

1

THE FOUNDATIONS OF CHEMICAL EQUILIBRIUM COMPUTATION

1.1 Prologue

1.1.1 The history of equilibrium computation

Until the early 1940s, only two methods appear to have been in use for the computation of chemical equilibria.

The first of these was based on the assumption that only a few molecular species would be present in the final equilibrium composition. By making use of mass action relationships, a limited number of non-linear equations specifying the composition were obtained. These were then solved numerically with such techniques as were available in the standard numerical analysis texts of the time (e.g. Scarborough, 1930).

The second method employed a cumbersome and time-consuming trial and error approach, in which the user's intuition played a crucial part. In fact, the solution of the problem often depended entirely on the user's intuition.

Furthermore, all such calculations were done on the calculators that were available until that time and those were, by present-day standards, very unsophisticated and mainly mechanical in nature. The principles first enunciated by Babbage in the nineteenth century had not yet resulted in the development of electronic, decision-making digital computers.

The development of rockets in the Second World War, particularly in Germany, led to a reconsideration of computational procedures for the solving of chemical equilibrium problems, because the technology of rockets such as the V2 required an accurate knowledge of the chemical equilibria of the propulsion gases formed in the chemical decomposition of the propellants within the rockets. Several articles describe the attempts at obtaining more accurate and, in particular, faster computational procedures for finding chemical equilibria. It is not surprising to

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2 COMPUTATION OF CHEMICAL EQUILIBRIA

find that two authors working at the Hermann Goering Air Force Research Institute in Germany published, as early as 1943, a paper entitled: 'The Composition of Dissociating Gases and Calculation of Simultaneous Gas Equilibrium'. The article was published as a Goering Institute Report, but also as a more generally available article (Damköhler and Edse, 1943). These authors describe a method wherein the non-linear equations, obtained on insertion of mass action equations into mass balance equations, are solved by a graphical estimation technique. They apply their method to an equilibrium mixture of gases, consisting of the elements carbon, hydrogen, nitrogen and oxygen, at specified pressure and temperature. For this system the procedure consists in estimating two starting values, viz. the partial pressures of H_2O and of O_2 , or, instead of the latter, the partial pressure ratio of CO_2 to CO can often be used advantageously. The other partial pressures are then calculated from these two initial estimates with the appropriate equilibrium constants. Changes in initial estimates are made until both the desired total pressure and the total oxygen balance equations are satisfied.

Algebraic procedures, very similar in nature to the graphical one mentioned in the previous paragraph, were proposed after computers became available (Winternitz, 1949; Donegan and Farber, 1956; Harker, 1967). Several later articles describe methods wherein all composition variables are related to one estimation variable (Von Stein and Voetter, 1953; McEwan, 1950).

The above mentioned schemes suffer from a number of serious disadvantages. The main problem is that the procedure employs mass action and mass balance equations written specifically for the system under consideration, and these equations have to be re-written for each new system. Furthermore, the procedure does not always succeed in converging to the desired equilibrium composition. Also, the amount of time involved in graph plotting, particularly when many different sets of pressure and temperature have to be investigated, is usually prohibitive.

The first major advance was made after the Second World War and most of the credit for the development of a generalized scheme is due to S. R. Brinkley. In 1946, Brinkley paved the way for a systematic approach to equilibrium computation, by giving an

analytical criterion for the number of independent components in a multi-constituent system (see §1.3.2). Subsequently, the same author published the outline of a method with which equilibria could be computed (Brinkley, 1947). The method is described in considerable detail in §4.2, so it should suffice to state here that Brinkley's procedure is basically a method wherein, first, a number of components is selected (see §1.3.2), with which, through the use of chemical equilibrium constants, the concentrations of all other chemical species in the equilibrium mixture are computed. These 'derived' species concentrations then serve as corrections to the atom balance equations and the correction procedure consists in solving a set of these corrected equations, with as many unknowns as there are elements (or components). Brinkley applied several methods, amongst others the standard Newton–Raphson linearization method for solving such sets of equations. Brinkley's method requires less set-up time than the method described by Damköhler and Edse, and furthermore, the finding of the numerical solution of a given problem, for instance that of the combustion of propane, actually requires much less time than the graphical method described above. But, and this is the main contribution that Brinkley's method made, his calculation scheme is very amenable to the use of digital computers. It is perhaps not entirely a coincidence that Brinkley's method first achieved success at the time when digital computers made their entry into the market and became generally available to research institutions, particularly in the United States.

