

THE CHEMICAL
EQUILIBRIUM
OF GASEOUS
SYSTEMS

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Preface

It is the purpose of this book to present a concise and sufficiently detailed description of the present state and possibilities of calculating chemical equilibria of gas mixtures. It is based on a book by one of the authors, published in Czech by the Publishing House Academia in Prague. The rapid development of the topic during the two years since publication of the Czech edition has made it necessary to revise practically all the sections in order to bring them up to the present level of knowledge.

One reason for writing this book was the practical requirement of contemporary industry, where a rational utilization of equilibrium composition calculations may provide valuable information concerning processes under study in all stages of their implementation. A second reason was the need of a text-book for studying this part of chemical thermodynamics in the scope as taught at the Institute of Chemical Technology, Prague.

These two basic motives determine the overall structure of the book, as well as the proportions and arrangement of the chapters. The book includes fundamental thermodynamic concepts as well as the mathematical apparatus needed to solve the problems involved, care being taken that the discussion should always lead to a practical procedure of performing equilibrium calculations in gas-phase systems of any degree of complexity whatever. Knowledge of chemical thermodynamics on the level of a fundamental university course is assumed.

The book is divided into seven chapters. A brief definition of the topic in Chapter 1 is followed by stoichiometric analysis of chemically reacting systems, leading up to an absolutely generalized description of the application of linear algebra methods.

Chapter 3 discusses the thermodynamic fundamentals of equilibrium behaviour, defines equilibrium criteria and indicates briefly the possibilities of their characterization.

Chapter 4 includes the calculation of chemical equilibria in simple systems in the ideal gas state, and the determination of the influence of simple reaction variables.

Chapter 5 is a review of methods employed to calculate complicated chemical equilibria in the ideal gas state. By means of detailed analysis, four very reliable and quite generalized procedures were selected. These have been practically tested and are described in complete detail up to the stage of block diagrams, from which prac-

tical programmes can be developed easily. Thus the procedures can readily be used to solve practical tasks in isothermic and adiabatic arrangements.

Chapter 6 describes the application of the individual methods for calculating equilibria in real gas systems.

Chapter 7 presents a critical survey of sources of thermochemical data, their calculation or estimation, method of tabulation, instructions for carrying out calculations with respect to maximum technological utilization of the results of calculations and an example of the treatment of a system of practical interest; errors, which may cause some uncertainty in the calculation, are briefly analyzed.

The book is amplified by a number of Appendices summing up some non-conventional mathematical procedures, proofs and some of the most important thermochemical and physico-chemical data. In order to facilitate the understanding of illustrative problems and — at the same time — to stimulate the interest of the workers active in the industrial branches, we retained the traditional units (cal, K, atm).

We hope that this book will contribute to a more intensive application of methods of chemical equilibrium calculation, for which modern data processing equipment provides all necessary conditions. We also hope to have contributed a little towards making this branch of chemical thermodynamics as well known as it deserves to be in view of its practical application.

Finally, we should like to express our sincere thanks to Prof. Dr. Ing. Eduard Hála, Dr.Sc. and Prof. Dr. Ing. Jiří Pick, Dr.Sc. for valuable advice, Ing. Milan Šolc for carefully reading the manuscript and for helpful discussion, Dr. Ota Sofr for the translation and last not least, Mrs. Jaroslava Margoliusová for carefully typing the manuscript and drawing the pictures.

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Robert Holub
Petr Voňka

List of Symbols

a	constant of the relationship C_p as function of T
a_i	constant of the relationship $(C_p)_i$ as function of T
a, a_i	constant of the Beattie-Bridgman equation
a, a_i	constant of the Benedict-Webb-Rubin equation
a_i	activity of the constituent i
a_{ij}	constitution coefficient (denotes the number of atoms of the element j , present in the compound i)
A_i	chemical formula of the compound i
A_0	constant of the Beattie-Bridgman equation
A_k	constant of the power series K_a as function of T
b	constant of the relationship C_p as function of T
b_i	constant of the relationship $(C_p)_i$ as function of T
b, b_i	constant of the Beattie-Bridgman equation
b, b_i	constant of the Benedict-Webb-Rubin equation
B	constant
B, B'	second virial coefficient
B_{jk}	second virial coefficient of the interaction between constituents j and k
B_r	reduced second virial coefficient
B_j	chemical symbol of an element, or chemical formula of a basic particle species
B_k	constant of the relationship of the second virial coefficient as function of T
B_0	constant of the Beattie-Bridgman equation
B_0	constant of the Benedict-Webb-Rubin equation
c	constant of the relationship C_p as function of T
c_i	constant of the relationship $(C_p)_i$ as function of T
c, c_i	constant of the Beattie-Bridgman equation
c, c_i	constant of the Benedict-Webb-Rubin equation
c_i	constituent concentration
c_i	$= (G_i^o/RT) + \ln P$
C, C'	constant
C_p	molar heat

