2 retained on Pt/Al2O3 is similar to that on Rh/Al2O3 and greater than that on Pd/Al2O3. There is less self-hydrogenation of C6H6 on Pd/Al2O3 than on Rh/Al2O3.

The Study of Catalysts and Adsorbents by the Thermal Desorption Method. II. Platinised Alumina
There exists for Pt/Al2O3 a direct connection between the amount of adsorbed gas and the intensity of exoelectronic emission. Maxima on curves of temperature against emission, for Pt/Al2O3, depend on the existence of centres on the Al2O3 surface which are activated by adsorption of H2O and O2. Tests were carried out in the range 20-300°C.

Investigation of the State of Platinum in Platinum Catalysts for Dehydrocyclisation by the Extraction Method
Pt dehydrocyclisation catalysts treated by air at 20-800°C and by H2 at 250-550°C were studied by extraction methods, which showed that, in reduced Pt/Al2O3, the Pt bonded chemically to Cl and Al2O3 has specific activity for the formation and closing of ring compounds but
does not catalyse the dehydrogenation of cyclo-

hexane.

Investigation of the Selectivity of Platinum
Catalysts on Various Supports in the Hydro-
genolysis of Methylcyclopentane
V. V. VORONIN, KH. M. MINACHEV and I. I.
1967, (12), 2616-2619

H₂ treatment up to 550°C of Pt/zeolite, Pt/SiO₂
and Pt/C catalysts does not alter their selectivity
for hydrogenation of methylcyclopentane. The
C₅ ring is split away from the side chain. Activity
is either decreased or remains constant. Similar
treatment of Pt/Al₂O₃ causes a sharp increase in
activity and a change in selectivity so that the
Al₂O₃ group. The change is caused by changes in the
Pt surface by the chemisorption of O₂.

Chemisorption and Catalysis on Platinised
Silica. III. Chemisorption of Oxygen
V. S. BORONIN, V. S. NIKULINA and O. M. POLTORAK,

Studies at 20-470°C, 10⁻¹⁻¹-1.5 mm Hg on the
sorption of O₂ on Pt/SiO₂ with various amounts of
Pt form the basis for a method of measuring the
Pt surface by the chemisorption of O₂.

Vapour-phase Hydrogenation of Benzene on
Pt/Asbestos Catalyst with Control of
Catalyst Potential
N. I. UT EGULOV, V. S. D R U Z and D. V. SOKOL’SKII, 
Ibid., (12), 3128-3131

The possibility of measuring the catalyst potential
during vapour-phase hydrogenation of C₆H₆
on Pt/asbestos was studied. Equilibrium and
stationary catalyst potentials, and catalyst
activity, depend on catalyst pretreatment and
perhaps on processes of exchange adsorption
on the support. The limiting factor is activation and
reactivation of H₂ weakly bonded to the support.
The apparent order of the reaction depends on the
gaseous phase ratio C₆H₆: H₂.

Effect of Noble Metal Concentration upon
the Isomerisation Activity of Molecular
Sieve Zeolite Catalysts
M. A. LANEWALA, P. E. PICKERT and A. P. BOTTON, 
J. Catalysis, 1967, 9, (1), 95-97

Tests on isomerisation of N-C₆H₁₄ showed that the
optimum catalyst concentrations for methyl-
pentane formation were 0.05 wt.% Pd or 0.10 wt.% Pt, and for dimethylbutane formation were
0.25 wt. % Pd and ~0.40 wt. % Pt. The metals are
equally effective when compared on an atomic
wt. % basis. Results suggest that ion exchange
incorporation of noble metals on to zeolites
allows for almost atomic dispersion. The
Pt(NH₃)₄Cl₂·H₂O and Pd(NH₃)₄Cl₂ salts intro-
duced Pt(NH₃)₄²⁺ and Pd(NH₃)₄²⁺ ions into the
zeolite and calcing deposited the metal atoms.

Metal Sulphide Catalysts for Hydrogenation
of Halonitrobenzenes to Haloanilines
1967, 32, (11), 3670-3671

Hydrogenations of chloro- and bromo-substituted
nitrobenzenes over metal sulphide catalysts
showed that Pt sulphide is probably best because
of its good selectivity and commercial availability.
Sulphides of Ni and Pd are satisfactory for
reduction of chloronitro- but not bromonitro-
aromatic compounds. Pt sulphide was also
suitable for quantitative hydrogenation of 2,5-
dichloronitrobenzene to 2,5-dichloroaniline.

