

# Practical Aspects of Metallurgical Thermodynamics

## APPLICATIONS TO THE PLATINUM METALS

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*Thermodynamic principles and data are very useful in the solution of industrial problems, particularly in assessing the feasibility and economics of a projected process. This article reviews the application of thermodynamics to the oxidation of platinum and to the life expectancy of platinum coatings on base metal substrates when operating at high temperatures, and describes the derivation of equilibrium diagrams of platinum alloys from the thermochemical properties of the constituent phases.*

As yet metallurgists have hardly appreciated the immense potentialities of chemical thermodynamics for the application to industrial and other practical problems. This is partly due to the belief that the application of chemical thermodynamics requires complicated mathematics. Students of science at university are fed, it is true, with involved derivations of thermodynamic equations and are then left "hanging in the air" with no indication how thermodynamic principles and data are to be put to practical use. No wonder that the puzzled student asks: "So what?"

In fact, all that is required is a working knowledge of arithmetic, the ability to think in terms of molar quantities and a good portion of metallurgical "commonsense". Once a problem has been broken down into one or more chemical equations, the evaluation of the equilibrium conditions becomes mere routine.

An important equation is the reaction isochore which connects the equilibrium constant of a chemical reaction ( $K_p$ ) with the standard Gibbs energy change ( $\Delta G^\circ$ ) in calories per mole,

$$\Delta G^\circ = -RT \ln K_p = -4.574T \log K_p \quad [1]$$

Since the Gibbs energy is a function of temperature, it is convenient to list the thermodynamic properties of chemical substances in terms of entropies ( $S$ ) and heat contents ( $H$ ). The three functions are connected by the equation:

$$G = H - TS \quad [2]$$

For a chemical reaction involving several substances, the heat of reaction is obtained by a simple summation,

$$\Delta H = \sum H_{\text{products}} - \sum H_{\text{reactants}} \quad [3]$$

Equation [3] is known as Hess' Law and is the form in which the chemist uses the First Law of Thermodynamics. Likewise, the entropy of reaction is obtained by the following summation:

$$\Delta S = \sum S_{\text{products}} - \sum S_{\text{reactants}} \quad [4]$$

In the first approximation and for the present purpose,  $\Delta H$  and  $\Delta S$  may be taken to be independent of temperature.

Of course, for the appraisal of a chemical reaction, not only a knowledge of the equilibrium is important but also the rate with which it is attained. Unfortunately in reaction chemistry, the prediction of the kinetic conditions is far more difficult than that of the thermodynamic ones. However, the higher the temperature the more rapidly equilibrium is approached and the less the influence of the kinetic delays. This is why chemical thermodynamics finds important applications in the field of metallurgy.

The main restriction on the application of thermodynamics is imposed by the relative scarcity of accurate values for the heats and entropies. These are usually tabulated as standard heats of formation from the component elements and standard entropies, both quantities at a temperature of 25°C. Several tabulations of critical values are available of which only one by the present author and his colleagues (1) will be mentioned here.

These tabulations show that relatively little thermodynamic information is available for systems involving the platinum metals, perhaps because their relatively high cost has discouraged measurements. On the other hand, experiments with platinum metals present few difficulties in general because of their *relative* inertness towards oxidation.

Such experimental thermodynamic data as are available have been obtained in a rather haphazard manner. The investigators either wanted to understand the fundamental nature of chemical bonding on the basis of systematic studies or had no reason other than that the particular metallic system suited an available apparatus. Neither of these approaches is very helpful to the applied thermochemist.

Before turning to some practical examples, there is one more fact that should be explained. The applied thermochemist is more often than not confronted with chemical reactions involving solutions of metals or non-metals in metals. In most of these cases it is more appropriate to work with partial rather than integral thermodynamic functions, i.e., heat, entropy, and Gibbs energy. The integral thermodynamic functions pertain to the formation of a compound or a solution of given composition from the component elements, e.g.,  $x\text{A} + y\text{B} = \text{A}_x\text{B}_y$ , whereas the partial thermodynamic functions pertain to the solution of one mole of A or B in the substance  $\text{A}_x\text{B}_y$ , the latter being assumed to be so much in excess that no change in concentration takes place on assimilation of the extra mole of A or B. It is usual to denote partial thermodynamic values by bars over the respective symbols, where *i* denotes the solute.

