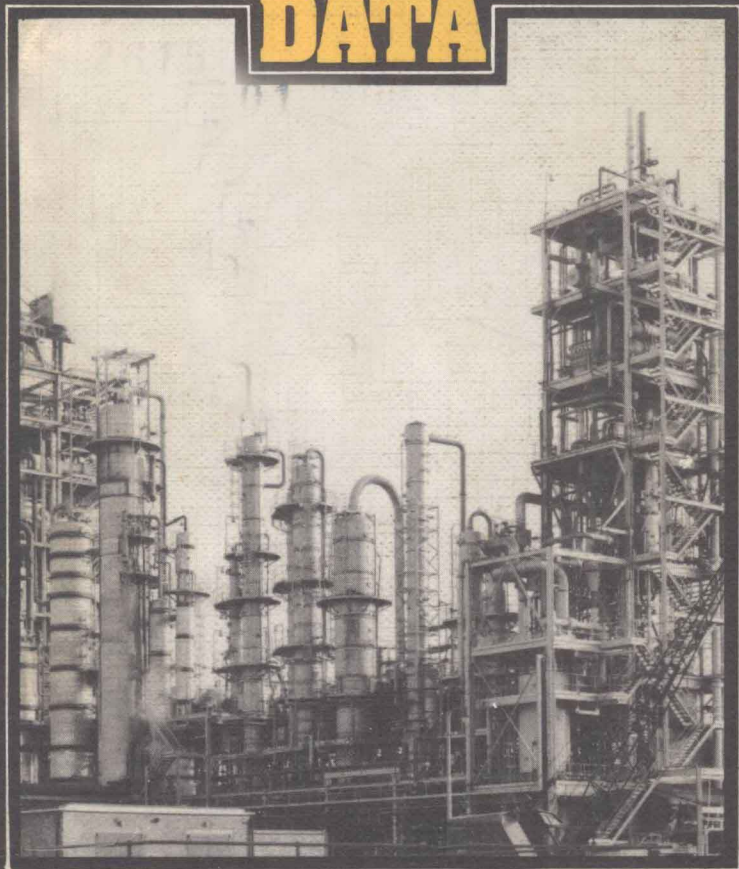


THE INDUSTRIAL USE OF THERMOCHEMICAL DATA



== EDITED BY T.I. BARRY ==

Special Publication No 34

The Industrial Use' of Thermochemical Data

The Proceedings of a Conference organised by
The National Physical Laboratory and The
Industrial Division of The Chemical Society

University of Surrey, September 11th–13th, 1979

Edited by
T. I. Barry,
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The Chemical Society
Burlington House, London, W1V 0BN

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British Library Cataloguing in Publication Data

The industrial use of thermochemical data. –
(Chemical Society. Special publications; no. 34
ISSN 0577-618X).

1. Heat engineering – Congresses
2. Thermodynamics – Congresses
3. Information storage and retrieval systems
– Thermodynamics – Congresses

I. Barry, T I	II. Chemical Society.
<i>Industrial Division</i>	III. National Physical
Laboratory	IV. Series
536'.7'02466	TJ260

ISBN 0-85186-930-0

Cover photograph of acetic acid manufacturing complex by
courtesy of BP Chemicals Ltd

Printed in Great Britain by
Whitstable Litho Ltd., Whitstable, Kent

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OF THERMOCHEMICAL DATA**

PREFACE

The conference on Industrial Use of Thermochemical Data, of which this book is the proceedings, was organised with the purpose of bringing those wishing to apply inorganic and metallurgical thermodynamics to practical problems together with those whose aim is to provide the necessary information, both reliably and in a convenient form. In 1971 when National Physical Laboratory last organised a conference on a similar topic, the use of computers formed only a small part of the conference subject matter. With this thought in mind a stated aim of the conference organisers was to illustrate the increasing potential of computer based methods. Accordingly there are papers on their use ranging from assessment of raw experimental data, through calculation of equilibria and phase diagrams to the modelling of complete industrial processes.

The purpose of this book is essentially the same as that of the conference. On the one hand it is to provide for technical management and development staff a key to the sources of data and methods and examples of their use in overcoming practical problems, demonstrated by the data needs for efficient and safe use of nuclear power. On the other hand this book will help students and researchers to appreciate industrial problems and the contribution they can make to these problems. The book can also do what the conference could not, provide a solid source of information with references to the literature, hard copy and on-line data sources and organizations able to undertake sponsored research.