Liquid-phase Hydrogenation of Organic
Compounds on Mixed Ruthenium Catalysts.
Ruthenium-Platinum Catalysts
D. V. SOKOL’SKII, K. K. DZIHDAMALIEVA, A. G.
SARMURZINA and T. TONMANOV, Dokl. Akad.
Nauk SSSR, 1967, 176, (5), 1093-1095
Tests showed that two maxima occur on each
graph of catalyst activity against alloy composition
for liquid-phase hydrogenations of a number of
organic compounds on Ru-Pt catalysts. These
maxima are related to the nature of the reduced
compound, and to the solvent used in the case
of the maximum at the higher Ru concentration.
The surface area decreases with increasing Ru
content.

Catalytic Reduction of Waste Nitrogen
Oxides
S. JAR č 8 and J. KATZKI, Chem. Prumysl, 1967, 17, 
(11), 581-586
Pt/Al₂O₃ and Pd/Al₂O₃ pellet or bead catalysts
have the greatest activity for reduction of
nitrogen oxides, according to laboratory tests.
Gases with low ignition and operating tempera-
tures are most suitable for reduction of the oxides.
High temperature affects the catalyst adversely;
it's life is reduced and more catalyst
is needed because of the lower space velocity. Results of
this work form the basis for a new reactor
design.

On the Catalytic Properties of Platinum
Group Metals and their Alloys Containing
Palladium
R. G. DAVLESMPOVA and D. V. SOKOL’SKII, Kinet.
Kataliz, 1967, 8, (6), 1378-1381
A study of the activity of the Pt group metals,
Re, and Pd₄Me-type alloys as catalysts for the
reduction of dimethylmethynylcarbinol in H₂O,
96% C₂H₅OH and 0.1 N KOH in H₂O or
C₂H₅OH at 10-40°C showed that the alloys
possess more activity than Raney catalysts of the
individual elements. Raney Ru, Os, Re and Ir
were completely inactive. The rate of the
process was lower in alkaline solution. In the

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alcoholic alkaline solution the process was checked at the semireduction stage.

The Effect of Sulphur-organic Compounds on the Purification of Gases from Nitric Oxide and Acetylene by the Method of Catalytic Hydrogenation


Thiophene, ethylmercaptan and CS₂ all reduce the degree of hydrogenation of NO over Pd-Ru catalysts. CS₂ has the greatest deactivation effect. CS₂ also reduces the activity of Pd catalysts more than Ru-Pd catalysts for hydrogenation of C₂H₆ and C₃H₆. However, the degree of hydrogenation of C₂H₆ is reduced far more than that of C₃H₆, hence Pd catalyst is more selective. Mercaptans do not form between H₂S and C₂H₆ or C₃H₆ in N₂ but ethylmercaptan is formed in a H₂ atmosphere as the product of reaction between C₂H₆ and C₃H₆ with CS₂, formed by hydrogenation of S-organic compounds.

Catalytic Conversions of Alkyl Derivatives of the Benzene and Naphthalene Series under Pressure of Hydrogen in a Flowing System


Studies of dehydrocyclisations of N-octyl and dodecylbenzene, and of 2-N-butyl and 2-N-octyl-naphthalene, in the presence of 0.5% Pd/clay or of activated clay at 450°C, 30 atm. H₂ in a flowing system showed that polycyclic aromatic hydrocarbons with high capacity for luminescence are formed. The yield rose as the molecular weight of the aromatic ring increased.

The Catalytic Activity of Rhodium in Relation to its State of Dispersion


Studies of the catalytic activity of Rh for hydrogenolysis of C₄H₁₀ using Rh/SiO₂ and Rh as catalysts, showed that the specific catalytic activities of unsupported Rh and of severely calcined Rh/SiO₂ are much lower than those of well-dispersed Rh crystallites 40 Å or smaller. Catalytic activity ultimately falls again when the dispersion is extremely fine.

Ruthenium Catalysts for the Liquid-phase Hydrogenation of Sulpholene


Ru catalysts, with high activity for liquid-phase hydrogenation of sulpholene and sulpholane, are more effective when prepared by applying potassium ruthenate to C than RuCl₃ to the support. 5% Ru catalysts were tested on a number of supports and are shown to enhance the activity of Pt/Al₂O₃.


H. PICHLER and W. BURGERT, Brennstoff-chem., 1968, 49, (1), 5-9

Discontinuous synthesis for paraffin formation at various temperatures and pressures of the reacting gases showed that stirring of special shape increased the exchange of gas at the double bond. At 1000-2500°C, this exchange was pressure-independent, unlike the molecular weight of polyethylene. At <100°C, 2000 atm. the molecular weight of the polyethylene produced was >200,000.

