# Catalysed Reduction of Water by Ketyl Radicals

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Ultraviolet irradiation of a wide variety of ketones in aqueous solution containing a low concentration of an alcohol results in the formation of the two corresponding ketyl radicals, which are strong reducing agents. In the presence of colloidal platinum particles, these radicals will reduce water to hydrogen gas with high overall quantum efficiency. This is a general reaction, able to operate in sunlight, for which the mechanism is discussed in detail. The importance of the colloidal catalyst is stressed and, by changing the catalyst, different reaction products are obtainable.

Over the past decade or so, photochemists have become increasingly more aware of the interesting possibilities offered by the incorporation of colloidal catalysts into their reaction mixtures. The nature of the reaction products can be changed markedly by using different types of colloidal catalyst and, indeed, useful products can be obtained from seemingly wasteful reactions. This situation is best exemplified by the photochemistry of benzophenone in aqueous alcohol solution. Under normal conditions, ultraviolet irradiation of benzophenone results in quantitative population of the lowest energy excited triplet state; which is of n,π^* character and which rapidly abstracts a hydrogen atom from the alcohol. The resultant ketyl radicals undergo addition and/or disproportionation reactions and benzpinacol is formed with high quantum yield.

$$2Ph_2CO^* + RCH_2OH =$$
$$Ph_2C(OH)C(OH)Ph_2 + RCHO \quad (i)$$
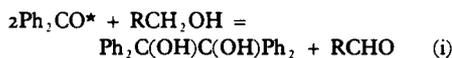
However, when the photolysis is carried out in the presence of small amounts of colloidal platinum, benzpinacol formation is inhibited and copious yields of hydrogen are obtained (1). This change arises because the intermediate ketyl radicals are powerful reducing agents and can reduce water to hydrogen on the surface of the platinum colloid (2). Similar reactions are observed with other ketones having lowest energy n,π^* excited states, including acetone

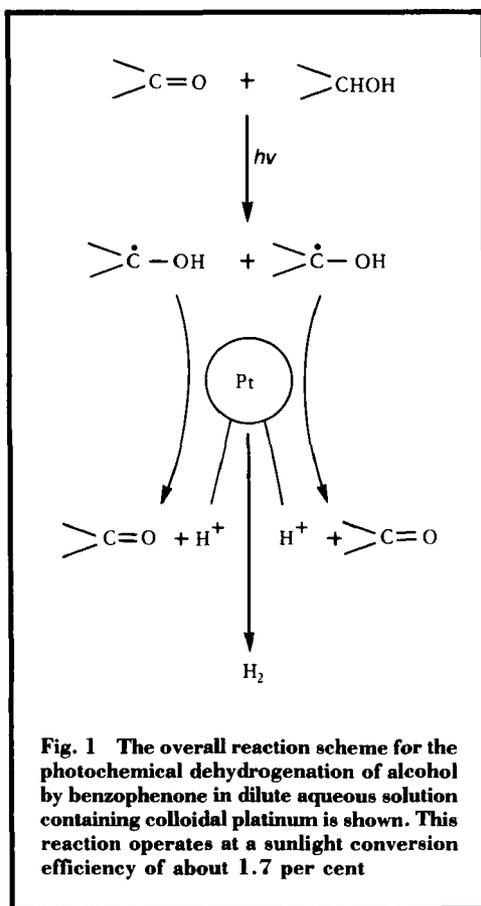(3), and with other metal colloids, including gold and iridium (4).

