Chemical thermodynamics in industry: models and computation

edited by T.I. Barry

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Contents

Editor's introduction

The latter part of the twentieth century is a period of rapid economic and technological change. The changes stem from:

1 diminishing resources of fossil fuel and other raw materials and a consequent need both to husband resources and develop new ones;

2 greater awareness of the dangers of pollution of the environment and other hazards;

3 the trend to automatic process control;

4 the need for new materials for energy efficient processing, lightweight structures and electronics;

5 the explosion in computing power.

Our ability to respond to these changes can be greatly enhanced by applications of chemical thermodynamics. The developments in computing power provide both the means and the stimulus. It is not surprising, therefore, that there should be a strong emphasis in this report on the computer-based methods for processing thermodynamic data and applying them to chemical and metallurgical processes.

Aims

The aims of this report are as follows.

1 To provide for project managers, insights into how thermodynamics can help in decision making, process design and materials selection and to indicate what resources will be necessary to exploit the methods available.

2 To provide for research workers an entry into a field that is new to them or which is on the periphery of their main activities.

3 To provide a guide to latest ideas, methods and data sources, highlighting key features of ideas and methods, and hence reducing the barriers to their adoption.

4 To give examples of how the thermodynamic approach has been applied.

5 To indicate future trends; for example, in correlation and modelling methods and in the impact of developments in communication and computers on data sources, calculation methods and process design.

6 To provide in a single volume, chapters covering fields in different branches of chemistry which have developed rather separately and to show the points convergence in methods and applications.

Why use thermodynamics?

Undoubtedly there is still resistance to the use of chemical thermodynamics in

industry, and it is easy to see why. Thermodynamics has the reputation of being an intimidating topic in which interesting and memorable information is converted into faceless numbers. Numerous conventions are used and it is easy for the infrequent operator to make mistakes and consequently distrust the calculated results. Lack of data is often a problem, since only one item of data need be missing to prevent a solution being reached.

The remedy for these difficulties is clear. Thermodynamics has to be made reliable and readily useable. These objectives can be achieved only by providing data and methods in ways that eliminate confusion. The underlying complexities are likely to be of no interest to the ultimate employer of the information. They must, in the jargon of computer systems, be made 'transparent to the user'. The most effective way of achieving this transparency until recently has been through the provision of compilations of tables and diagrams which allow phase equilibria, solubilities, vapour pressures, etc. to be read off as a function of the independent variables. Now the use of computer-stored data, coupled to the power of the computer to undertake complex calculations, offers great opportunities and has stimulated mathematically-inclined physicists and chemists to develop thermodynamic models which can exploit computers fully.

Until relatively recently the application of chemical thermodynamics was confined mainly to pure substances, their ideal solutions or those of real solutions for which there was a great deal of experimental data. The situation now is greatly changed. Mathematical models have been developed which express the thermodynamic properties of solutions with an accuracy appropriate to the application. Furthermore, an important principle can be invoked. The thermodynamic properties of a species in a solution phase depend (i) on its individual nature, e.g. whether it is an iron atom or a benzene molecule, (ii) on its interaction with neighbouring species and, less importantly, (iii) on ternary interactions. In most cases quaternary interactions have been ignored. Thus, the properties of a multicomponent solution can be calculated from those of the pure species and the binary and ternary interactions between them. Adding more species to a solution does not increase the complexity of the modelling, even though the amount of data required can become rather large and the individual calculations are made possible only by the availability of computers.

Topics
The subject matter of this report covers three topics which are normally kept distinct, namely:
1 metallurgy and high temperature chemistry;
2 aqueous solutions;
3 organic systems, especially the properties of mixtures.
Though specializing in the first of these areas I occasionally attend conferences on the other two topics. It is always a shock to hear the same concepts and methods

being discussed but credited to an entirely different set of authors. The wheel is continuously being reinvented. There is often much more contact between researchers in different continents than between those in these closely-related fields in the same laboratory. Certainly this was true of my own institute.

A major difference between inorganic and organic systems, responsible for many of the differences in approach, lies in the very large enthalpy changes involved in the formation of compounds and solutions in inorganic systems, and the comparatively small enthalpy changes in mixing organic fluids. However, alloys between similar metals also often have low enthalpies of formation. Thus, metallurgists interested in calculation of phase diagrams may have much to learn from methods that have been developed for the calculation of phase equilibria of organic mixtures. The subroutines used in these calculations must be efficient because they are called frequently during the optimization of the design and operation of large petro-chemical plants.