$(C_p)_i$	molar heat of constituent i
C, C'	third virial coefficient
C_{jkl}	third virial coefficient of the interaction between the constituents j, k and l
C_k	constant of the relationship C_p as function of T
C_r	reduced third virial coefficient
d	total differential of the quantity denoted by the following symbol
d	bond length
D, D'	fourth virial coefficient
D_{jklp}	fourth virial coefficient of the interaction between the constituents j, k, l , and p
e_j	value of (G°/RT) corresponding to the j -th element or basic particle species
E°	standard electromotoric force
f	fugacity
f_i	fugacity of constituent i
f_r	function symbol
F	free energy (Helmholtz function)
F_i	free energy (Helmholtz function) of constituent i
F	Faraday constant
F	function symbol
G	free enthalpy (Gibbs function)
G_i	free enthalpy (Gibbs function) of constituent i
G_f	free enthalpy of formation
H	rank of a matrix of constitution coefficients
H	enthalpy
H_i	enthalpy of the constituent i
H_f	enthalpy of formation
H_r	enthalpy of chemical reaction (heat of reaction)
I_H	integration constant of the heat of reaction vs. temperature relationship
I_K	integration constant of the equilibrium constant vs. temperature relationship
K	Kelvin
K, K_a, K_r	equilibrium constant
K_f	equilibrium constant of reaction of formation
M	number of elements (basic particle species) in a closed system
M_i	molecular weight of compound i
n	overall number of moles in a system
n_i	number of moles of constituent i
N	number of compounds in a closed system
p_i	$= \sum_{k=1}^M a_{ik} \lambda_k - c_i$

P	number of linear combinations of columns of the matrix of constitution coefficients
P	overall pressure in a system
P_i	partial pressure of constituent i
P_c	critical pressure
P_r	reduced pressure
r_{jk}	coefficient of a system of linear equations
R	number of linearly independent reactions
R	gas constant
q_i	$= n_i + \sum_{r=H+1}^N v_{ri} n_r$
Q	function symbol $V, G/RT$
S	entropy
t	reciprocal value of the overall number of moles ($1/n$)
T	absolute temperature
T_c	critical temperature (K)
T_r	reduced temperature
u	function symbol
u	$= (n^{(p+1)}/n^{(p)} - 1)$
U	internal energy
v	molar volume
v_i	molar volume of the constituent i
V	overall volume
W	function symbol
y_i	molar fraction of constituent i
z	linking condition
z	compressibility factor
z_c	critical compressibility factor

Superscripts

e	quantity in equilibrium
M	quantity of mixing
o	quantity in standard state (or pure constituent)
0	initial value (zero-th approximation)
p	step (p -th approximation of the quantity denoted by the preceding symbol)
$'$	notation of alternative quantity, denoted by the preceding symbol
$-$	partial molar quantity
$*$	under conditions close to ideal ones

Subscripts

c	critical state
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f	for reaction of formation
i	index of summation for compounds (1, 2, ..., N)
j	index of summation for elements (basic particle species) (1, 2, ..., N)
k	index of summation
l	index of summation
m	relating to mixture
p	index of summation
r	index of summation for reactions (1, 2, ..., R)
r	reduced state
s	index of summation
x	required value of quantity denoted by the preceding symbol