This type of reaction scheme is fairly general and, in principle, could be applied to the conversion and storage of solar energy. To do this successfully it is necessary to manufacture extremely effective colloidal catalysts since the colloid must be able to intercept the ketyl radicals before they combine together in the bulk solution. Also, it should be realised that the production of hydrogen, although attractive, might not be the most appropriate means of energy conversion under the circumstances. There is, therefore, a need to make the overall reaction more versatile and this can be achieved by changing the type of colloid used as the catalyst.
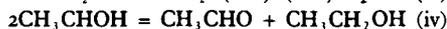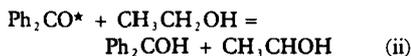
The Photosystem

Water-soluble benzophenone derivatives are readily available (5), a typical structure being shown below:
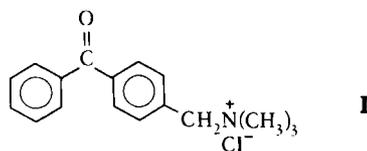
This compound (I) and its close relatives absorb less than 5 per cent of the total energy available in sunlight and require ultraviolet excitation

Fig. 1 The overall reaction scheme for the photochemical dehydrogenation of alcohol by benzophenone in dilute aqueous solution containing colloidal platinum is shown. This reaction operates at a sunlight conversion efficiency of about 1.7 per cent

(6) but the lowest energy triplet state, which is of n,π^* character, is formed with unit quantum efficiency. Ultraviolet irradiation of **I** in water containing 4 per cent ethanol results in quantitative formation of the benzpinacol and acetaldehyde, and the intermediate formation of the benzophenone ketyl radical can be detected by flash photolysis techniques.

$$Ph_2CO^* + CH_3CH_2OH =$$
$$Ph_2COH + CH_3CHOH \qquad \text{(ii)}$$
$$2Ph_2COH = Ph_2C(OH)C(OH)Ph_2 \qquad \text{(iii)}$$
$$2CH_3CHOH = CH_3CHO + CH_3CH_2OH \quad \text{(iv)}$$

Addition of colloidal platinum (2×10^{-4} mol/dm^3) to the above solution causes evolution of hydrogen upon irradiation. The reaction mechanism for this is pictured in Figure 1 and, under optimised conditions, the quantum yield for formation of hydrogen was found

to be 0.34 (7). The initial reaction involves abstraction of a hydrogen atom from an ethanol molecule by the triplet excited state benzophenone derivative. This produces two ketyl radicals within a solvent cage. Geminate recombination can occur to reform the original reactants but some of the radicals escape from the cage into the solvent bulk. Radical recombination and addition reactions can occur in the solution but these bimolecular processes are in competition with electron transfer to a platinum particle. The particle functions as a microelectrode and accepts an electron from each ketyl radical. This oxidises the ketyl radical to the corresponding carbonyl compound, hence recycling the benzophenone, and stores electrons on the colloid. Discharge of the platinum colloid occurs via the reduction of surface-bound protons so that hydrogen gas is evolved and the overall reaction corresponds to the photochemical dehydrogenation of ethanol.

$$C_2H_5OH = CH_3CHO + H_2 \qquad \text{(v)}$$

This overall reaction stores some 42 kJ/mol but, since the benzophenone derivative collects such a small fraction of the incident sunlight, it operates with only a low sunlight conversion efficiency (about 1.7 per cent). Of course, this is a problem as far as developing the system for practical purposes is concerned, but to some degree, it is offset by the simplicity and versatility of the system. This situation is exemplified by the experimental results collected in the Table. Here, the quantum yields for formation of hydrogen, Φ_{H_2}, have been measured for a variety of different organic substrates (7). It is clear that almost any hydrogen containing organic material can be photodehydrogenated under such conditions. The turnover numbers refer to the ability of the benzophenone to be recycled before pinacol formation finally destroys it. The relatively high numbers obtained show that the platinum colloid used in these experiments is extremely efficient at intercepting the intermediate ketyl radicals and directing them towards water reduction. The limiting yields of hydrogen obtainable upon exhaustive photolyses are impressive and compare favourably with all other photosystems

reported to date. Also, it should be noted that the reaction employs only low concentrations of organic materials. With efficient donors, the required concentration of organic substrate is only about 1 per cent v/v in aqueous solution. This is the order of concentration that might be found in effluents from industrial processes and the photosystem could be used to purify water supplies.