HOMOGENEOUS CATALYSIS

The Reactivity of Pt(II) Complexes in the Oxidation of Carbon Monoxide in Aqueous Solutions


K₃PtX₄ complexes in the oxidation of CO show decreasing reactivity in the order: PtI₄ > PtBr₂ > Pt(CNS)₄ > PtCl₄ > Pt(NO₃)₄ > Pt(NH₃)₄ > Pt(CN)₄.

Application of the Mobile Equilibrium of Isomerisation to the Polymerisation of Olefin Mixtures. I. Prototropic Displacement by Salts and Complexes of Noble Metals


The addition of TiCl₃ to PdCl₄ produced a new catalytic system more active than PdCl₄ alone. It encouraged different stoichiometry in the polymer.

Olefin Oxidation with Palladium(II) Catalyst in Solution


A review of process for the oxidation of C₄H₁₀ and other olefins using Pd(II) catalysts in aqueous and non-aqueous solvents. The Pd-olefin complexes are considered as reaction intermediates and their structures and mechanisms are examined. (85 references.)

The Catalytic Activity of π-Complexes of Straight-chain Olefins with Palladium Chloride

G. PREGAGLIA, M. DONATI and F. CONTI, Chim. e Ind., 1967, 49, (12), 1277-1283

The π-complexes were synthesised by direct interaction of PdCl₄ with straight-chain olefins or by exchange between (C₉H₁₈)₂PdCl₄ π-com-
plexes and other olefins. Exchange with 1,5-cyclooctadiene displaces the coordinated olefin with unchanged configuration. When PdCl₂ dissolves in α-olefins the free olefin isomerises until the trans:cis ratio is greater than one, a result due perhaps to different rates of reaction of the α-olefin with the cis- and trans-π-complexes. An intramolecular mechanism for rearrangement of the π-complex of an α-olefin is inferred from the lack of isomerisation of the olefin while entering or leaving the complex.

Organic Syntheses by Means of Noble Metal Compounds. XXXIII. Carbylonylation of Azobenzene-palladium Chloride Complexes


The preparation and carbylonylation of PdCl₂ complexes of several symmetrically and asymmetrically substituted azobenzenes took place smoothly under mild conditions. Study of their structure indicated that PdCl₂ formed a σ bond with the benzene ring by electrophilic substitution, substitutes exerting inductive influences. The carbylonylation mechanism was not clear.

Polymerisation by Transition Metal Derivatives. IV. Investigations on the Mechanism of Butadiene Polymerisation by Rhodium Salts


Tests on the polymerisation of butadiene using RhCl₃ as catalyst showed the effects of catalyst concentration, different activation energies, requirements in emulsifier structure and concentration, and the effects of other diolefins. Mixtures of butadiene and piperylene were also polymerised.

Rhodium Complexes for Allene Polymerisation in Polar Media


Polyallenes are produced in high yield at relatively low temperatures and pressures in polar solvents using as catalysts the Rh complexes [RhCl(CO)₅], [RhCl₂(C₆H₄)₃], [RhCl(PPPh₃)₃] and [RhCl₂(PPPh₃)₂]. The rate of polymerisation is faster with [RhBr(CO)₅], than with [RhCl(CO)₅], and [Rhacac(C₆H₄)₃] is also effective in C₆H₄OH as solvent. Ru complexes, such as RuCl₃nH₂O₃, RuCl₃-PPh₃ and RuCl₃(PPPh₃)₃, catalyse allene polymerisation similarly but Pd complexes, such as Pd(PPPh₃)₃ and PdCl₃-SnCl₂, are ineffective.

Polymerisation of Allene with Rhodium Complexes


Most active catalysts for polymerisation of allenes to a regular structure were combinations of Rh(I) with appropriate donor ligands, e.g. [RhCl(CO)₅]-2PPh₃. Almost quantitative polymerisation is possible in 95% C₂H₅OH at 60–70°C in <5h. Studies of the reaction mechanism suggest insertion of σ-coordinated allene monomer to the asymmetric π-allyl- or σ-π-allyl-metal bonding.

The Catalytic Hydrogenation and Deuteration of Steroids in Homogeneous Phase


Olefin reduction by (PPh₃)₃RhCl suggested a new method for specific hydrogenation of double bonds in steroids. The effects of the solvent, the pressure and the rate of reaction on reactions at the C=π double bonds of steroids were studied. D₄ labelling depended on the solvent and on the catalyst concentration.