The papers have been divided into four groups, each with at least one keynote paper.

1. Fundamentals and databanking.
2. Chemistry and chemical vapour transport.
3. Phase diagrams and phase relationships.
4. Steel making, slags and ceramics.

The range of industries covered is very wide and the subject matter of the book is highly interdisciplinary. Thus the book cannot be regarded as a text book, covering all aspects of inorganic and metallurgical thermodynamics and their applications. In order to increase its general utility a subject index is provided. The reader should consult the notes at the head of the index before using it.

The editor would like to thank all those who have contributed to the conference and this volume: the authors, especially of the keynote papers, the other conference organisers Mr R P Miller of NPL and Drs K J Matterson and R Thompson of Borax Holdings Ltd., representing The Chemical Society, colleagues at NPL, Dr T G Chart, Mrs F H Putland, Mrs J M Ellender, Mr A T Dinsdale and Mr G O'Neill, and Mr A G Cubitt of The Chemical Society.

T.I. Barry

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Fundamental aspects of the use of thermodynamic data

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Abstract

The fundamental basis which is needed for the calculation of equilibrium is very limited and the difficulties encountered by students and engineers are largely of mathematical nature. Due to the high calculating capacity of a computer, it should be possible to construct a computer program based on simple thermodynamic principles and not using various tricks and mathematical operations in order to handle different kinds of equilibria. A method is suggested by which such a computer program may be constructed. It seems to be capable of calculating the equilibrium under many different circumstances. In the future there will probably be programs available which are so general that the user only needs a basic knowledge of thermodynamics.

Introduction

When considering what fundamentals are required in order to use thermodynamic data for practical purposes it may be helpful to consider thermodynamics as a game and to consider the question how one can learn to play that game well. For inspiration we may first look at another game, the game of chess. The rules are very simple to learn but it was always very difficult to become a good player. This situation has now changed due to the application of computers. Today there are programs for playing chess which allow any beginner to beat almost any expert. It seems reasonable to expect that it should be possible also to write programs for playing thermodynamics, programs which should be almost as good as the very best thermodynamics expert.

In order to teach a computer to play chess one must instruct the computer about the rules and teach the computer some strategy. If the strategy is primitive, it may also be necessary to teach the computer a number of tricks to be used in special situations, in particular during the opening part of the game. However, the better the strategy, the less tricks are required. In the game of thermodynamics, the question is whether such a good strategy could be found that no tricks would be required. In order to find such a strategy it is necessary to go back to the fundamentals of thermodynamics and to find a way to instruct the computer about them, such that the same instruction can be used by the computer in various kinds of situation

In order to simplify the discussion, we shall only consider the calcula-

tion of equilibria under constant temperature and pressure. In principle, the problem is then to find the minimum of Gibbs energy of the system under consideration. This can be done directly with a computer using a so-called hill-climbing technique. However, it requires special tricks in many cases. For example, if one wants to calculate an equilibrium under a constant value for the chemical potential of one component, one can use the trick of introducing an artificial phase which consists of that component alone and has the prescribed chemical potential. A more complicated example is the case where one likes to calculate the equilibrium between some prescribed phases without prescribing anything about the content of the system.

A second type of strategy makes use of equilibrium conditions expressed in terms of chemical potentials. The resulting system of equations is solved either directly or after an initial elimination of the chemical potentials.

In the former case the main drawback is that there will be a very large number of equations which must be solved simultaneously when the system contains many phases and many components. In the latter case, the new system of equations takes different forms for different cases and it may not be possible to find a general strategy.

The various methods which have been suggested were recently reviewed by van Zeggeren and Storey (1). Since then Ericsson (2,3) has suggested a new method based upon the equilibrium conditions and using an initial elimination of the composition variables. The remaining system of equations only contains one equation for each phase and one equation for each component in the system. That method seems to have some advantages and will be further developed in this paper. The new development was recently outlined (4) and will now be given in more detail.