Equations of the form of equation [2] apply equally to partial and integral values, i.e.,

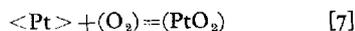
$$\Delta G = \Delta H - T\Delta S \quad [5]$$

and 
$$\Delta \bar{G}_i = \Delta \bar{H}_i - T\Delta \bar{S}_i \quad [6]$$

where equation [6] refers to the *i*<sup>th</sup> component.

## Reactions Involving Gaseous Platinum Metal Oxides

One problem frequently encountered by the technologist dealing with platinum metals is their volatility in the presence of air or oxygen at elevated temperatures. This problem has attracted the attention of thermochemists for some time. Schneider and Esch (2), thirty years ago, recognised that platinum reacts with oxygen to form a gaseous oxide of composition  $\text{Pt}_x\text{O}_2$  and determined the value for the equilibrium constant,  $K_p = p_{(\text{Pt}_x\text{O}_2)} / p_{(\text{O}_2)}$ , at 1200°C, although the original paper contains some inconsistencies. Later, Alcock and Hooper (3) established that  $x=1$  and that hot platinum reacts significantly with oxygen according to the reaction\*



The thermodynamic data they obtained agree with the results of Schneider and Esch. The integral Gibbs energy change in cal/mole  $\text{O}_2$  of reaction [7] may be represented by the equation:

$$\Delta G^\circ = 39,750 - 1.35T$$

Platinum coatings have been, and are being, repeatedly suggested as protection against oxidation, be it for gas turbines or materials designed for even higher temperatures. The thermodynamic data, converted into equilibrium constants by means of equation [1], indicate that significant losses of platinum may occur above, say, 900°C. This can be seen from the table which gives the vapour pressure of the oxides in terms of mm Hg rather than atmospheres. To estimate the rate of loss from these data is difficult. For evaporation from a surface into a vacuum, the Langmuir equation is needed which states that

$$m/t = 44.3 p.A \sqrt{M/T} \quad [8]$$

\* Brackets are used to indicate states of aggregation: <solid>, (gaseous).

where  $m$  (g) is the mass of material of molecular weight  $M$  which evaporates from an area  $A$  ( $\text{cm}^2$ ) in time  $t$  (sec) at a vapour pressure of  $p$  atm.

However, the result for any given temperature would represent no more than a maximum value, because the presence of oxygen would reduce the rate of evaporation of  $\text{PtO}_2$  gas, so that a platinum coating of, say, 0.0025 cm thickness would have a lifetime of at least a few hundred hours at  $900^\circ\text{C}$  and a coating ten times as thick would last for several thousand hours.

Having introduced a kinetic argument, it may be added that diffusion of platinum into the matrix might limit the life of the coating even further. There is a simple equation that is very useful for such estimates, namely,

$$\bar{s}^2 = 2Dt \quad [9]$$

where  $\bar{s}^2$  is the mean square of the displacement of the solute atoms in a solvent in a given direction in time  $t$  (sec) and  $D$  is the diffusion coefficient in  $\text{cm}^2/\text{sec}$ . In other words,  $\bar{s}$  is the distance in cm which the bulk of the solute atoms have moved in a concentration gradient in a given direction. The present author has used equation [9] on many occasions, for instance to estimate the decarburisation rate of steel sheet or the time necessary to homogenise a compact made of a metal powder mixture, and has usually found it to agree well with practical observations.

In the present case, one may again take thicknesses of a platinum layer on a steel base of 0.0025 cm and 0.025 cm respectively. At  $900^\circ\text{C}$ , the diffusion rate of platinum is estimated to be of the order of  $10^{-10} \text{ cm}^2/\text{sec}$ . Thus the time required for the bulk of the layer to diffuse into the matrix is of the order of tens of hours for the thinner but thousands of hours for the thicker layer.

As a rule, diffusion rates in metals and alloys are similar at their melting points. Consequently, the diffusion rate is much less in a high-melting-point metal such as molybdenum than in steel at a given temperature, and the life of a coating that much longer.

