

# Thermochemistry of the Platinum Metals and their Compounds

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The word "thermochemistry" may seem to have an unduly academic ring to it, far removed from the world of the experimental chemist, and indeed in the case of the platinum metals the information on the subject is so widely scattered in the literature (and often in obscure journals) that it may seem to have little practical relevance. However, when properly handled, such data on the stabilities of the elements and their compounds can be helpful to the experimentalist for they afford a quantitative basis to the very fundamental problem of whether a given chemical reaction will proceed or not.

The appearance of a comprehensive and critical review on the thermochemistry and oxidation potentials of the six platinum group metals and their compounds is therefore timely and welcome. This, prepared by R. N. Goldberg and L. G. Hepler (1) at the Carnegie-Mellon University, Pittsburgh, brings together a mass of previously uncorrelated information, more particularly concerned with the aqueous solution chemistry of the compounds. It is the purpose of this note to indicate the scope of the review, the information that it presents and the use that may be made of it.

For each element there is a brief but well-informed discussion of its descriptive chemistry, followed by a table of thermodynamic data for the metal and its compounds; the approach here is selective and critical, and the authors clearly indicate the value they attach to the reported results. Each section also includes data on oxidation potentials, equilibrium constants and related matter, while oxidation potential diagrams are given for various metal oxidation states in acidic and in

basic solutions. The general arrangement of material is very similar to that in Latimer's well-known book (2) and to anyone acquainted with that work the present review should cause no difficulties.

For each metal and such compounds for which data are available the following three quantities are listed (all refer to the standard temperature of 298°K):

$\Delta H_f^\circ$ , the standard heat of formation of the compound from its elements;

$\Delta G_f^\circ$ , the free energy of formation of the compounds from their elements;

$S^\circ$ , the standard entropies of the elements and their compounds.

The  $\Delta H_f^\circ$  values are obtained from calorimetric or vapour pressure data,  $S^\circ$  by calculation from specific heat or spectroscopic measurements, and  $\Delta G_f^\circ$  from the equation

$$\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S^\circ$$

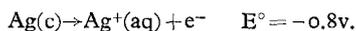
where  $T=298^\circ\text{K}$  and  $S$  is the *difference* between  $S^\circ$  values of the reaction products and reactants.

For species in aqueous solution,  $\Delta G_f^\circ$  values are difficult to measure accurately but may be obtained by measurements of the standard electrode potential  $E^\circ$  of the reaction under consideration:

$$\Delta G^\circ = -nFE^\circ = -23.06nE^\circ$$

(where  $n$  is the number of electrons involved in the cell reaction and  $E^\circ$  the standard oxidation potential, in volts;  $\Delta G^\circ$  is then in Kcals/mole). The sign convention used here for  $E^\circ$  is (regrettably) not the one recommended by the IUPAC convention but is that used in Latimer's book and a number of

other texts; e.g. for the cell reaction



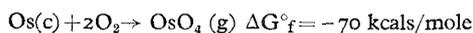
All the cell reactions are written as oxidations; i.e. with the electrons on the right-hand side.

The equation

$$\Delta G^\circ = -RT \ln K = -1.360 \log_{10} K$$

is also used to calculate  $\Delta G^\circ$  for some reactions ( $T=298^\circ\text{K}$ , and  $K$  is the equilibrium constant of the reaction).

From these data  $\Delta G^\circ_f$  values are tabulated for a number of compounds in the solid and (occasionally) gaseous states and for aqueous solutions. This standard free energy of formation is the most useful thermodynamic quantity for practical application; if it is negative, as in



the reaction should proceed spontaneously in the direction indicated. However, this tells us nothing of the rate of such a reaction, merely that it is thermodynamically possible. If  $\Delta G^\circ_f$  were large and positive the reaction could not proceed spontaneously, with or

without a catalyst. Of course, by proceeding to non-standard states of reaction the balance may be changed. It is also possible to calculate equilibrium constants for reactions involving the compounds quoted by using these  $\Delta G^\circ_f$  values together with other readily available data.

Potential diagrams are given for the various oxidation states of the elements, and these provide a useful shorthand way of summarising information on the relative stabilities in solution of their various oxidation states.

In short, this review provides at least a foundation for the more quantitative aspects of platinum metal chemistry. It should stimulate further research in a field which, for the platinum group elements, has received less attention than it deserves.

### References

- 1 R. N. Goldberg and L. C. Hepler, *Thermochemistry and Oxidation Potentials of the Platinum Group Metals and their Compounds*, *Chem. Rev.*, 1968, **68**, 229.
- 2 W. M. Latimer, *Oxidation Potentials*, Prentice Hall, Second edition, 1959.

## One Million Ounces of Platinum

### RUSTENBURG'S INCREASED OUTPUT

Since 1964 there has been a fourfold increase in the output of platinum from Rustenburg Platinum Mines, for whom Johnson Matthey are the refiners and distributors. The last big increase was announced a year ago, when extensions to mining and refining operations were put in hand to provide an output of 850,000 ounces of platinum a year.

It has now been decided to expand the rate of production to approximately 1,000,000 ounces of platinum a year, with of course corresponding increases in the supply of rhodium, ruthenium, palladium and iridium.

This decision has been made in the light of current assessments of demand during the next five years, notwithstanding the announcement by Universal Oil Products of a new petroleum reforming catalyst that will utilise platinum more efficiently for a given reforming capacity. This new catalyst will give higher yields, improved stability in operation and increased quantities of by-product hydrogen in the widely used Platforming process while it will also help in reducing the amount of contaminants in high-octane fuels which are contributory to air pollution.



A new shaft headgear in course of construction at Rustenburg