Some other water-soluble benzophenone derivatives can be used in much the same manner as reported here for I (5, 6). These compounds are cheap, easily prepared on a large scale, non-toxic and relatively stable. Opportunities do exist for improving their light harvesting properties without detracting from their high efficiencies. Indeed, we are actively engaged in modifying the structure of the benzophenone photosensitiser in order to collect a much higher fraction of the solar spectrum.

The Catalyst

It is important that the catalyst is able to intercept ketyl radicals generated in the bulk solution before they react with each other. This kinetic problem can be solved by careful control of the light intensity and concentration of each reactant in such a way that the steady-state concentration of ketyl radicals is kept at a minimum. To ensure high rates of hydrogen formation, it is necessary to use high concentrations of catalyst and this is best achieved by employing ultrafinely dispersed particles. Indeed, for a given molar concentration of platinum the pseudo first order rate constant for trapping a ketyl radical (k_1) can be expressed in the following form:

$$k_1 = 0.027D \, (Pt)/R^2 \qquad (vi)$$

Here, D is the diffusion coefficient of the ketyl radical (D = 8×10^{-6} cm^2/s) and R is the radius of the platinum particle (expressed in nm). It is seen clearly that k_1 increases with decreasing particle size. Thus, smaller particles give a definite advantage in this type of competitive reaction system.

Producing small particles is not the only means of ensuring that the catalyst can intercept self-annihilation of the reducing radicals. And, by the same reasoning, having small particles does not guarantee that trapping will be

	Quantum yield of hydrogen ΦH_2	Turnover number	Hydrogen (0.01 mol/dm^3)
Donor			
Triethylamine	1.03	112	5.6
Ethylamine	0.53	112	5.6
Diethylamine	0.09	55	2.7
Methanol	0.24	125	6.3
Ethanol	0.34	139	6.9
Isopropanol	0.32	83	4.1
Tert-butanol	0.23	105	5.3
Lactic acid	0.13	81	4.0
Acetamide	0.12	63	3.1
Glucose	0.10	56	2.8
Acetonitrile	0.075	54	2.7
Acetaldehyde	0.014	18	0.9
Acetic acid	0.0002	1	0.6

