

The Gaseous Oxides of the Platinum Metals

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This paper reviews the experimental techniques used in the elucidation of the thermodynamics of the volatile oxides of the platinum metals in the temperature range 1200 to 1800°C. It is shown how the molecular formulae of the gases were obtained, and free energy equations of the two-term type are given for PtO₂, RhO₂, IrO₃, RuO₃ and OsO₃. At other temperatures oxides of different compositions may predominate, and approximate methods for calculating the thermodynamics of these from the present data are given.

The platinum metals all show an increased volatility when heated in oxidising atmospheres, compared with the volatility due to evaporation as metal atoms that occurs in vacuum or inert gas atmospheres. The study of the thermodynamics of volatile oxide for-

mation has recently been advanced to a stage where it can reasonably be said that we now have a practically complete knowledge of both the molecular composition and the free energies of formation of all of the important species. Therefore the calculation of the *maximum* rates of volatilisation of the elements, both as a function of temperature and of oxygen partial pressure, can be made with a high degree of accuracy, both over pure metals and over alloys where the activities of the noble metals are known.

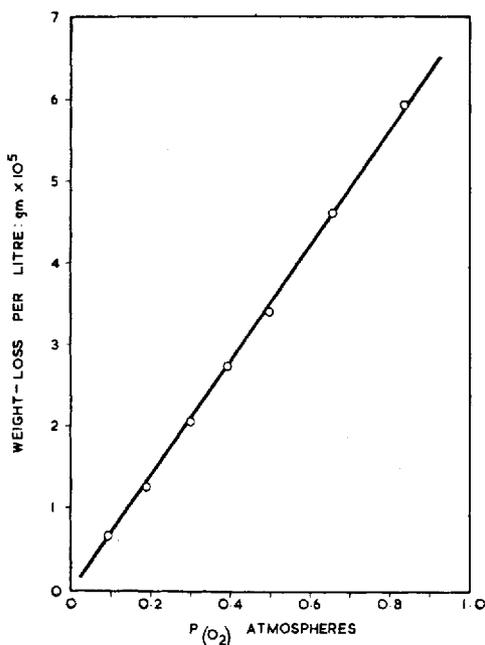
The experimental techniques that have yielded these results are best described by dealing with the individual elements, and we will first discuss the oxide of platinum, PtO₂(l).

Platinum

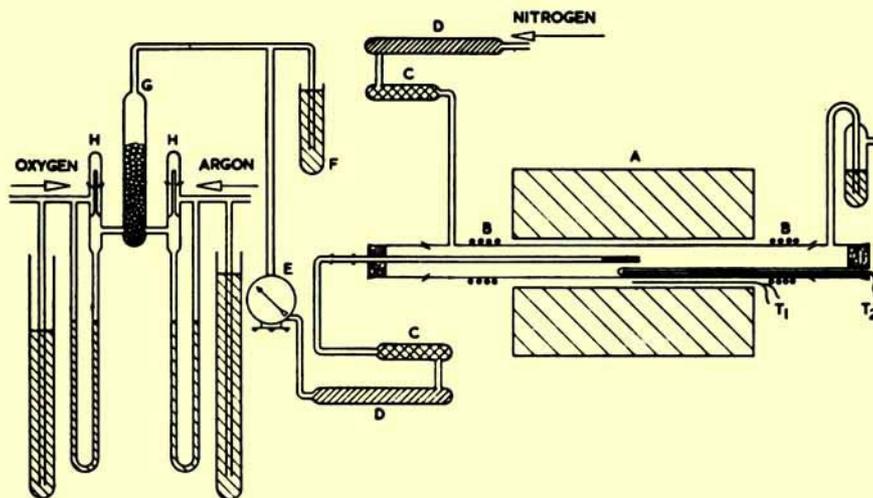
If platinum forms the gaseous oxide Pt_xO_y, then the equilibrium constant for the formation of the oxide from metal and oxygen at a temperature, T, is expressed by

$$K_T = \frac{p_{\text{Pt}_x\text{O}_y}}{a^x_{\text{Pt}} \cdot p^{y/2}_{\text{O}_2}} \quad (1)$$