A topic which appears to be more advanced for inorganic systems is the solution of problems of *chemical* equilibrium. The method of solving a system of explicit chemical equations is now seldom used for inorganic systems. The number of chemical equations involved in a typical problem in inorganic materials research is very large, and this characteristic requires automatic procedures for setting up the problem. In organic systems, physical mixing of species which retain their molecular identity during change of phase is usually of greater concern than true chemical reaction. This may be the reason why automatic procedures for solving *chemical* equilibria are less prominent for organic systems. However, particularly in the development of synthetic fuels, processes are being developed where chemical reactions between hydrocarbons must be optimized so as to achieve the desired balance in the product.

The stability of dissociated ionic species in the dielectric medium of water makes the thermodynamics of aqueous solutions of special interest: because of the ubiquity of water and its role in geochemistry, inorganic processing, energy conversion, electrochemistry, corrosion, life processes and pollution it is important as well as special. Moreover, in many of these areas the thermodynamics involve other substances, such as rock minerals, alloys and weak or non-electrotypes, requiring a multidisciplinary approach for problem solving. This is particularly so for many geological processes in which high temperature–high pressure water plays a major role.

Symbols

No attempt has been made to unify the symbols used in the four chapters because to do so would have prevented one of the aims from being achieved; namely, that of providing an entry to fields which are new to the reader. Each of the fields has developed its own set of commonly-used symbols.

Future developments

The view shared by all the authors of this report is that the future will be shaped by developments in the following areas.

1   Development of better models to represent the thermodynamic properties of non-ideal systems.

2   Theoretical estimation of thermodynamic properties.

3   Provision of experimental data.

4   Development of databases of experimental data that can be used for validating new models and improving critically assessed data as new experimental data becomes available.

5   Parallel development in computing power and improved methods for calculating equilibria.

6   Development of comprehensive computer databases, from which stored data can be readily retrieved and used as a basis for calculation.

7   Incorporation of modules for solving equilibria into programs to solve kinetic problems in diverse areas, e.g. normal and abnormal operation of plant, diffusion and solid state transformation.

8   Further development of procedures for optimizing the design of chemical plant and devices in which there is only localized equilibrium. These procedures may involve finite element analysis.

The Cinderella of these developments, but ultimately the most important, is the organized provision of good experimental data. There has been an unfortunate trend to reduce the funding of experimental work in many countries, mainly because the time taken to produce experimental data is usually longer than the time from realization of future need to the actual need. International cooperation on an experimental programme would be invaluable because this could justify the expenditure of national funds and ensure a balanced programme. Even if the time comes when theoreticians are able to estimate properties with useful accuracy, key experiments will still be required to validate the theories.

An area not covered in this volume concerns the thermodynamics of surfaces. Surface chemistry is important to many processes including nucleation, crystal and droplet growth, adsorption, corrosion, catalysis, coating, joining and grain boundary segregation. There is an extensive literature on the applications of thermodynamics in these fields but no attempt has yet been made to develop a computer databank incorporating comprehensive data on the thermodynamics of surfaces.

T.I. Barry

# High temperature inorganic chemistry and metallurgy

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This chapter is concerned with the attainment or drive to chemical equilibrium, the state where the Gibbs energy of the system is minimized not only with respect to

physical mixing but also with respect to *chemical combination*. The subject matter divides into three parts: the first deals with pure substances and ideal solutions, the second with non-ideal solutions and the third with applications. Emphasis is placed on inorganic systems, because relatively few organic compounds are thermochemically stable.

Even this restriction leaves an enormous range of applications for inorganic and metallurgical thermodynamics, simply because so many materials are processed and used at temperatures where chemical reactions can occur. Readers concerned mainly with the applications rather than the principles of the thermodynamic methods should turn to section 3 on p. 24.

1   Pure substances and ideal solutions

Any chemical reaction, such as

$$2CO + 2H_2 = CO_2 + CH_4$$
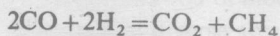
can be written in the form

$$\sum_j v_j \alpha_{ij} = 0 \tag{1}$$

where α_{ij} is the number of atoms of element i in species j, and v_j is the stoichiometry number, i.e. the number of moles, of species j participating in the equation, negative for reactants, positive for products.