Analytical derivation of the equilibrium conditions

In order to define the state of a system one needs several properties. Some of the most important ones are the pressure P , volume V , absolute temperature T , entropy S and internal energy U . In addition, it is useful to define the following related quantities

$$\text{Enthalpy} \quad H = U + PV \quad (1)$$

$$\text{Helmholtz energy} \quad F = U - TS \quad (2)$$

$$\text{Gibbs energy} \quad G = U + PV - TS \quad (3)$$

From the second law of thermodynamics it is known that

$$dS \geq dQ/T \quad (4)$$

where dS is the change in entropy of a system at temperature T when it receives the heat dQ from the surroundings. The equality holds for a reversible change and the inequality for a so-called natural reaction. If the system is under pressure P , there may be an accompanying change of volume dV and the amount of work performed by the system is then PdV . According to the first law,

$$dU + PdV - TdS \leq 0 \quad (5)$$

For a system at rest in a state of equilibrium there can be no natural reaction and we thus find

$$dU = -PdV + TdS \quad (6)$$

The following relation thus holds at equilibrium

$$dG = d(U + PV - TS) = VdP - SdT \quad (7)$$

We can thus find the equilibrium state from the condition

$$dG = 0 \quad (8)$$

provided that pressure and temperature are kept constant. The present treatment will be limited to that case.

P and T are intensive properties and V and S are extensive properties. It follows from the relations already given that U, H, F and G are also extensive properties. The value of G for a poly-phase system is thus equal to the sum over all the phases

$$G = \sum_i G^i \quad (9)$$

By the same reason, the Gibbs energy of a phase is proportional to the number of moles in the phase, n^α . By introducing the molar Gibbs energy of the phase, G_m^α , we can write

$$G^\alpha = n^\alpha G_m^\alpha \quad (10)$$

It is also evident that G^α varies with the amount n^α as well as with P and T. Eq. 7 should thus be modified as follows,

$$dG^\alpha = \left(\frac{\partial G^\alpha}{\partial P}\right)_{T,n^\alpha} dP + \left(\frac{\partial G^\alpha}{\partial T}\right)_{P,n^\alpha} dT + \left(\frac{\partial G^\alpha}{\partial n^\alpha}\right)_{P,T} dn^\alpha \quad (11)$$

$$\text{where } \left(\frac{\partial G^\alpha}{\partial P}\right)_{T,n^\alpha} = V^\alpha \quad (12)$$

$$\left(\frac{\partial G^\alpha}{\partial T}\right)_{P,n^\alpha} = -S^\alpha \quad (13)$$

$$\left(\frac{\partial G^\alpha}{\partial n^\alpha}\right)_{P,T} = G_m^\alpha \quad (14)$$

For a multicomponent phase, the Gibbs energy should vary with the amount of each component and we can write

$$dG^\alpha = V^\alpha dP - S^\alpha dT + \sum_j G_j^\alpha dn_j^\alpha \quad (15)$$

where G_j^α is the partial Gibbs energy for component j

$$G_j^\alpha = \left(\frac{\partial G^\alpha}{\partial n_j^\alpha}\right)_{P,T,n_k} \quad (16)$$

The subscript n_k indicates that the amounts of all the other components are kept constant. Let us now consider a poly-phase equilibrium state in a system with a given amount of several components, n_A etc. The distribution of the components on the various phases is unknown but for the total amount of each component we have

$$\sum_i n_A^i = n_A \quad (17)$$

We would now like to find the state of equilibrium under constant P and T and should thus calculate the minimum of G . In view of the side conditions given by eq. 17 for each component the minimum can be found by the use of the Lagrange multipliers, one for each side condition. By denoting them as μ_A etc we formulate the function

$$L = \sum_i G^i + \sum_j \mu_j (n_j - \sum_i n_j^i) \quad (18)$$

and calculate the minimum of this new function. The following kind of equations are obtained:

$$\frac{\partial L}{\partial n_A^\alpha} = \frac{\partial G^\alpha}{\partial n_A^\alpha} - \mu_A = 0 \quad (19)$$

The partial derivatives are taken with all the other variables constant. All the n_j^i and μ_j can be calculated by solving the system of equations formed by eqs. 17 and 19, altogether $c + cp$ equations if c denotes the number of components and p the number of phases.

It is evident from eq. 19 that the partial Gibbs energy of a component must have the same value in all the phases at equilibrium. That value is denoted by μ_A etc and is usually called the chemical potential of the component.