Table

Efficiency of Hydrogen Generation upon Ultraviolet Irradiation of Compound I in Nitrogen-Saturated Aqueous Solution at pH9 Containing Colloidal Platinum (2×10^{-4} mol/dm^3) and a Donor (usually 4 per cent v/v)
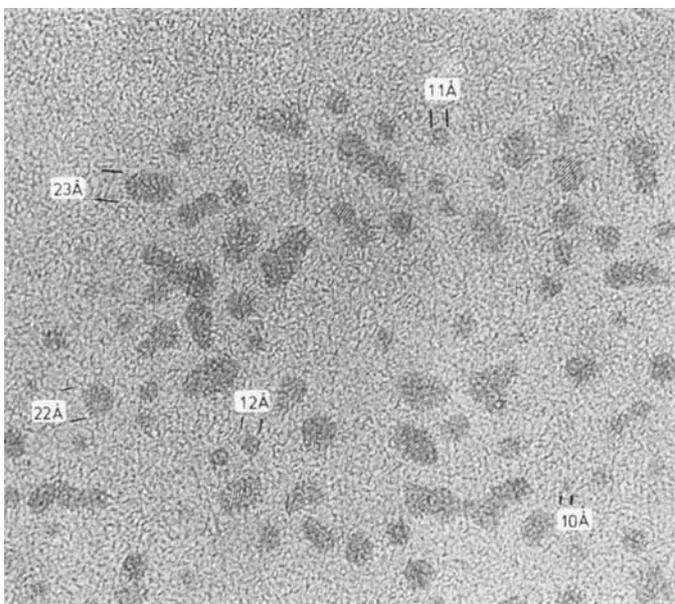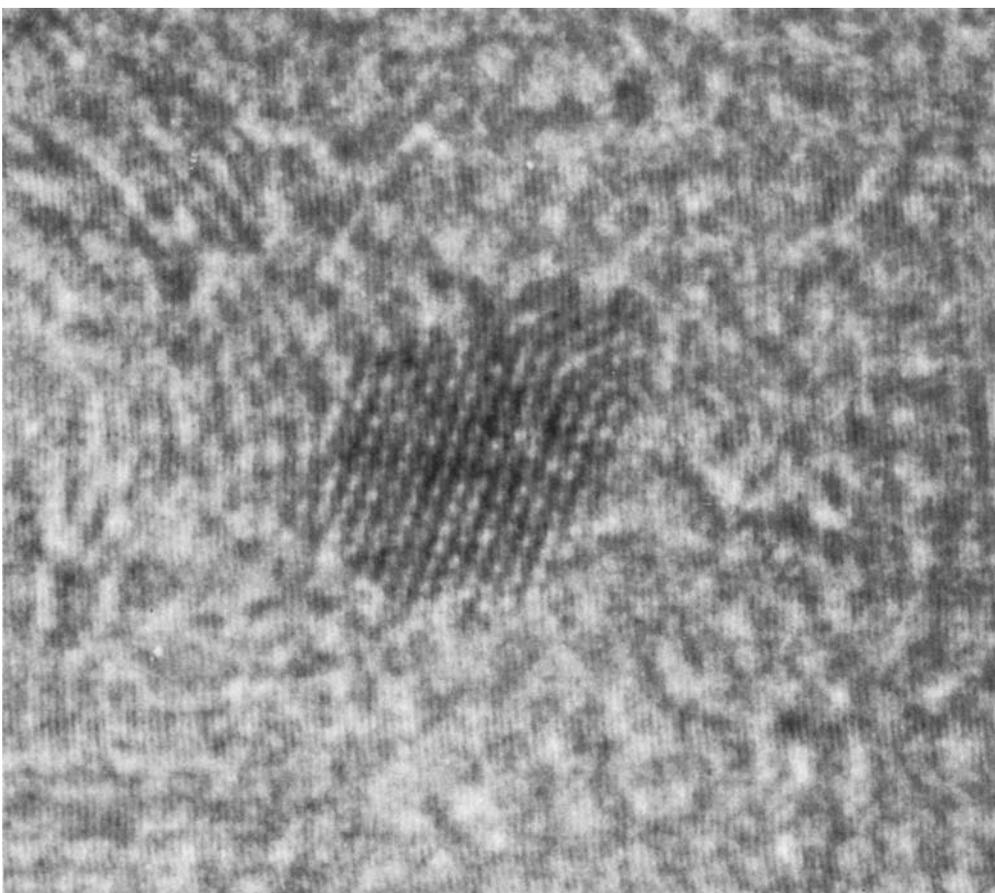
Fig. 2(a) This electron micrograph shows freshly prepared colloidal platinum particles. The colloid is stable against flocculation for several months

Fig. 2(b) (below) A high resolution transmission electron micrograph of a colloidal platinum particle showing the arrangement of the platinum atoms within the lattice. Further details are given in (12)

effective. Consideration must be given to other factors, especially electrostatic forces and radical mobility. The colloidal particle will carry a surface charge due to ionisable groups. The sign and magnitude of this charge can be varied by pH and by adsorbing charged surfactants to the metal surface. In this way, charged radicals in the bulk solution will be attracted to or repelled from the colloid surface. In general, it is not good policy to use strong electrostatic forces to attract radicals of the opposite charge to the colloid. This is because the catalyst surface becomes coated with highly reactive intermediates, such as hydrogen atoms, during the reaction. These species react with most organic and inorganic compounds, either to short-circuit the overall reaction or to reduce unsaturated bonds. The importance of these side-reactions is increased markedly in cases where the contact time between catalyst and reactant is increased by electrostatic binding (6).