**Reaction Pressures of Rhodium, Iridium, and Platinum Oxides in mm Hg when the Metals are in Equilibrium with Oxygen at 1 atm Pressure (3,5). Vapour Pressure of Metallic Palladium in mm Hg.**

$^\circ\text{C}$	$\text{RhO}_2$	$\text{IrO}_3$	$\text{PtO}_2$	Pd
900		0.57	$6 \times 10^{-5}$	$4 \times 10^{-6}$
1100	$6 \times 10^{-4}$	0.74	$7.5 \times 10^{-4}$	$5.2 \times 10^{-4}$
1300	$5 \times 10^{-3}$	0.90	$4.5 \times 10^{-3}$	$2 \times 10^{-2}$
1500	$2.5 \times 10^{-2}$	1.05	$1.8 \times 10^{-2}$	0.32
1700	$9 \times 10^{-2}$	1.2	$5.5 \times 10^{-2}$	2.9

The reaction pressures of other platinum metal oxides in oxygen are listed in the table at various temperatures to enable the reader to make comparisons for practical purposes. Gaseous palladium oxide ( $\text{PdO}$ ) is not very stable; its reaction pressure in oxygen is of the same order as the vapour pressure of the metal (3), data for which are also given in the table.

One important problem encountered in industry is the loss of precious metals to the vapour phase at elevated temperatures: for instance, where these are used as catalysts. Whether vaporisation occurs by direct evaporation ( $\text{Au}$ ) or through the formation of a gaseous oxide ( $\text{Pt}$ ), or both ( $\text{Pd}$ ), the thermodynamic potential and thus the rate of loss can be reduced by alloying. Hayes (6) has measured the heats of formation in the ternary system platinum-palladium-gold. The results can be converted into partial heats of solution of either of the component metals in the alloys. As an example, the partial values for platinum are presented in Fig. 1. Use can be made of these data in the following way. Let us take a concentration of 30 atomic per cent Pt in an alloy with the atomic proportion of  $\text{Au}:\text{Pd} = 1:9$ . The partial Gibbs energy of solution ( $\text{cal}/\text{g-atom}$ ) may be represented by the equation,

$$\Delta\bar{G}_{\text{Pt}} = \Delta\bar{H}_{\text{Pt}} + 4.574T \log N_{\text{Pt}} \quad [10]$$

The value for  $\Delta\bar{H}_{\text{Pt}}$  ( $-1200 \text{ cal}/\text{g-atom}$ ) is taken from Fig. 1 and the logarithmic term arises from the assumption that the solid solutions are "regular", meaning that the

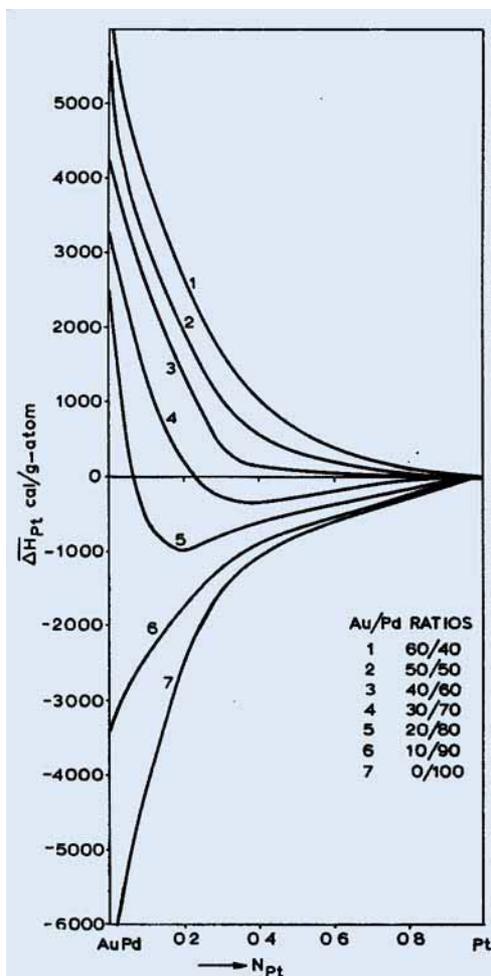


Fig. 1 Partial heats of solution of 1 g-atom of platinum in solid platinum-palladium-gold alloys (6)