For the reaction to be in equilibrium the Gibbs energy change, $\Delta_r G$, for the conversion of one mole of reactants to products in an infinite total amount must be zero.

$$\Delta_r G = \sum_j v_j G_j = 0 \tag{2}$$

where G_j is the partial molar Gibbs energy of species j, otherwise known as the chemical potential. Thus, in order to calculate the conditions of chemical equilibrium, data are required to enable the Gibbs energy to be calculated as a function of the amount and composition of the substances present, the temperature and pressure. For the example of ideal gases

$$G_j = G_j^0 + RT \ln p_j \tag{3}$$

where G_j^0 is the standard chemical potential of species j and p_j its partial pressure.

1.1   Data

1.1.1   *Standard and reference states.* As implied by equation (3), Gibbs energy values are not absolute but are always defined in relation to some standard conditions and reference states. Unfortunately, there are almost as many ways of

representing Gibbs energies as there are compilations, and, therefore, it is important to check at least the following points when using data from different sources.
(a) The data are expressed in the same form or that sufficient information is available to convert from one form to another.
(b) The reference states chosen for the elements are the same.
(c) When the data were compiled the same or known values were used for important secondary reference substances.

The variations in representation referred to above partly arise from differences in definition of standard states and reference substances. Therefore some comments on these points are necessary.

Standard states. A liquid or solid substance has standard properties when it is pure and at a pressure of 1 bar (10^5 Pa). The former standard, 1 atm. $= 1.01325$ bar, is still frequently used. The standard properties of a gaseous substance are those of the ideal gas at a pressure of 1 bar, the superscript ^{0} being used to denote a standard property. Even for real gases at 1 bar the difference between standard properties and real properties will not usually be very great; for methods of treating high pressure gases the reader should consult Chapters 3 and 4. For substances in solution, the pure substance at 1 bar is often taken as the standard state but other states, e.g. 1 wt%, may be found. Aqueous solutions present a special case (see Chapter 2).

Reference substances. The Gibbs energy of a substance must be defined with reference to other substances, usually the elements from which it is composed. The most stable form of the element is chosen, except in the case of phosphorus, for which white rather than red phosphorus is normally taken. For gaseous elements existing in various molecular states one form is usually assigned for all temperatures above the boiling or sublimation point.

Reference temperatures. The temperature 298.15 K (25 °C), often abbreviated to 298 K, is used as a reference temperature for many thermochemical calculations. However, some compilations, notably those originating in USSR, use zero K as a reference temperature.

Stable element reference state. The concept of a stable element reference (SER) state is introduced here to simplify the expression of thermodynamic quantities. The SER properties of a substance are the sum of those of its constituent elements in their standard states at 298.15 K, the elements being normally in the most stable form as discussed above. The usefulness of this definition will become apparent later.

Gibbs energy and equilibrium constant. For calculation of the equilibrium in an equation it is necessary to know the standard Gibbs energy change for the reaction which is given by

$$\Delta_r G^0 = \sum_j v_j G_j^0 \tag{4}$$

since $\Delta_r G$ is related to the equilibrium constant, K_p, by the equation

$$\Delta_r G^0 = -RT \ln K_p \tag{5}$$

and

$$\ln K_p = \sum_j v_j \ln a_j \tag{6}$$

For pure condensed substances, the activity, a_j, is equal to 1 and for ideal gases it is the pressure divided by the standard pressure. For calculations of chemical equilibria using equations (5) and (6) it is important to have convenient sources of reliable data and consistent Gibbs energy data, G_j^0, to be applied in equation (4). These Gibbs energy data can be interpolated from the compilations below or they may be computed as indicated in section 1.1.3.

1.1.2   Compilations. The most useful compilations are those in which thermo-dynamic quantities are tabulated as a function of temperature. The most comprehensive are listed below together with their particular features.

JANAF[1]: *Reference temperature 298.15 K.* Separate tables are provided for each phase of a substance in addition to a combined table in which the data relate to the phase stable at the temperature in question. Gibbs energy is expressed as $\Delta_f G^0$ and as $-(G^0 - H^0_{298})/T$. Equilibrium constants can be evaluated from $\Delta_f G^0$ or from the listed values of equilibrium constants of formation, $\log K_f$. C_p and S^0 are also tabulated. Additional data are provided on $H^0(298) - H^0(0)$ and transition enthalpies. Useful information describing the origins of the data chosen is provided.