Also, when considering the problems of kinetic control of the reaction balance, some thought should be given to the mobility and electron transferring properties of the reducing radical. For example, ketyl radicals generated by hydrogen atom abstraction are produced in very close proximity such that their interaction is favoured. Unless the radicals can freely migrate away from each other recombination will dominate. The ease of mobility is expressed by the diffusion coefficient D in Equation (vi) and it is related to the solvent viscosity and the molecular volume of the ketyl radical. Furthermore, it is desirable that electron transfer to the colloidal particle occurs with high efficiency so that each encounter transfers an electron to the particle (8). If the electron transferring properties of the reducing radical are poor, due to a large reorganisation barrier or slow self-exchange rates, many encounters between a radical and a colloidal particle might be needed before electron transfer occurs. Competitive addition or dimerisation reactions might dominate over electron transfer in such cases, even if the reaction conditions favour encounter with a catalyst particle.

A further point to take into account concerns the actual structure of the colloidal particle. It is possible that much of the surface is inert due to adsorbed surfactant or unreactive groups. Electron transfer will occur only at clean metal surfaces and this introduces the concept of "active sites". For such catalysts, a reducing radical might have to encounter many different particles before it finds an active site where it can disgorge its electron.

Ultrafine Colloidal Particles

It is now possible to produce ultrafine dispersions of many different metals by controlled hydrolysis and reduction of the corresponding metal salts. Extremely small particles (R<1.0 nm) are afforded by gamma radiolysis of the metal salts in aqueous alcohol solution under an inert atmosphere (8–10). Slightly larger, but still very finely dispersed, colloids are obtained by reduction with citrate ions in water at elevated temperatures (11). We have found that reduction of sodium hexachloroplatinate (8×10^{-4} mol/dm^3) in neutral water with sodium citrate (3×10^{-3} mol/dm^3) at 70°C occurs over 3 to 4 hours. After cooling overnight, the excess citrate ions can be removed by ion-exchange chromatography and the colloid protected by a low molecular weight polyethyleneglycol. The resultant colloid, which is stable against flocculation over many months standing, has an average particle radius of only 0.7 nm, as determined by high resolution electron microscopy. This is shown in Figure 2(a).

Recently, the structures of platinum and gold colloids were studied by transmission electron microscopy (12). It was shown that the platinum colloids are highly crystalline with the interplanar spacings, atomic environments and degree of translational symmetry as expected for crystalline bulk platinum electrodes. However, the colloids show a high tendency for micro-twinning and there is considerable surface roughness. Such factors can be seen by close examination of the high resolution electron micrograph shown as Figure 2(b).

Colloids of other metals, such as gold, silver, thallium, iridium, ruthenium, palladium and

nickel, can be produced by similar methods. In general, the average particle sizes and distributions depend upon the rate of reduction of the metal salt and upon the nature of the metal. For example, under the same experimental conditions, colloids of platinum and iridium tend to give very small particles with average radii of 0.7 to 1.0 nm, colloids of silver tend to be somewhat larger with average radii 3.0 to 4.0 nm and colloids of gold possess radii around 6.0 to 7.0 nm. The crystal structures of these colloids are being studied by high resolution electron microscopy and, very recently, bimetallic particles of gold and platinum have been prepared in colloidal form (13).

All the above colloids show catalytic properties and many are efficient catalysts for promoting the reduction of water to hydrogen. In particular, colloids of platinum or iridium favour hydrogen evolution when brought into contact with reducing species, such as ketyl radicals. Kinetic parameters associated with these reactions can be obtained from pulse radiolysis or flash photolysis studies and are useful for optimising experimental conditions.