entropy of solution is due only to atomic disorder. The atomic fraction of Pt is  $N_{Pt}=0.3$ , and a temperature of  $T=1173$  K may be selected. Then,  $\Delta\bar{G}_{Pt}$  equals  $-4000$  cal/g-atom and the logarithm of the value of  $p_{PtO_2}$  in the table must be corrected by  $\Delta\bar{G}_{Pt}/4.574T$ . The result of this calculation is that the reaction pressure of  $PtO_2$  at  $900^\circ\text{C}$  changes from  $6 \times 10^{-5}$  to about  $1 \times 10^{-5}$  mm Hg for platinum dissolved in an alloy consisting of 30 atomic per cent Pt, 63 Pd and 7 Au.

Such calculations may be carried out for other compositions to give quantitative

information on the change of thermodynamic potential of platinum in the alloys and thus provide relative data for its rate of loss *via* the gas phase or the recovery of platinum by a gold-palladium alloy from a gas carrying  $PtO_2$ . From the results presented by Hayes (6) partial thermochemical data for gold and palladium in the ternary alloys corresponding to those in Fig. 1 can also be obtained, and the calculations repeated for the same alloy compositions. It is thus possible to arrive at numerical information for the relative evaporation of precious metals from the alloys under consideration and to minimise the losses.

### Reactions Involving Platinum Oxide in Solid Solutions

The inclusion of platinum particles in glass laser rods has caused the laser industry considerable problems, the platinum obviously originating from the container in which the glass is melted. The present author has been aware of this problem for some time and thermodynamic reasoning has led him to similar conclusions as those arrived at by Woodcock (7) on experimental grounds. Although pertinent thermodynamic data are not available, it may be of interest to follow the arguments.

The solubility of platinum metal in glass seems to be very small (7); and so are the solubilities of copper, silver, and gold in the absence of oxygen. However, thirty-five years ago, the present author (8) studied the dissolution of silver and copper in glass at  $540^\circ\text{C}$  and found that both diffuse into the glass significantly only in the presence of oxygen. When the oxygen pressure was reduced to below about 10 mm Hg, the silver uptake dropped sharply. No matter what mechanism one envisages, it seems to be certain that diffusion of the metal oxides rather than the metals is involved.

Platinum does not appear to form any thermodynamically stable oxides in the condensed state, but this does not rule out the possibility of metastable platinum oxide

dissolving in glass in quantity. Thermodynamic considerations are best based on an equation similar to [10], viz.,

$$\Delta\bar{G}_{\text{PtO}_x} = \Delta\bar{H}_{\text{PtO}_x} + 4.574T \log N_{\text{PtO}_x} \quad [11]$$

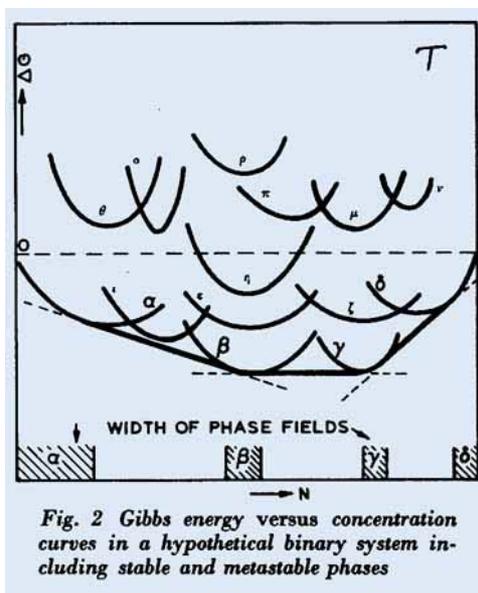
In order to enable platinum oxide, denoted  $\text{PtO}_x$ , to dissolve in the glass, the value of  $\Delta\bar{G}_{\text{PtO}_x}$  must be more negative than the Gibbs energy of formation of  $\text{PtO}_x$  from the elements at any given temperature. Neither the latter value nor the value for  $\Delta\bar{H}_{\text{PtO}_x}$  are known, but the degree of metastability of platinum oxide is probably not very pronounced: as a very rough guess one might say it is of the order of 10 kcal/mole. On the other hand, the concentration-dependent term in equation [11] can easily overcompensate this order of energy. At a concentration of, say, 0.1 mole per cent  $\text{PtO}_x$ , the logarithmic term contributes 17,500 cal to the stability of  $\text{PtO}_x$  in solution.