The fact that the partial Gibbs energy must have the same value in all the phases is often applied directly when calculating phase equilibria. That procedure is identical to eliminating the multipliers from eq. 19 as the first step in the calculation

$$\begin{aligned} G_A^\alpha &= G_A^\beta = \dots \\ G_B^\alpha &= G_B^\beta = \dots \end{aligned} \quad (20)$$

A system of equations is thus obtained, which can be used to calculate all the n_j^i . After the equilibrium state has thus been calculated, it is possible to calculate the chemical potentials of all the elements present in the system by inserting the n_j^i values in some of the expressions for G_j^i .

This procedure cannot always be used. A complication arises as soon as there is some restriction to the variation in composition of a phase, which may occur for instance if the atomic sites in the phase belong to different sublattices. It is then impossible to express G_A^α analytically using the derivative of G^α with respect to n_A^α because all the other n_j^α cannot be kept constant.

The use of mole fractions

In order to derive the equilibrium conditions in a more general way, one can introduce the mole fractions to describe the composition of a phase,

$$x_A^\alpha = n_A^\alpha / \sum_j n_j^\alpha = n_A^\alpha / n^\alpha \quad (21)$$

For each phase we now have a new side condition,

$$\sum_j x_j^\alpha = 1 \quad (22)$$

The previous side condition for each phase, eq. 17, is now written as

$$\sum_i n_i^i x_A^i = n_A \quad (23)$$

A new set of multipliers, one for each phase, λ^α , must be introduced due to eq. 22 and one can calculate the equilibrium state by finding the minimum for the following function, which makes use of the molar Gibbs energy from eq. 10,

$$L = \sum_i n_i^i G_m^i + \sum_j \mu_j (n_j - \sum_i n_i^i x_j^i) + \sum_i \lambda^i (\sum_j x_j^i - 1) \quad (24)$$

By putting the partial derivatives equal to zero we now obtain two types of equations,

$$\frac{\partial L}{\partial n_m^\alpha} = G_m^\alpha - \sum_j \mu_j x_j^\alpha = 0 \quad (25)$$

$$\frac{\partial L}{\partial x_A^\alpha} = n^\alpha \frac{\partial G_m^\alpha}{\partial x_A^\alpha} - \mu_A n^\alpha + \lambda^\alpha = 0 \quad (26)$$

Eq. 25 is usually written as

$$G_m^\alpha = \sum_j x_j^\alpha \mu_j \quad (27)$$

$$\text{or } G^\alpha = \sum_j n_j^\alpha \mu_j \quad (28)$$

By differentiating eq. 28 we obtain

$$dG^\alpha = \sum_j n_j^\alpha d\mu_j + \sum_j \mu_j dn_j^\alpha \quad (29)$$

Comparison with eqs. 15 and 19 yields the Gibbs-Duhem relation

$$\sum_j n_j^\alpha d\mu_j - V^\alpha dP + S^\alpha dT = 0 \quad (30)$$

This is a useful relation between the variations in the intensive properties, P , T , μ_A etc. In a phase with c components their number is $c + 2$ but due to the relation only $c + 2 - 1$ of them may be regarded as independent. In a system with p phases, there will be p equations like eq. 30 and the number of independent intensive properties in such a system is thus given by

$$f = c + 2 - p \quad (31)$$

This is Gibbs phase rule and f is regarded as the number of degrees of freedom. In many cases, the state of a system is defined by fixing some extensive property. Gibbs phase rule can be derived for such a case as well but should then be used with care.

The new multiplier in eq. 26, λ^α , can be identified using the well-known computational rule for the partial Gibbs energy of a solution phase

$$\mu_A = G_A^\alpha = G_m^\alpha - \sum_j x_j^\alpha \frac{\partial G_m^\alpha}{\partial x_j^\alpha} + \frac{\partial G_m^\alpha}{\partial x_A^\alpha} \quad (32)$$

We obtain

$$\lambda^\alpha / n^\alpha = G_m^\alpha - \sum_j x_j^\alpha \frac{\partial G_m^\alpha}{\partial x_j^\alpha} \quad (33)$$

However, it should be emphasized that the equilibrium state can be calculated by first eliminating all the multipliers and it is not necessary to concern oneself with their interpretation. In particular, it is possible to eliminate λ^α by taking the difference between eq. 26 applied to two components in the same phase and one thus obtains a relation which is sometimes useful:

$$\mu_A - \mu_B = \frac{\partial G_m^\alpha}{\partial x_A^\alpha} - \frac{\partial G_m^\alpha}{\partial x_B^\alpha} \quad (34)$$

The advantage of eqs. 25 and 26 as compared to eq. 19 is that a stoichiometric phase can be handled without changing the strategy. Eq. 26 will simply be left out for such a phase but eq. 25 applies. In order to handle a phase with some variable compositions but also some restrictions, the method outlined in the next section can be used.