Wilkes (1956) gives an excellent summary of the history of digital computers. He describes in some detail how Babbage came to stop the development of his analytical engine in 1843, and how the first model of the 'Automatic Sequence Controlled Calculator' was conceived by H. H. Aiken in 1937 and completed, at Harvard University, in 1944. This device was operating mechanically, but only two years later, in the summer of 1946, the first electronic computer (ENIAC) was built at the Moore School of Electrical Engineering at Pennsylvania State University. The same school built the EDVAC, wherein the von Neumann principle, of using words for both storage and commands, was utilized. This principle gives modern computers their real power in that they can modify

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Excerpt

[More information](#)

4 COMPUTATION OF CHEMICAL EQUILIBRIA

their own behaviour to cope with changes in external or internal conditions. The first computer to be designed (at Cambridge University) and used in England was the EDSAC, in May 1949. From the late 1940s until the present time, in a time-span of only two decades, the advances in computer technology have been almost unbelievably rapid. The extreme speed with which calculations could be performed led to the development of a whole new body of science: computer science, of which the field of equilibrium computation may be considered to form part.

During the last twenty years, fast and efficient methods for calculating equilibrium compositions have led to developments in three major areas of applied science. These are (see §1.1.2):

1. The development of rocket propellants.
2. The scientific evaluation of explosives.
3. The development of sophisticated chemical processing techniques, particularly high pressure and high temperature processes.

Of the three, the advance in propellant technology in particular has led to the development of a large number of sometimes very ingenious techniques for the solution of simultaneous chemical equilibrium problems. It is even possible that the development of propellants and rocket and space science, by creating a demand for rapid computation, contributed considerably to the development of computers sketched in the above paragraph. Certainly, only the development of larger and faster computers has made possible the development of propellants and rockets as they are in use today. Both these developments have had their main impetus in the United States, and is for this reason that most of the references to computational procedures in this monograph are to papers published in the United States (or in Canada).

1.1.2 Applications of equilibrium calculations

As was pointed out in §1.1.1, there has been a large interaction between computational procedures on the one hand, and applications of such computations on the other. There have been, during the past two decades, four main areas of applications.

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5

(a) The main application, and one that is important from the point of view of illustrating the need for accurate chemical equilibria, is the calculation of properties of propellants and rocket motors. One of the most important characteristics of propellants in a rocket motor is the specific impulse, which determines the apogee of the rocket that can be attained. The specific impulse is directly related to the exit velocity of the gas from the nozzle attached to the rocket motor. The exhaust velocity is determined by the difference ΔH in enthalpy H between nozzle exit and chamber:

$$I_s = \frac{V_e}{g} = \frac{\sqrt{(\Delta H)}}{g}, \quad (1.1.1)$$

where g is the gravitational constant. Thus, the enthalpies of the gas mixtures at the nozzle exit and in the chamber have to be calculated and since these depend on the chemical compositions of the respective gas mixtures, it can be seen that it is necessary to evaluate the equilibrium compositions of these mixtures. Solving these problems is now a standard exercise for propulsion engineers (Sutton, 1963). Computation of chemical equilibria is done by a standard subroutine in computer programs for the computation of specific impulse and of many other significant rocket design parameters and characteristics. Such important characteristics are, e.g. thrust, mass flow rate (propellant consumption), nozzle design, etc.

(b) Another application is found in the calculation of properties of explosives. The standard thermohydrodynamic theory of explosives (Cook, 1958) requires the knowledge of the thermodynamic properties of the gas mixture at the Chapman–Jouguet plane at the end of the reaction zone accompanying the detonation (or reactive shock) wave. These thermodynamic properties can only be found after having calculated the chemical equilibrium of the gas mixture in the reaction zone. In explosive property calculations, the problem is more complex than in the calculation of propellant or rocket properties and characteristics, because explosives give gas mixtures at extremely high pressures (of the order of millions of p.s.i.) and temperatures (several thousand °K). The equation of state describing such high pressure and temperature mixtures is one that cannot yet be predicted on the

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Excerpt

[More information](#)

6 COMPUTATION OF CHEMICAL EQUILIBRIA

basis of theoretical considerations, such as the virial equation of state. The virial equation of state has been applied, but only for standard mixtures consisting of the elements carbon, hydrogen, nitrogen and oxygen; for most other mixtures empirical equations of state have to be used (see §1.4.1). The non-ideality of the explosion products makes it necessary to develop special techniques for equilibrium computation (van Zeggeren and Storey, 1969).