In the case of the oxidation of pure platinum ($a_{\text{Pt}} = 1$) the pressure of the oxide will depend on the $y/2$ th power of the oxygen pressure



The weight loss of platinum, under equilibrium conditions at 1400°C, for unit volume of transporting gas, as a function of oxygen pressure



Apparatus for the measurement of vapour pressures by the transportation method

- | | |
|---|--|
| <i>A Resistance-heated furnace</i> | <i>F Blow-off</i> |
| <i>B Reaction tube and cooling coils</i> | <i>G Gas mixing chamber</i> |
| <i>C Drying tubes (anhydron) for transporting gas</i> | <i>H Capillary flowmeters</i> |
| <i>D Silica gel drying tubes</i> | <i>T₁ Thermocouple for furnace control</i> |
| <i>E Gas meter</i> | <i>T₂ Thermocouple for the measurement of even-zone temperature</i> |

only. Thus if we compare the weight losses of a piece of platinum which is brought successively to equilibrium with gases of known oxygen partial pressure passing at a known flow rate for a known time, and at a constant temperature, then a plot of the weight loss of platinum per litre of gas passing over the sample against pO_2 will be linear when the correct choice of y has been made. A typical result at $1400^\circ C$ with $y=2$ is shown in the graph on page 134.

The weight loss of the sample has here been used as a measure of the partial pressure of the gaseous oxide. Of course the pressure of a species containing two atoms of platinum per molecule would be half that of one containing one atom per molecule, but although this would affect the scale on the ordinate, it would not affect the linearity test.

The transportation method used in these experiments was arranged so that the metal, in the form of 80 mesh gauze, was brought

into intimate contact with all of the oxygen passing through the apparatus, thus assuring the attainment of equilibrium. This was achieved by passing the metered mixture of oxygen and nitrogen through a narrow bore refractory tube which ended at the thermal centre of the furnace. At the open end of this tube a weighed roll of gauze was inserted so as nearly to fill the tube. It was found, by varying the flow rate of the gas, that the weight loss of platinum per litre of gas passed at constant temperature was independent of gas flow rate over a wide range of flow rates, thus clearly indicating that equilibrium had been achieved. Details of the transportation apparatus are shown in the diagram above.

The next part of the research was to establish the number of platinum atoms in the molecule by measuring the weight losses, at constant temperature and oxygen pressures, of platinum alloys. The choice of an alloying element was very restricted here since the

alloying element must have the following properties.

- (1) It must not form a volatile oxide or a condensed oxide under the conditions of the experiments.
- (2) The metal must have a measurable, although not too high, vapour pressure so that its thermodynamic activity in the alloys could be measured and from these the platinum activities could be calculated. With the low vapour pressure and chemical inertness of platinum it was clearly necessary to be able to measure the activity of the alloying element in order to arrive at the otherwise unmeasurable activity of platinum by means of the Gibbs-Duhem relation.
- (3) It must form alloys with platinum over a reasonable range of compositions.

Fortunately gold has all of these properties.

It was not necessary to know the absolute values of the platinum activities since the value of x could be obtained from experiments where the *difference* in platinum activities was known at two atom fractions N and N' .

Thus

$$\frac{p' \text{Pt}_x \text{O}_2}{p \text{Pt}_x \text{O}_2} = \frac{a'^x_{\text{Pt}}}{a^x_{\text{Pt}}}$$

from equation (i) at constant T and $p\text{O}_2$.

Hence $\log p'_{\text{Pt}_x \text{O}_2} - \log p_{\text{Pt}_x \text{O}_2} = x (\log a'_{\text{Pt}} - \log a_{\text{Pt}})$ (ii)

But by the Gibbs-Duhem relationship

$$\log a'_{\text{Pt}} - \log a_{\text{Pt}} = - \int_N^{N'} \frac{N_{\text{Au}}}{N_{\text{Pt}}} d \ln a_{\text{Au}} \quad (\text{iii})$$