Barin, Knacke & Kubaschewski[2]: *Reference temperature 298.15 K.* In most cases one table is used to cover all phases of a substance. Coefficients are listed that enable thermal functions to be calculated by means of an equation for heat capacity. Gibbs energy, tabulated under the heading '*G*', is the function $G^0 - H(\text{SER})$, i.e. the Gibbs energy of the substance at temperature less the enthalpy of its constituent elements at 298.15 K. The Gibbs energy of reactions, including formation from the elements, can readily be calculated using this function in equation (4), because the unknown term $H(\text{SER})$ for each substance cancels out over a chemical equation. Similarly the function $H^0 - H(\text{SER})$ is tabulated under the heading '*H*'. The logarithms of equilibrium constants can be calculated by summing over the equation the quantity listed under the column headed '*BT*', which is the function $(H(\text{SER}) - G^0)/RT \ln 10$.

Institute for High Temperature Chemistry (Moscow)[3]: *Reference temperature, zero K.* Combined tables are provided for condensed phases of substances and

separate tables for gaseous species. Columns list C_p, ϕ, S^0, $H^0 - H^0(0)$, log K, where $\phi = -[G^0 - H^0(0)]/T$ and K is the equilibrium constant for a specified reaction. Also listed are $\Delta_f H^0(0)$, $\Delta_f H^0(298)$ and transition data, and ϕ expressed as equations, usually for temperatures greater than 500 K.

The Gibbs energy change on reaction can be determined from

$$\Delta_r G = \sum_j v_j(\Delta_f H(0) - T\phi) \tag{7}$$

There is a comprehensive commentary in Russian and an English language version of the tables is in preparation.

Other useful sources are, *The NBS Tables of Chemical Thermodynamic Quantities*[4] and *Thermochemical Constants for Substances*[5]—which both cover many substances not included in the other compilations but are restricted to 298 K—and Kubaschewski & Alcock[6]. The CODATA key values for compounds[7] have particular importance because they are internationally agreed and can therefore be used with confidence as a foundation for further assessment. In addition to these general sources there are more specific compilations for some elements or groups of elements[8,9]. Many other sources as well as details of underlying theory and examples are given by Chart *et al.*[10].

1.1.3   Computer-based databanks. Many data centres and major industrial companies throughout the world have now set up computer-based databanks, i.e. databases coupled to software enabling calculations to be undertaken on the stored data. Some of the centres offer on-line access to the databanks and consultancy services using them, whereas others use databanks mainly to systematize and facilitate their effort on data assessment and to serve the individual needs of their organization[11,12]. Usually the data stored for each substance comprise:

$\Delta_f H^0(298)$, the standard enthalpy of formation at 298.15 K;
$S^0(298)$,   the standard entropy at 298.15 K;
C_p^0,   the heat capacity, expressed as sets of coefficients relating C_p to temperature. The function normally used is

$$C_p = A + BT + CT^2 + DT^{-2} \tag{8}$$

If data for various phases of a substance are stored in the same data set then enthalpies of transition and transition temperatures must also be incorporated. Instead of heat capacity, any thermal function such as $H^0(T) - H^0(298)$ or $(H^0(0) - G^0(T))/T$ may be stored so long as it enables thermodynamic properties to be referred to a fixed temperature. The following equations are used for calculating thermodynamic quantities as a function of temperature.

$$H^0(T) = H^0(298) + \int_{298}^{T} C_p \, dT \tag{9}$$

$$S^0(T) = S^0(298) + \int_{298}^{T} C_p/T \, dT \tag{10}$$

The functions used during computation to express enthalpy and Gibbs energy with respect to the elements are the same as those of the Barin, Knacke & Kubaschewski tables[2], namely.

Enthalpy: $H^0(T) - H(\text{SER}) = \Delta_f H^0(298) + H^0(T) - H^0(298)$ $\qquad$ (11)

Gibbs Energy: $G^0(T) - H(\text{SER}) = \Delta_f H^0(298) + H^0(T) - H^0(298) - TS^0(T)$ $\quad$ (12)

Computer-based databanks have a number of important advantages for users of thermochemical data as indicated below.

(a) No matter in what form the data are stored or what methods of internal calculation are used, the computer can in principle be programmed to produce tables to suit the user, for example mimicking the major compilations whilst using various units or intervals of temperature, energy, pressure and concentration.