(c) There are numerous examples of applications of complex equilibrium calculations in chemical processing. With the rapidly advancing technology that chemical processing has experienced over the past ten years, particularly with the increase in the number of high pressure, high temperature processes with their attendant rapid chemical kinetics, and in view of the increasing complexity and size of chemical processing plants, a large impetus has been given to rapid, computer control of such plants. Computer control usually requires a knowledge of the exact compositions encountered at each stage of the process under consideration. Also, with increase in competition, optimization of processes to give either maximum yield, efficiency, safety or any other extreme property, has led to the development of a considerable volume of optimization theory (Wilde and Beightler, 1967). In the optimization of chemical processes, chemical equilibria must be computed. It is rather interesting to note that, conversely, several techniques developed as optimization methods can be used as methods for calculating equilibria (see §3.2). Typical examples of high temperature, high speed commercial processes are combustion processes, such as in power plants, magnetohydrodynamic developments, plasma jet techniques, etc.

(d) The fourth main area of application is to problems of such complexity that manual calculation could never be attempted, even with all possible approximations and simplifications. Typical of such applications are the RAND methods for calculating the behaviour of multiphase biological cell systems (see e.g. Dantzig and DeHaven, 1962). Some applications have even been made in studies on the geological origin of organic materials (Eck *et al.* 1966); the study in question indicated that organic compounds such as aromatics may be formed, under conditions of thermodynamic equilibrium, from inorganic ingredients such as carbo-

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naceous chondrites, at moderate temperatures and low pressure. It seems that the next logical step in such studies could well be the investigation of the origin of life. (For an interesting and stimulating discussion of chemical evolution, see Calvin, 1965). It is hoped that some of the methods described in this book will be able to cope with problems of such formidable complexity.

1.2 Thermodynamics of chemical equilibria

1.2.1 Introduction

The computation of chemical equilibria is essentially a problem which relies on the solving of equations which can be derived from classical thermodynamics. In this section an outline will be given of those thermodynamic principles which are usually encountered in the solving of the computation problem. Although the thermodynamic principles are equally valid for ideal gases, non-ideal gases, and condensed compounds, and for mixtures thereof, this section will deal only with ideal gases and gas mixtures. The next section (1.3) will treat heterogeneous systems, and §1.4 will illustrate some of the added complexities encountered in the treatment of non-ideal gaseous systems.

1.2.2 Dalton's Law

The equation of state for ideal gases can be written as (Zemansky, 1957):

$$pV = nRT, \quad (1.2.1)$$

where n is the number of moles of all gases present in the system, thus:

$$n = n_1 + n_2 + \dots + n_N = \sum_{i(g)=1}^N n_i, \quad (1.2.2)$$

where N is the number of chemical species present in the (gaseous) system.* Equation (1.2.1) can also be written as:

$$p = \sum_i \frac{n_i RT}{V}, \quad (1.2.3)$$

$$p = p_1 + p_2 + \dots + p_N = \sum_i p_i, \quad (1.2.4)$$

* The word species here denotes a distinct chemical constituent in a given phase. The same constituent in another phase will be considered as the same species.

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Excerpt

[More information](#)

8 COMPUTATION OF CHEMICAL EQUILIBRIA

where it is postulated that p_i can be called a partial pressure of the system, thus: $p_i = (n_i RT/V)$. Equation (1.2.4) is known as Dalton's law (Zemansky, 1957). Equations (1.2.1) and (1.2.4) can be combined into

$$p = \sum_i \frac{n_i}{n} p = \sum_i p_i. \quad (1.2.5)$$

A useful value is the mole fraction of the i th gas which is denoted by x_i , viz. $x_i = n_i/n$, etc. Also $p_1 = x_1 p$, etc. It follows that

$$\sum_i \frac{n_i}{n} = x_1 + x_2 \dots x_N = 1 \quad (1.2.6)$$

so that, of the total number of N mole fractions, only $N-1$ are independent of each other; the last one can be determined from the other $N-1$ fractions.

1.2.3 Entropy and Gibbs free energy of gas mixtures

The entropy of an ideal gas (species i) at temperature T and pressure p is given by (Zemansky, 1957):

$$(S_T)_i = (S_{298})_i + \int_{298}^T (C_p)_i \frac{dT}{T} - R \ln p. \quad (1.2.7)$$