Thus combining (ii) and (iii) and noting that $\log p'_{\text{Pt}_x \text{O}_2} - \log p_{\text{Pt}_x \text{O}_2}$ is equal to $\log W'_{\text{Pt}} - \log W_{\text{Pt}}$ where W is the weight loss/litre of gas

$$\log \frac{W'_{\text{Pt}}}{W_{\text{Pt}}} = -x \int_N^{N'} \frac{N_{\text{Au}}}{N_{\text{Pt}}} d \ln a_{\text{Au}}$$

Therefore gold partial pressures over a range of liquid compositions at a temperature of 1550°C were measured in the transportation apparatus using nitrogen as the transport-

ing gas and the same alloys were then oxidised in pure oxygen at the same temperature in the apparatus. The weight losses under nitrogen were used to calculate the difference in platinum activities, and the weight losses in oxygen minus those in nitrogen were used to fix x as having the value one.

Finally now that the composition of the volatile oxide was known, the heat and entropy of formation of PtO_2 were obtained by measuring the weight loss of platinum in pure oxygen as a function of temperature since

$$- \frac{\Delta H^\circ}{R} = \left(\frac{d \ln p \text{PtO}_2}{d \frac{1}{T}} \right) p\text{O}_2$$

$$\text{and } \Delta G^\circ = -RT \ln p \text{PtO}_2;$$

$$-\Delta S^\circ = (\Delta G^\circ - \Delta H^\circ)/T$$

under these conditions with the standard states of pure solid platinum, and oxygen and platinum dioxide at one atmosphere pressure.

Rhodium

Exactly similar studies of the dependence of the weight loss of a spool of rhodium wire as a function of oxygen pressure at constant temperature served to establish the number of oxygen atoms in this molecule as two.

Alloying with gold was not useful, due to the very narrow range of gold-rich alloys which are formed at about 1500°C , as a means for establishing the number of rhodium atoms. A less rigorous method was used relying on the established knowledge of PtO_2 .

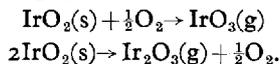
The platinum-rhodium phase diagram shows a continuous range of solid solutions together with a narrow solidus-liquidus lens. This suggested that the alloys were approximately ideal in the Raoult sense, that is that the activity of each component was equal to its atom fraction in the alloy. Weight loss studies in pure oxygen at 1400°C were therefore made on a series of platinum-rhodium alloys and from these, after deduction of a PtO_2 pressure which was calculated assuming ideality for platinum in the alloys, the weight loss assuming $x=1$ and $x=2$ in Rh_xO_2 were

calculated and compared with the measured ones. It was found that close agreement could be obtained if $x=1$ and $a_{\text{Rh}}=N_{\text{Rh}}$, but if $x=2$ there would have to be large positive deviations from ideality in the platinum-rhodium alloys. Thus the molecule was RhO_2 .

Iridium

The oxygen dependence measurements gave three atoms per molecule for the gaseous oxide of this element, and the number of iridium atoms was found by an interesting method devised by Schäfer (2).

Iridium forms a solid oxide in air which is stable up to about 1200°C . If one studies the weight loss, under saturation conditions, of IrO_2 samples as a function of oxygen pressure then this should depend on $p^{3/2}\text{O}_2$ for IrO_3 and $p^{-1/2}\text{O}_2$ for Ir_2O_3 thus



The former dependence was established by Schäfer and Heitland (2).

Ruthenium

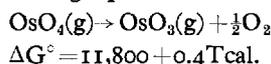
In preliminary studies, it was shown that the weight loss of a ruthenium sample heated in oxygen-nitrogen mixtures at 1280°C varied as $p^{1/2}\text{O}_2$. Schäfer, Gerhardt and Tebben (3) have subsequently shown that the solid oxide RuO_2 is stable at this temperature and oxygen pressures and thus it may be concluded that the gaseous molecule is RuO_3 . The stability of RuO_2 is confirmed by the recent work of Shchubarov and Ryabov (4), who have shown, calorimetrically, that the heat of formation of RuO_2 is -73 ± 1 Kcal/mole and not -52.5 Kcal as previously thought. Hence by combining this result with an estimated entropy content of RuO_2 of 14.5 e.u. at 298°K , and using the results for the volatility of RuO_2 in oxygen, the equation given below for the formation of RuO_3 was calculated.