FUEL CELLS


Fuel cells with BPO₄-H₃PO₄ paste electrolyte and Pt/Ta or Pt/C electrodes were operated continuously on H₂ and O₂ at 200°C for up to 3 months and produced up to 110 mw/cm², although 65–70 mw/cm² was more usual. The thermally stable electrolyte rejects CO₂, has high ionic conductivity and good mechanical properties and needs no regeneration with H₂O. Pt/Ta gauze electrodes were 20% superior to Pt/porous C. Similar cells operated on dilute H₂, steam-reformed CH₃OH and shifted CO gave 70–90% the performance of those on pure H₂. Carbonaceous fuels including hydrocarbons led to lower efficiency due to high activation polarisation, partly caused by oxidation of Pt anode. When operated on steam-reformed CH₃OH and air, the cell produced 45 mw/cm².

The Effect of Preoxidation and Meniscus Shape on the Hydrogen-Platinum Anode of a Molten-carbonate Fuel Cell


Studies at 723°C of a H₂-O₂ fuel cell with Pt electrodes and molten electrolyte, composed of a eutectic mixture of Li, K and Na carbonates, showed that smooth Pt anodes are activated by hydrogen to give bigger currents. Contact angle of unactivated Pt with the eutectic is 90°, of activated Pt is 0° and decreases with deactivation. H₂ diffuses to the reaction site along the Pt/molten carbonate interface and/or diffusion through the Pt but not appreciably through the molten carbonate film above the meniscus.
CHEMICAL TECHNOLOGY

The Process of Activated Sintering of Tungsten with Palladium Additives

0.05-1.0% amounts of Pd in the form of aqueous PdCl₂ solution were added to 75% W powder and, after mixing, drying, sieving, reduction, and sieving, were compressed and sintered in H₂ at a process which gave the highest density of >17g/cm³ at 0.2% Pd and 1600°C. These samples had microhardness <300 kg/mm² and compressive strength of 105 kg/mm². The activating effect of Pd occurred by transfer of nonlocalised electrons from Pd to W with an accompanying decrease in free energy and increase of statistical weight of the stable electron configurations of the Pd and W atoms.

GLASS TECHNOLOGY

Creep of Alloys of Platinum with Rhodium at Temperatures 1350-1500°C

Strip samples of 7, 10 and 15% Rh-Pt were examined for creep by metallography at 1350, 1400 and 1500°C and at 0.2, 0.15 and 1.3 kg/mm² for up to 5 h. Graphs of test results show that creep increases with temperature. Creep was most intense at 1500°C, 1.3 kg/mm² and 7 and 10% Rh-Pt alloys failed after 90 and 240 min. in these conditions. No other failure occurred at other temperatures and loadings for any alloy. Creep decreases with greater Rh content. 10% Rh-Pt is recommended for glass-melting as 15% Rh-Pt is more expensive but not much stronger.

Experience in Industrial Determination of Glass Viscosity at a Tank Furnace Feeder

Cylindrical Pt electrodes of diameter 10 mm were placed 40 mm apart in the furnace and 20 mm deep in the molten glass. The viscosity of the glass was calculated from the resistance measured between the electrodes. A Pt:Rh-Pt thermocouple measured the temperature, whose fluctuations are matched by fluctuations of viscosity.

ELECTRICAL AND ELECTRONIC ENGINEERING

Fluorescence of Rhodium-activated Aluminium Oxide

Fluorescence emission of 0.1-1.0 at.% Rh-activated Al₂O₃ consists of a broad band in the far red at 680 nm, probably due to the spin-forbidden 3TIg → 1Ag₁g transition but other Rh³⁺-activated aluminates had very weak photoluminescence.

TEMPERATURE MEASUREMENT

Apparatus for Measuring the Hall Effect of Low-mobility Samples at High Temperatures

A thermocouple is a more desirable sensor than a resistance thermometer for high stability of the sample temperature and a Pallador I thermocouple with output 65μV/deg C was found to be suitable. The double a c measuring method uses a c at 510 Hz with a 2 Hz magnetic field.

NEW PATENTS

METALS AND ALLOYS

Tungsten-base Alloys
Mallory Metallurgical Products Ltd.
British Patent 1,090,561

Tungsten alloys with improved tensile strength and ductility are produced by incorporating 0.5-10 wt.% Ru. Small amounts of Mo, Ni and Fe give another range of alloys of high strength and ductility.

Treatment of Palladium and Palladium-base Alloys
Johnson, Matthey & Co. Ltd.
British Patent 1,091,051

When placed under conditions of stress these materials tend to give “discontinuous yield” due to the presence of Si in the material. This defect is now prevented by adding an alloying element which more readily combines with Si than Pd, e.g. Ca, Ba, Sr, Ti, Zr, etc.