(b) The user has no need to rewrite or retype stored data, so the possibilities for errors during data transfer are minimized. However, if necessary the user can supplement or modify the data for a particular problem from his own knowledge.

(c) Tabulations can be made for any combinations of substances of interest to the user. Thus, enthalpy changes and equilibrium constants can be determined for innumerable chemical reactions.

(d) Once properly programmed, computers are highly reliable. Thus, complicated error-free calculations can be undertaken.

(c) When coupled to a graphics package, output can be presented in a variety of graphical forms.

(f) As will be seen in the following sections, the databank can be programmed to undertake calculations of equilibria involving several components and phases. If these include non-ideal solution phases, there are further advantages, as discussed in section 2.7.

1.2   Calculation and presentation of thermochemical equilibria

Real problems in thermochemistry can seldom be solved by the determinations of equilibria for individual chemical equations. Almost invariably a number of alternative reactions are possible, even before considering the possibility that the products may react with the material of the plant. For this reason, methods are required which will reveal the behaviour of a system as a whole, preferably as a

function of variables that can be controlled in plant operation. Various types of diagram devised for this purpose have been classified and exemplified by Pelton & Thompson[13]. The purpose of this section is to describe some types of calculation and diagram, and briefly to indicate how they can be used to solve problems.

1.2.1   Relative stability diagrams.

To simplify plotting and interpolation of diagrams it is very desirable that they comprise sets of straight lines. Starting from the general equation for chemical equilibrium

$$K_p = \prod_j a_j^{v_j} \tag{13}$$

one obtains

$$\log K_p = \sum_j v_j \log a_j \tag{14}$$

and hence for the log activity of component i

$$v_i \log a_i = \log K_p - \sum_{j \neq i} v_j \log a_j \tag{15}$$

For small ranges of temperature $\log K_p$ can be expressed as a linear function of reciprocal temperature and therefore

$$v_i \log a_i = A + B/T - \sum_{j \neq i} v_j \log a_j \tag{16}$$

Thus, the potential—expressed as the logarithm of activity of component i—can be plotted as a linear function of the log activity for the other components or reciprocal temperature. Alternatively, if it is desired to use T rather than $1/T$ as an axis variable it is usual to plot $RT \ln a_i$ or $RT \ln p_i$ versus T.

If a set of these curves is prepared for various elements for equivalent reactions as exemplified in Fig. 1, it is possible to get a rapid appreciation of the relative stability of the elements towards the reactions. Such a set was produced by Richardson & Jeffes[14] for reactions of the elements and lower oxides with one mole of oxygen. The lines define the conditions of coexistence of the element (or a sub-oxide) and its oxide, both of which have unit activity on the line. Below the line the oxide is stable, above the line it decomposes. Thus, in a system of two elements plus oxygen the element lying lower on the diagram will reduce the oxide of an element lying higher up the diagram. In practice the result may be rather more complicated because the elements may react together to form alloy solid solutions, and the oxides may also react to form compounds or solid solutions. Moreover, where either the oxide or the element (or sub-oxide) is gaseous, allowance must be made through equation (16) for departure of its activity from unity. Nevertheless, the diagrams do offer a very simple visual way of categorizing the suitability of materials for various processes.
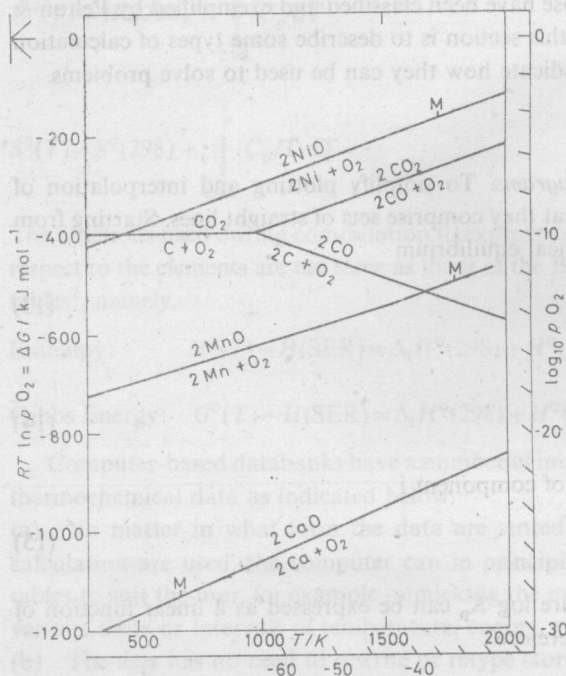
Fig. 1. Relative stability diagram for a few oxides. Lines of constant $p\,O_2$ radiate from the point corresponding to $T =$ zero K, $G = 0$. $p(CO) = p(CO_2) = 1$ atm.