Osmium

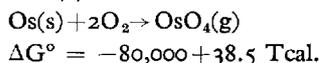
Recent studies using the mass spectrograph (5) have shown that at high tempera-

tures the species OsO_3 and OsO_4 are formed. In these experiments a sample of osmium was heated in a refractory Knudsen cell in which a low pressure of oxygen could be maintained. The vapour effusing from the cell was analysed mass spectrographically and found to contain ions derived from OsO_3 and OsO_4 molecules.

From the results given in this letter, the following equation was obtained



and using data given by Kubaschewski and Evans (6)

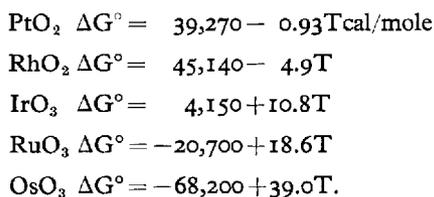


Palladium

This metal has a far higher vapour pressure than the other members of the series, and consequently the metal volatility interfered with attempts to measure the volatility due to gaseous oxide formation by the transportation method. An increase in weight loss of about 20 per cent was found at 1500°C when oxygen was substituted for nitrogen.

Summary of the Results

The results of all of these measurements can now be collected together to give free energy of formation equations. These are:



The standard states for these equations are the pure solid metal, and oxygen and the volatile oxide at one atmosphere pressure. Thus the pressure of the volatile oxide over the metal in pure oxygen at a temperature T is given by

$$p\text{MO}_x = \text{antilog} \frac{-\Delta G^\circ_T}{4.576T} \text{ in atmospheres.}$$

In surveying the results of these measurements, one is led to ask why the particular

species have been found to be stable in the experimental temperature region. Thus why PtO₂ rather than PtO or PtO₃? (We shall neglect the possibility of polymer formation, e.g. Pt₂O₂.) The answer to this question can be indicated by the following considerations.

The bond energies in a series of gaseous oxides of a given element, that is the energy evolved when the separated atoms are brought together to form the molecule divided by the number of linkages which are formed, usually follows thus

$$E_{M-O}^{MO} \geq E_{M-O}^{MO_2} > E_{M-O}^{MO_3} > E_{M-O}^{MO_4}$$

and so on, thus as each extra bond is formed the extra amount of energy which is gained decreases, excepting possibly when going from one oxygen atom bonded to two atoms bonded. If this value were constant, then the energy of formation of MO_n from metal M and oxygen gas would be given by

$$\Delta E = n(E_{M-O} - E_{O-O}) + \Delta E \text{ evap.}$$

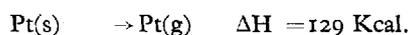
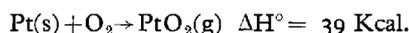
where E_{O-O} is half the dissociation energy of oxygen gas, O₂, and ΔE evap. is the vapourisation energy of the metal M.

Summing up, we would expect the heat of formation from metal and oxygen gas (O₂) to be the greatest, that is most negative, for the species involving the greatest number of oxygen atoms. Thus for example, OsO₄(g) should have a greater heat of formation than OsO₃(g), and so on. However the entropy changes of formation will be, very approximately, +20, 0, -20, -40 entropy units for

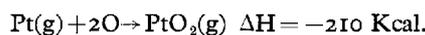
the formation of one mole of MO, MO₂, MO₃, MO₄ from metal and oxygen (O₂) gas.

Therefore at low temperatures MO₄ is predominant, but at the highest temperatures MO must predominate. Hence we see that it is untrue to speak of one molecular species of gaseous oxide being formed by a metal, and it is better to say that there is a temperature range in which one species will be predominant.

Applying these considerations to platinum, we know that for the reaction



Therefore



$$E_{\text{Pt-O}}^{\text{PtO}_2} = -105 \text{ Kcal.}$$

Then

$$\Delta H_{\text{PtO}}^\circ \sim (-105 + 60 + 129) = 85 \text{ Kcal.}$$

$$\Delta G_{\text{PtO}}^\circ \sim 85,000 - 20T \text{ cal.}$$

$$\Delta H_{\text{PtO}_3}^\circ \sim (-315 + 180 + 129) = -6 \text{ Kcal.}$$

$$\Delta G_{\text{PtO}_3}^\circ \sim -6,000 + 20T \text{ cal.}$$

These equations clearly apply to the formation of the gaseous oxide from metal and diatomic oxygen gas.