On thermodynamic grounds, it is, therefore, conceivable that platinum follows a similar pattern to silver when dissolving in glass. The actual concentrations,  $N_{\text{PtO}_x}$ , cannot be calculated because the pertinent thermochemical data are missing, but it follows from equation [11] that the solubility of  $\text{PtO}_x$  decreases with decreasing temperature so that  $\text{PtO}_x$  would be precipitated on cooling. Since this is unstable, platinum inclusions in laser gases would form. The excess oxygen is possibly squeezed into some supersaturated solution, and this might be the cause for the explosive fracture of rods operated at high peak powers.

The obvious conclusion to be drawn from these considerations is that oxygen should be largely eliminated from the atmosphere when melting glass in platinum crucibles. The tolerable oxygen pressure may be obtained by making systematic experiments simulating those mentioned for silver (8).

### Calculating Equilibrium Diagrams from Thermochemical Data

A major object of research in the laboratory of the present author is the application of thermodynamic data of alloys to the calcula-



tion of phase boundaries in binary and ternary equilibrium diagrams. The advantage of this over the conventional methods is that heats and free energies can often be determined under conditions where equilibrium is easily achieved whereas the results of conventional methods are frequently subject to kinetic checks. The principle of the thermochemical method (9) is to measure two of the three quantities in equation [5] for every phase in a given system, to calculate the Gibbs energies as a function of composition at various temperatures and to draw the tangents to the  $\Delta G-N$  curves as illustrated in Fig. 2 for a hypothetical, binary system at one temperature. Since it is always the phase or mixture of phases with the lowest Gibbs energy which is stable, the concentrations at which the tangents touch the curves indicate the phase boundaries at that temperature.

The systems so far evaluated do not include any involving platinum, but work by Pratt, Bryant and Bugden (10) on the palladium-silver-copper system in which the results of thermodynamic measurements are correlated with phase boundaries obtained by conventional methods may be mentioned. The thermochemical work of the Metallurgical Thermodynamics Section of the National

Physical Laboratories has been directed mostly to the establishment of equilibrium diagrams pertaining to alloyed steels (11). In the present paper, one can only indicate the type of system for which the thermochemical approach appears to be particularly suitable.

Platinum and iridium form a complete series of solid solutions at higher temperatures and a miscibility gap at lower temperatures, the phase boundary of which is difficult to establish because of the slowness with which equilibrium is attained (12). If the heats and entropies for the solid solutions were determined at some kinetically convenient temperature, the boundary of the miscibility gap could be calculated at any temperature. A corresponding example is the system chromium-molybdenum to which this calculation has been applied (9, 11). It should be noted that an 18-month annealing period at 800°C was needed to confirm the formation of the miscibility gap, and even after this time the phase boundary could only approximately be assessed by conventional methods. Of course, at lower temperatures, the rate of equilibration would eventually be so slow that, for most practical purposes, the existence of a phase change would be irrelevant.

However, cases may occur in practice at lower temperatures where even the tendency to a change in phase is important and phase boundaries ought to be known. Although the problem is now one of the past, one may recall that before the spectroscopic standard of length was introduced, one relied on the standard meter, bars made of 10 per cent iridium-platinum alloys. The reported changes in physical properties and the suspected changes in dimensions (13) indicated some solid state reaction even at room temperature which, of course, make such an alloy unsuitable for standardisation purposes. In such cases, only the thermochemical method can supply quantitative information on the position of the phase boundaries.