For a number of different gases i , prior to mixing, the total entropy at p and T is equal to the sum of each of the entropies of the gases:

$$S_T^n = \sum_i n_i (S_{298})_i + \int_{298}^T \sum_i n_i (C_p)_i \frac{dT}{T} - \sum_i n_i R \ln p, \quad (1.2.8)$$

where the superscript u indicates: unmixed. After mixing, assuming no chemical reaction takes place, the total entropy of the mixture is, according to Gibbs, equal to the sum of the partial entropies. The partial entropy s_i is the entropy that gas i would have if it occupied the whole volume alone at T , in which case it would exert a pressure equal to p_i . Thus:

$$S_T^m = \sum_i n_i (S_{298})_i + \int_{298}^T \sum_i n_i (C_p)_i \frac{dT}{T} - \sum_i n_i R \ln p_i, \quad (1.2.9)$$

where the superscript m indicates: mixed. Thus, from equations (1.2.8) and (1.2.9) follows an expression for the entropy of mixing:

$$(\Delta S)_{\text{mixing}} = - \sum_i n_i R \ln \frac{p_i}{p} \quad (1.2.10)$$

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which, according to equation (1.2.5) becomes:

$$(\Delta S)_{\text{mixing}} = -\sum n_i R \ln x_i \quad (1.2.11)$$

which has always a positive value: the spontaneous mixing process is accompanied by an entropy increase. This is in accordance with the second law of thermodynamics (Zemansky, 1957).

The Gibbs free energy G (also called the Gibbs function or the free enthalpy) is given by:

$$G_T = H_T - TS_T. \quad (1.2.12)$$

Thus, since $H_T = H_{298} + \int_{298}^T C_p dT$, equation (1.2.12) becomes:

$$G_T = H_{298} - TS_{298} + \int_{298}^T C_p dT - T \int_{298}^T \frac{C_p}{T} dT + RT \ln p. \quad (1.2.13)$$

Zemansky (1957) writes this expression as follows:

$$G_T = RT (\psi + \ln p), \quad (1.2.14)$$

where ψ is a function of T only. In a manner similar to that described for the entropy, the Gibbs free energy of mixing can be derived. One obtains:

$$(\Delta G)_{\text{mixing}} = RT \sum_i n_i \ln x_i. \quad (1.2.15)$$

In this case, $(\Delta G)_{\text{mixing}}$ is always negative, in accordance with the knowledge that mixing is a spontaneous process.

Many other thermodynamic variables such as the volume, enthalpy and specific heats, are purely additive for ideal gas mixtures (Prigogine and Defay, 1954). Thus, for these variables:

$$(\Delta V)_{\text{mixing}} = 0, \quad (\Delta H)_{\text{mixing}} = 0 \quad \text{and} \quad (\Delta C_p)_{\text{mixing}} = 0.$$

Equations (1.2.14) and (1.2.15) can be combined to give the frequently used expression for G at p and T for any (ideal) gas mixture:

$$G = RT \sum_i n_i (\psi_i + \ln p + \ln x_i). \quad (1.2.16)$$

1.2.4 Chemical equilibrium conditions

A chemical equilibrium can be defined as the thermodynamic state of a system which, for a given set of thermodynamic variables, is unalterable in its mechanical, thermal and chemical properties. The

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Excerpt

[More information](#)

10 COMPUTATION OF CHEMICAL EQUILIBRIA

conditions for chemical equilibrium can be derived as follows: Consider a system of constant mass, in mechanical and thermal but not chemical equilibrium. The system is in contact with its surroundings at temperature T , and undergoes an infinitesimal irreversible process involving an exchange of heat dQ with the surroundings. If dS_{sys} and dS_{sur} are the changes in entropy of system and surroundings, respectively, the total entropy change of system + surroundings is $dS_{\text{sys}} + dS_{\text{sur}}$ and since the process is irreversible this sum has to be greater than zero. Thus:

$$dS_{\text{sys}} + dS_{\text{sur}} > 0.$$

The entropy change of the surroundings is due merely to entropy transfer (Lewis and Randall, 1961), thus:

$$dS_{\text{sur}} = \frac{dQ_{\text{sur}}}{T} = -\frac{dQ_{\text{sys}}}{T}.$$

Then, by deleting the subscript 'sys' one obtains for the system:

$$dQ - TdS < 0. \quad (1.2.17)$$

In the irreversible process, the internal energy of the system changes by dE , and the amount of work performed is $p dV$. Thus, according to the first law:

$$dE + p dV - TdS < 0. \quad (1.2.18)$$

This is a very fundamental inequality in thermodynamics, that leads to the basic condition for chemical equilibrium, viz. that $dE + p dV - TdS = 0$ at equilibrium. Usually, the irreversible process is restricted in that two of the thermodynamic variables are maintained constant. The usual selection of these two variables is pressure and temperature. For p and T constant, inequality (1.2.18) becomes (Zemansky, 1957)

$$d(E + pV - TS) < 0 \quad \text{or} \quad dG < 0, \quad (1.2.19)$$

or, in other words, the Gibbs free energy of a system at constant p and T decreases during an irreversible process, becoming a minimum at the final equilibrium state. Another selection of variables, viz. that of V and T being kept constant, leads to

$$d(E - TS) < 0 \quad \text{or} \quad dA < 0. \quad (1.2.20)$$