Interfacial Electron Transfer

Once the reducing radicals reach the surface of the colloidal particle, an electron transfer reaction can occur. This reaction must take place across a liquid/solid interface, as occurs in conventional electrochemistry. As such, it seems appropriate to consider the particle as a microelectrode and to describe the redox reaction in electrochemical terms. Two aspects of the overall reaction should be considered; namely, charging the particle with electrons and discharging the particle by transferring the electrons to protons or other reagents in the bulk solution. Kinetic parameters associated with the charging process are readily obtainable by pulse radiolysis methods and there have been many such studies. It is more difficult to follow the discharge process but some success has been obtained from time-resolved conductivity studies.

Both the benzophenone ketyl radical and the 1-hydroxyethyl radical produced in Reaction (ii) are powerful reducing species that are thermodynamically able to reduce water to hydrogen. The two radicals donate electrons to colloidal platinum particles at the diffusion controlled rate limit, at least in neutral aqueous solution. The rate constants for these electron transfer reactions have been evaluated by pulse radiolysis studies (3, 6). Thus, the ketyl radical derived from I, which retains a single positive charge in neutral solution, can be monitored by optical absorption spectroscopy since it absorbs at 540 nm. Decay occurs by second order kinetics, due to rapid dimerisation ($k_3 = 4.8 \times 10^8$ dm^3/mol/s), with a half-life of about 1 ms. The addition of colloidal platinum increases the rate of decay but the kinetics remain complex until the concentration of added platinum exceeds about 10^{-4} mol/dm^3. Using a platinum concentration of 2×10^{-4} mol/dm^3, the observed half-life of the ketyl radical is only 85 μs. This suggests that all the ketyl radicals are trapped by the platinum particles under such conditions. In contrast, a ketyl radical bearing a single negative charge under identical experimental conditions had a half-life of 1.25 ms and corresponded to only 25 per cent trapping.

The platinum colloid used in these experiments had a particle radius of 1.0 nm, as determined by electron microscopy. This means that there is an average of 280 platinum atoms clustered into a single particle. Taking this factor into account, the bimolecular rate constant for interaction between the particle and a ketyl radical derived from I was 1.4×10^{10} dm^3/mol/s. This interaction is assisted by electrostatic terms since the platinum colloid has a negative surface charge. Consequently, the bimolecular rate constant for the corresponding reaction with a negatively charged ketyl radical was found to be some twenty times lower.

This interfacial reaction involves transfer of an electron from a ketyl radical to the platinum particle. The added electron can migrate around the crystalline platinum particle or it may be trapped at the surface in the form of a hydrogen atom by reaction with an adsorbed

proton. Further electrons can be added to the same platinum particle, although the rate constant for the electron transfer step may depend upon the number of electrons already residing on that particle. These accumulated electrons may be discharged by reduction of adsorbed protons to hydrogen. Where many electrons are added to a single particle, the discharge process will be intraparticle but in cases where few electrons are stored on a single particle, that is when high concentrations of catalyst are used, discharge may involve an interparticle reaction.

It is important to bear in mind that the particles may be discharged in ways other than via the reduction of surface bound protons. Thus, easily reducible substrates present in the system are liable to be reduced in preference to hydrogen liberation. This becomes especially important as the hydrogen evolution reaction proceeds since the platinum particles retain a number of hydrogen atoms on the surface which can be added to unsaturated groups.

Reaction Products

The above photosystem has been optimised for the generation of hydrogen. Over the early part of the reaction at least, the benzophenone photosensitiser is recycled and it is not destroyed. During the later stages of the reaction, when the catalyst is charged with hydrogen atoms, the benzophenone is reduced to the corresponding alcohol. This stops further hydrogen evolution since the alcohol is not photoactive. As shown by Equation (v), the evolved hydrogen comes from the organic donor and, as such, the system is sacrificial. The advantage of the present system is that it is extremely simple and it will operate with a very wide range of donors, some of which are genuine waste products. It is not dependent upon any particular type of donor or pH, and it is not easily poisoned so that a mixture of waste organic materials could be fed into a reactor charged with the photosensitiser. It seems possible that a practical system could be developed based on this type of photosystem.

