Thermodynamic Properties of the Platinum Metals

AN ANALYSIS AND EVALUATION OF THE DATA

The six platinum metals form a very compact and coherent group, which occupies a strategic position at the right-hand end of the second and third periods of the transition elements. Although very complex, their electronic structure ensures very strong bonding forces, which are reflected by their high melting points, low vapour pressures and extremely high elastic moduli. They also have a strong affinity for metals at the beginning of the second and third long periods and, because of the violent exothermic nature of the reactions that occur, the electronic structure of the platinum metals is of considerable theoretical and practical importance.

Reliable thermodynamic data are therefore needed to provide the raw material from which lattice dynamics, electronic distributions and energy states can be inferred by serious students of the solid state. The thermal data hitherto available on the platinum metals have been scattered among many journals, some of which have not been easily obtainable. The Institute of Basic Standards, National Bureau of Standards, Washington, has therefore satisfied a very real demand by publishing a comprehensive review and critical evaluation of the thermodynamic properties of the six platinum metals from 0 to 300 K. (G. T. Furukawa, M. L. Reilly and J. S. Gallagher, "Critical Analysis of Heat Capacity Data, and Evaluation of Thermodynamic Properties of Ruthenium, Rhodium, Palladium, Iridium, and Platinum. A Survey of the Literature Data on Osmium", *J. Phys. Chem. Ref. Data*, 1974, **3**, (1), 163–209).

This review is written by specialists for specialists. The authors are scrupulous in remaining inside their self-imposed boundaries, so that no effects occurring above 300 K are referred to, nor are the interesting thermodynamic anomalies in the vicinity of superconducting transitions discussed. The importance of the work resides in part in the thorough and comprehensive manner in which the philosophy of modern low temperature calorimetry is discussed, and partly in the mathematical treatment used for the analysis of published thermodynamic information, so that the best values of heat capacity can be selected. An intercomparison between the literature data and the selected values is then provided as a derivative plot. The estimated limits of accuracy of the selected values are also shown in the same plot.

The ardent student of low temperature thermodynamics will find this survey of considerable interest. The physical metallurgist will, however, be somewhat disappointed to find that the sole purpose of this comprehensive tour de force has been to demonstrate that at room temperature, or 300 K, the thermal capacities of the six platinum metals are for all practical purposes almost identical. A slight tendency for the heat capacity value to increase with atomic weight can be detected but it is very marginal. Thus C_p at 300 K is 5.755 for Ru, 5.957 for Rh and 6.193 cal/K/mole for Pd. The corresponding values for Ir and Pt are, respectively, 6.000 and 6.200 cal/K/mole. At lower temperatures these differences are much accentuated and at 10 K, for example, the specific heat at constant pressure of palladium is 4½ times higher than that of ruthenium.

As earlier mentioned, no high temperature thermal information is reviewed in this paper. This is rather disappointing, as a critical analysis of the results of Jaeger and Rosenbohm, and of other early investigators who suggested the possibility of allotropic transformations in ruthenium, would have been of considerable interest. High temperature data would assist any systematic interpretation of the alloying characteristics of the transition elements, and a great weakness of the Engel–Brewer correlation is that the effect of temperature upon solubility does not clearly emerge from the various publications involved.

A surprising feature which emerges from this review is that very little systematic work has been undertaken on the thermodynamic properties of the platinum metals and that few of the measurements reported at temperatures above 20 K have achieved accuracies better than 0.2 per cent. Furthermore, the heat capacity data on ruthenium, rhodium and iridium originated essentially from the same group of laboratories and cover separate portions of the temperature range 0–300 K with no overlap. Data from different laboratories were not available to make intercomparisons and the possibility exists, although each group of results is compatible with the others, that systematic sources of error persist and affect the whole temperature range. So little data on osmium exist that the authors of the review made no attempt to derive the best thermodynamic values and simply present the published information.

More thermodynamic measurements have been made on platinum and palladium than on the other four metals in total, although the best and most accurate information relates to temperatures below 4 K. Two reliable sets of data on palladium do, however, cover the range 100–300 K and this metal is the only one in the platinum group which can be regarded as being fully documented over a reasonable temperature spectrum. In view of the way in which palladium is now regarded as the archetypal transition metal, this concentration of effort is understandable.

This review by three authors represents a considerable expenditure of time, effort and technical resources. It is, therefore, somewhat surprising that the Bureau of Standards was content to leave it as a neutral and impartial presentation of numerical information. Although the metallurgist spends his time attempting to correlate the properties and behaviour of metals with their structures and compositions, no such activity has been attempted in this review. The authors do not indicate the metallurgical condition of the specimens on which they report.

No doubt this information is presented in the original papers but since the object of any comprehensive review of this type should be an avoidance of the time and effort needed for a basic search of the literature one might expect a more rounded approach. No matter how refined and sophisticated the method of numerical analysis which is adopted, the results obtained are of little value if they relate to material which has been inadequately characterised.

A. S. D.

Platinum Catalysts for Odour and Fume Control

Atmospheric pollution by industrial processes is rightly regarded as something which must be eliminated or substantially reduced. At a symposium organised by the Society of Chemical Industry, R. A. Searles of Johnson Matthey Chemicals described how platinum catalyst systems were achieving abatement for three types of air pollution. (*Chem. & Ind.*, 1974 (22, Nov. 16), 895–899).

Odours result when complex organic chemicals are released into the atmosphere and a recent survey showed that catalytic incineration was the most successful means of preventing this. The disposal of waste solvents from processes such as paint drying is essential to avoid potentially explosive situations. Catalytic incineration achieves this and also gives fuel economies. Without preventive measures the production of nitric acid results in the discharge of nitrogen oxides detrimental to life. Reacting these fumes with a fuel over platinum gives harmless nitrogen and water, and by increasing heat recovery results in substantial cost savings.

Highly active catalysts marketed under the registered trade name 'Honeycat' have been developed by Johnson Matthey for use in such forms of pollution control.