Greek letters

α, α_i	constant of the Benedict-Webb-Rubin equation
α	directional angle
β	functional expression in the Beattie-Bridgman equation
β_r	correction factor, replacing the reaction coordinate ξ_r
γ	functional expression in the Beattie-Bridgman equation
γ, γ_i	constant of the Benedict-Webb-Rubin equation
Γ	dimension-less function of free enthalpy (equal to G/RT , or $\sum_{i=1}^N f_i$)
∂	partial differential
δ	functional expression in the Beattie-Bridgman equation
δ_{jk}	Kronecker's delta (unit diagonal matrix of the dimension $j \times k$)
Δ	final difference, or deviation of quantity following the symbol
ε	arbitrarily small positive number
λ	Lagrangian multiplier
$\dot{\lambda}$	magnitude of step
$\dot{\lambda}_i$	arbitrary chosen vector, substituting a stoichiometric coefficient
μ_i	chemical potential of constituent i
v_{ri}	stoichiometric coefficient (denotes the number of moles of the i -th constituent taking part in the r -th reaction)
ξ	reaction coordinate (degree of conversion, extent of reaction)
ξ_r	reaction coordinate of the r -th reaction
$\prod_{i=1}^N$	denotes the product over i ($i = 1, 2, \dots, N$)
σ	reciprocal molar volume ($1/v$)
$\sum_{i=1}^N$	denotes the sum over i ($i = 1, 2, \dots, N$)
φ_i	fugacity coefficient of constituent i
Φ	function symbol

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1 Introduction

Chemical equilibrium can be established when a system contains constituents between which chemical conversion can take place. Determination of the products which can be formed by chemical conversion of the initial constituents and of the composition of the system in equilibrium is one of the frequent, important and often highly interesting problems which have to be solved in practice.

Up to recent times, when the chemical industry was still mainly based on coal, organic syntheses set out from relatively pure individual compounds e.g. acetylene, ethylene, benzene, etc., reacting systems could generally be described by means of a simple chemical reaction. With conversion of the chemical industry to oil and petrochemical processes, it becomes increasingly important to utilize multi-component mixtures as raw materials. This development is supported by economic aspects as well as progress in chemical technology, instrumental analysis and engineering. Separation of the components from petroleum or its fractions is difficult and expensive, while on the other hand, contemporary technology, utilizing modern analytical techniques is able to study even highly complex reaction systems. In this situation it is essential to be able to calculate the chemical equilibrium of systems in which several chemical reactions will be taking place.

There is no difficulty in calculating the chemical equilibrium of a system, in which a single chemical reaction takes place. The calculation, however, becomes increasingly difficult with the rising number of simultaneous reactions, until application of the same procedure to systems with more than three reactions proceeding simultaneously is practically impossible. Therefore, techniques have had to be worked out for more complicated chemically reacting systems, based on principles somewhat different from those of simple equilibrium calculation. The result are methods which allow equilibrium compositions to be calculated for systems of any degree of complexity whatever, in the ideal as well as real gas state.

A survey of the most important and generally applicable procedures, together with practical instructions for their application in solving actual problems is the topic of this book.

2 Stoichiometry of chemical reactions

In chemistry, stoichiometry is conventionally understood to mean the relationship between elements or fundamental particles and components in their mutual conversions. In the field of chemical equilibria, stoichiometry permits investigation of concentration changes as well as an accurate determination of the maximum number of reactions which may take place in a system, and allows the optimum combinations of these reactions to be selected. For this reason, equilibrium considerations proper must be preceded by a detailed stoichiometrical analysis of the system involved. This purpose may well be achieved by utilization of linear algebra, and a closed system may be described formally as a system of linear algebraic equations.

2.1 DEFINITION OF A CHEMICAL REACTION

Let us consider a closed system consisting of M elements and N constituents. Let A_i stand for the i -th constituent and B_j for the j -th element. Then,

$$A_i = \sum_{j=1}^M a_{ij} B_j \quad i = 1, 2, \dots, N \quad (2.1)$$

where a_{ij} is the constitution coefficient, denoting the number of gram atoms of the j -th element in the i -th constituent.

For conventional use this intuitive concept of a compound is sufficient, and there is no difficulty in extending it to a radical. Provided an electron is additionally defined as one of the set of elementary particles B_j , ions may also be considered to be independent constituents.

When every compound is described as a line vector of constitutional coefficients, a system of N constituents may be defined by a matrix of $N \times M$ elements. Clearly the elements of this matrix must be non-negative integers. With regard to the physical sense of the matrix, none of its rows or columns may be composed exclusively of zeros.