Another case where thermochemical evaluation would be superior for the establishment of phase boundaries is exemplified by the

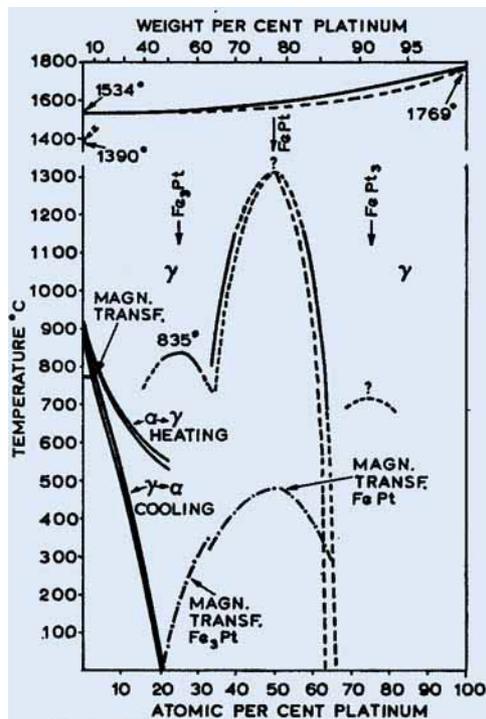


Fig. 3 Phase diagram of the system platinum-iron after Hansen (12)

system platinum-iron, the phase diagram of which is only incompletely known, the diagram in Fig. 3 being taken from Hansen's assessment (12). At high temperatures, f.c.c. iron and platinum form a continuous series of solid solutions. There exist several superstructures in equilibrium with the solid solutions, but the positions of the phase boundaries are obviously quite uncertain. The example that corresponds to this case and for which thermochemical studies have been made is the system chromium-iron (1, 9) which has one superstructure of the  $\sigma$  type in equilibrium with the b.c.c.  $\alpha$  solutions. For the thermodynamic investigation, the heats and Gibbs energies of formation were determined by high-temperature methods across the whole range of the  $\alpha$  solutions. Then  $\sigma$  alloys of various compositions were prepared by lengthy annealing and the heat and entropy of transformation from  $\sigma$  to  $\alpha$  was measured by adiabatic calorimetry. The results pro-

vided all the information for the calculation of the  $\sigma$ - $\alpha$  phase relationships (see ref. 1, 9 or 11). When required, one could deal with the system Pt-Fe and similar systems in the same manner, whereas conventional methods would be more cumbersome and lengthy, and probably less reliable.

More examples of past as well as potential applications of chemical thermodynamics to the platinum metals could be found. An early application involved the oxidation of alloys used for electrical contacts which are composed of either platinum or gold with copper or nickel; data for the minimum temperatures above which bulk oxidation ceases were given for various alloys and found to agree closely with observations (14).

However, it is not intended to overload the present article, and the examples given must suffice to indicate the potential practical uses of thermodynamic principles and data.

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## Ruthenium – a Compilation of Data

It might be imagined that ruthenium is one of the less-documented metals but its occurrence as a radioactive isotope in products of nuclear fission has stimulated research into its properties and chemistry. A work which demonstrates this point has been published recently by a team working under Dr. André F. LeRoy at the Bureau of Radiological Health, Winchester, Massachusetts. "A Comprehensive Bibliography of Element 44, Ruthenium" cites over 3,000 references dealing with some aspect of this metal and includes an author index, a patent index, a source index, and a computer-generated keyword-in-context (KWIC) English language title index. The bibliography is published by the U.S. Department of Health, Education, and Welfare.

Undoubtedly a remarkable collection of material has been assembled and so it is a pity that two criticisms must be made. First, the work was commenced in 1963 and only titles up to and including that year are indexed. Much labour was expended to

produce this volume, which is 10 cm thick, but since it only appears to have reached general distribution this year there is a gap of nearly eight years covering all the most recent work.

The second criticism concerns an assumption on which the work appears to have been based and which is mentioned in the foreword by the Director of the Bureau of Radiological Health. He writes: "Recent estimates of ruthenium production by fission in nuclear power reactors indicate that the present annual yield from this source exceeds today's consumption level in the United States (10,000 troy ounces per year). The ruthenium thus produced includes about 5 per cent  $^{106}\text{Ru}$  ( $t_{1/2} = 1$  yr). With long-term storage for decay, this source represents a significant supply of useable ruthenium". A recent evaluation of the possible use by industry of platinum metals from nuclear fission was published in this journal (*Platinum Metals Rev.*, 1971, **14**, (3), 88-92) and cast serious doubt on their practical use. F. J. S.