Fig. 1 shows a simplified and recalculated version for a few oxides. Other diagrams have been produced for oxides[17], sulphides[16,18] and carbides[15,19]. Pourbaix has prepared a number of diagrams of this kind for individual systems, e.g. $Fe-O$[20], and shown how they can give insight into materials' properties.

1.2.2   Predominance area diagrams. A closely related type of diagram is useful when it is necessary to calculate the behaviour of an individual component under a range of conditions of temperature or partial pressure of gaseous species. A convenient way of presenting information on such a problem is exemplified by Fig. 2. This type of diagram is used extensively for the consideration of chemical and electrochemical equilibria in aqueous solutions of electrolytes, as discussed in Chapter 2. The lines on the diagram define the conditions for coexistence of the substances identified between the lines.

Various methods have been described for calculating the diagrams[21], though all rely on the same principle[21,22]. The substances may be in pure condensed form and therefore at unit activity, or they may be gaseous or in a solution at a specified activity. Therefore, each line represents a chemical equation for the reaction between two coexisting compounds of which the components are those defined by the axes
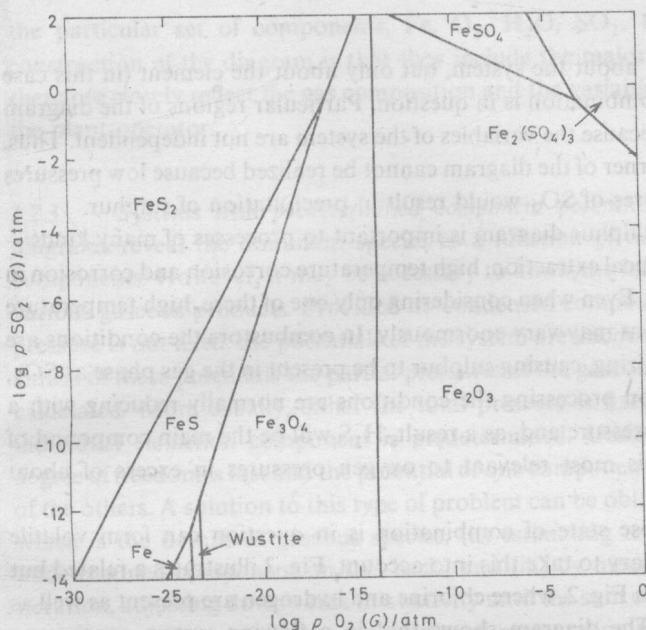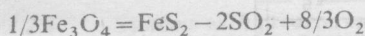
Fig. 2. Predominance area diagram for the iron–oxygen–sulphur system at 900 K.

variables. For example, Fig. 2 shows the behaviour of iron under a range of O_2 and SO_2 potentials. The coexistence line between FeS_2 and Fe_3O_4 is governed by the equilibrium equation for the reaction

$$1/3 Fe_3O_4 = FeS_2 - 2SO_2 + 8/3 O_2$$

$$\log K_p = 8/3 \log p(O_2) - 2 \log p(SO_2) \tag{17}$$

The slope of this line is 4/3, as determined by minus the ratio of the stoichiometry numbers of O_2 and SO_2. The position of the line is determined by the Gibbs energies of the two iron compounds involved, and it is terminated where reactions to form other compounds of iron can take place with a decrease of Gibbs energy. Thus, the lower end of the line is terminated at the condition where the reactions

$$FeS_2 = Fe + 2SO_2 - 2O_2$$

$$FeS = Fe + SO_2 + O_2$$

and $\quad 1/3 Fe_3O_4 = Fe + 2/3 O_2$
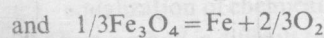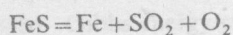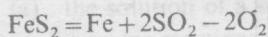
all result in the same Gibbs energy change when account is taken of the contribution from the non-standard pressure of O_2 and SO_2 as in equation (17). Note that the same amount of iron is involved in each chemical equation.

The diagrams must be used with some caution because they do not necessarily