Dehydrogenation of the organic donor could, in principle, give rise to some interesting products. With an alcohol as donor, the reaction forms an aldehyde which can be treated with ammonia to give a primary amine. The aldehyde will also react with hydrogen cyanide and subsequent hydrolysis will give a hydroxyacid. Further reaction with hydrogen cyanide and an amine permits formation of simple amino acids. Thus, a whole range of simple organic products are possible and the overall system has some interest as a model for the primordial synthesis of complex organic matter.

When platinum or iridium colloids are used to trap the intermediate ketyl radicals, the major reaction product is hydrogen, as described above. This is because these metals possess extremely low overpotentials for hydrogen evolution. Consequently, as soon as electrons are added to a particle they are discharged via hydrogen formation and, at any given time, there will be very few electrons stored on a particular particle. However, with other metal colloids this need not be the case. For example, gold colloids favour hydrogen liberation but silver colloids show a higher overpotential for hydrogen evolution and will exist for a finite time in aqueous solution with many tens of electrons stored on a single particle. Colloids of cadmium or thallium show even more resistance towards hydrogen liberation and many hundreds of electrons will reside on a particle. Upon addition of suitable substrates, these electrons can be discharged and used to drive multielectron reductions. Of particular importance are the reductions of carbon dioxide, on ruthenium colloids, and nitrate ions, on silver colloids. It is possible that future work will lead to the development of a system able to reduce nitrogen to ammonia, a reaction of tremendous significance.

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Coefficients of Thermal Expansion

NEW DATA ON PLATINUM AND PLATINUM-RHODIUM ALLOYS

The importance of an accurate knowledge of the properties of key reference materials such as platinum and its alloys has been emphasised here previously (1). For example, accurate values of thermal expansion are required in high temperature "constant volume" gas thermometry, where failure to take account of the unavoidable changes in the volume of the gas-containment bulb with temperature can lead to errors of several per cent in the measurement of the pressure ratios.

In support of its programme on gas thermometry, the National Bureau of Standards, Gaithersburg, U.S.A., has recently reported on the construction of apparatus for the measurement of thermal expansion, which allows changes in length to be measured to an accuracy of 1 part per million and temperature determinations to be made to within 0.01°C (2). In this paper, R. E. Edsinger, M. L. Reilly and J. F. Schooley also describe the use of the apparatus for measuring the thermal expansions of 99.95 per cent pure platinum and of two platinum-rhodium alloys, nominally containing 12 and 20 weight per cent rhodium, in the temperature range −27 to +570°C. The samples used were taken either from surplus materials used in the construction of bulbs for the Gas Thermometer or from pieces cut from used gas bulbs, all generally about 1mm thick.

Optical interferometry was selected as the means of measuring the dimensional changes, using the Merritt-Saunders technique, and the samples were heated in a multi-chambered, sealed furnace, based on a design by H. F. Stimson. A quartz window, to allow interferometric measurement, and a platinum resistance thermometer are incorporated into the furnace, which is capable of evacuation, so allowing variations in both the gas pressure and the type of gas employed. The platinum resistance thermometer was calibrated according to the IPTS-68 standard procedures.

The data obtained for the pure platinum and platinum-rhodium samples were analysed and fitted to 4th degree polynomial equations. From these equations, the values of the per cent linear expansion and hence the coefficient of linear expansion were calculated. These results show that substitution of rhodium into the platinum lattice reduces its thermal expansion in the range 0 to 350°C, then causes it to increase at higher temperatures.

A comparison of the results obtained in this study with previous work for pure platinum shows reasonable agreement, to within ±20ppm; the current work generally showing larger values for the linear expansion. Similar comparisons for platinum-20 per cent rhodium show very close agreement with some earlier results; but there were differences of about 50 ppm with the data of Barter and Darling (3).

In summary, this work has provided improved, more accurate data on the thermal expansions of platinum and platinum-rhodium alloys.

C.W.C.

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