Phases with sublattices

For a particular phase or problem it may be convenient to introduce new types of mole fractions. A particularly useful method is to introduce the occupancy on lattice sites, $y_A^{\alpha s}$. For each kind of site there is a condition

$$\sum_j y_j^{\alpha s} = 1 \quad (35)$$

and there will be a corresponding multiplier, $\lambda^{\alpha s}$. These sites form a sublattice and there will be a multiplier for each sublattice. It must be noticed that the fraction of vacant sites $y_{Va}^{\alpha s}$ must be included in the summation. Our first site condition, eq. 17, is now written as

$$\sum_i n_i^{\alpha s} \sum_s a_s^{\alpha is} y_A^{\alpha is} = n_A \quad (36)$$

where $a_s^{\alpha is}$ is the number of lattice sites of type s per one formula unit of the phase i and n_i^{α} is the amount of the phase measured as the number of formula

units. The minimum should now be calculated for the following function,

$$L = \sum_i n_i^i G_m^i + \sum_j \mu_j (n_j - \sum_i n_i^i a_j^{is} \cdot y_j^{is}) + \sum_{is} \lambda^{is} (\sum_j y_j^{is} - 1) \quad (37)$$

G_m^i is the value for one mole of formula units of the phase. The following equations are now obtained

$$\frac{\partial L}{\partial n^\alpha} = G_m^\alpha - \sum_j \mu_j \sum_s a_j^{\alpha s} y_j^{\alpha s} = 0 \quad (38)$$

$$\frac{\partial L}{\partial y^{\alpha s}} = n^\alpha \frac{\partial G_m^\alpha}{\partial y_A^{\alpha s}} - \mu_A^\alpha a^{\alpha s} + \lambda^{\alpha s} = 0 \quad (39)$$

Eq. 38 is identical to our previous eq. 25. However, it should again be emphasized that the individual chemical potentials cannot always be uniquely defined for a phase with sublattices if it is not in equilibrium with some other phase. Eq. 32 takes the following form when there are sublattices:

$$a_1 \cdot \mu_A + a_2 \cdot \mu_C + \dots \equiv G_{A_1 C_2 \dots}^\alpha = G_m^\alpha - \sum_j y_j^{\alpha s} \frac{\partial G_m^\alpha}{\partial y_j^{\alpha s}} + \frac{\partial G_m^\alpha}{\partial y_A^{\alpha 1}} + \frac{\partial G_m^\alpha}{\partial y_C^{\alpha 2}} + \dots \quad (40)$$

$G_{A_1 C_2 \dots}^\alpha$ may be regarded as the chemical potential for the compound $A_1 C_2 \dots$.

As a simplification we have here written $a^{\alpha 1}$ as a_1 etc. It is thus impossible to use any one of the eqs. 39 in order to identify the λ multipliers. However, by adding such equations, one for each sublattice in the phase, one obtains

$$\sum_s \lambda^{\alpha s} / n^\alpha = a_1 \cdot \mu_A - \frac{\partial G_m^\alpha}{\partial y_A^{\alpha 1}} + a_2 \cdot \mu_C - \frac{\partial G_m^\alpha}{\partial y_C^{\alpha 2}} + \dots \quad (41)$$

By using eq. 40 we thus find

$$\sum_s \lambda^{\alpha s} / n^\alpha = G_m^\alpha - \sum_j y_j^{\alpha s} \frac{\partial G_m^\alpha}{\partial y_j^{\alpha s}} \quad (42)$$

It may again be emphasized that the multipliers may be eliminated as the first step in the calculation of an equilibrium. As a consequence, it is not essential to concern oneself with their interpretation. In particular the $\lambda^{\alpha s}$ multiplier for any sublattice can be eliminated by taking the difference between the equations obtained by applying eq. 39 to two elements in that sublattice:

$$a^{\alpha s} (\mu_A - \mu_B) = \frac{\partial G_m^\alpha}{\partial y_A^{\alpha s}} - \frac{\partial G_m^\alpha}{\partial y_B^{\alpha s}} \quad (43)$$

The quantity $\mu_A - \mu_B$ may for instance be of practical value for the construc-