One of the most useful applications of these results is in the calculation of the weight losses of the elements in various atmospheres over a range of temperatures. The calculated

Weight Losses of the Platinum Metals in Grams of Metal per Litre of Gas						
Metal	T = 1500°K (1223°C)			T = 2000°K (1723°C)		
	Inert Atmosphere	PO ₂ = 10 ⁻³	PO ₂ = 1	Inert Atmosphere	PO ₂ = 10 ⁻³	PO ₂ = 1
Palladium	5 × 10 ⁻⁷	—	ca 7 × 10 ⁻⁷	4 × 10 ⁻³	—	—
Platinum	v. small	3 × 10 ⁻⁸	3 × 10 ⁻⁵	9 × 10 ⁻⁷	2 × 10 ⁻⁶	7 × 10 ⁻⁴
Rhodium	v. small	2 × 10 ⁻⁸	2 × 10 ⁻⁵	5 × 10 ⁻⁷	10 ⁻⁶	7 × 10 ⁻⁴
Ruthenium	v. small	10 ⁻⁶	4 × 10 ⁻¹	v. small	10 ⁻⁶	7 × 10 ⁻²
Iridium	v. small	4 × 10 ⁻⁸	9 × 10 ⁻³	v. small	5 × 10 ⁻⁸	10 ⁻³

losses will, of course, be the *maximum* losses, assuming that equilibrium is reached. The table shows some results for temperatures of 1500 and 2000°K, and for atmospheres of an inert gas, a rough vacuum, $pO_2 = 10^{-3}$ atmospheres, and 1 atmosphere of pure oxygen, in grams of platinum-group metal

per litre of gas. (The values have been rounded to the nearest integer.)

The weight losses for the elements were calculated by using Brewer's estimates (7) for the vapour pressures, except in the case of palladium for which results have been reported by Alcock and Hooper (8).

References

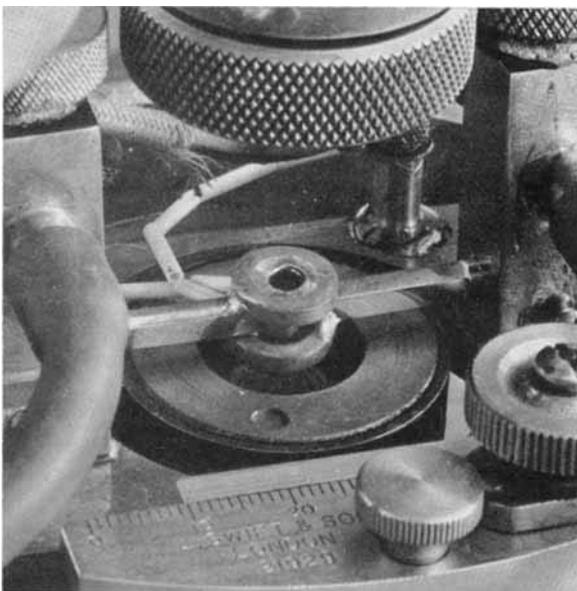
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A High Temperature Research Microscope

NEW DESIGN OF PLATINUM MICRO-FURNACE

For the study of crystallisation phenomena in glass and for the construction of phase diagrams a high temperature polarising microscope is needed capable of examining specimens at temperatures up to 1400°C. A new type of micro-furnace for use in this way on a microscope stage has recently been designed by N. Murphy, of Pilkington Brothers Research Laboratories. This consists of a 3 mm diameter vertical open-ended tube in 10 per cent rhodium-platinum, partitioned about its centre by a foil diaphragm which serves as a support for a cone-shaped rhodium-platinum crucible. The current leads are of 3 mm square section rhodium-platinum. Equilibrium temperatures are at-

tained very quickly, and can be measured accurately by means of a 0.012 mm diameter platinum thermocouple accurately located in contact with the specimen.



The platinum micro-furnace unit mounted on the stage of the microscope