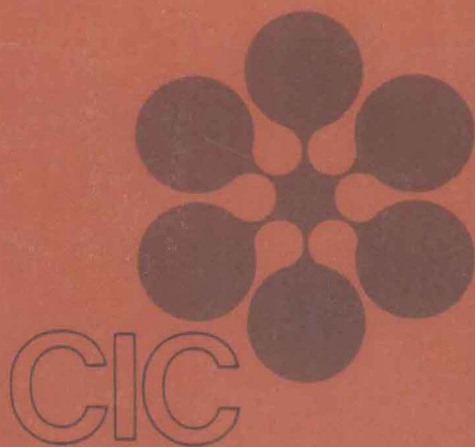


J. Gmehling (Ed.)

Software Development in Chemistry 5

Proceedings of the Workshop
„Computers in Chemistry“, Oldenburg



Springer-Verlag

J. Gmehling (Ed.)

Software Development in Chemistry 5

Proceedings of the 5th Workshop
"Computers in Chemistry"
Oldenburg, November 21-23, 1990

Organized by the working group

Springer-Verlag
Berlin Heidelberg New York
London Paris Tokyo Hong Kong
Barcelona Budapest

Prof. Dr. Jürgen Gmehling
Universität Oldenburg
Technische Chemie (FB9)
Ammerländer Heerstrasse 114-118
W-2900 Oldenburg
FRG

ISBN 3-540-53532-2 Springer-Verlag Berlin Heidelberg New York
ISBN 0-387-53532-2 Springer-Verlag New York Berlin Heidelberg

Library of Congress Cataloging-in-Publication Data

Workshop "Computers in Chemistry" (5th: 1990: Oldenburg, Germany) Software development in chemistry 5: proceedings of the 5th Workshop "Computers in Chemistry", Oldenburg, November 21-23, 1990; organized by the working group, CIC Computer in der Chemie der GDCh — Fachgruppe Chemie-Information / J. Gmehling (ed.). p. cm.
ISBN 0-387-53532 (U.S.)

1. Chemistry — Data processing — Congresses. 2. Information storage and retrieval systems — Chemistry — Congresses. I. Gmehling, Jürgen, 1946 - . II. GDCh-Fachgruppe Chemie-Information. Arbeitsgruppe CIC Computer in der Chemie. III. Title.
QD39.3.E56W67 1990 542'.85512—dc20 91-18942

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, re-use of illustrations, recitation, broadcasting, reproduction on microfilms or in other ways, and storage in data banks. Duplication of this publication or parts thereof is only permitted under the provisions of the German Copyright Law of September 9, 1965, in its current version, and a copyright fee must always be paid. Violations fall under the prosecution act of the German Copyright Law.

© Springer-Verlag Berlin Heidelberg 1991
Printed in Germany

The use of registered names, trademark etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

Geleitwort

Die Globalisierung von Wissenschaft und Wirtschaft hat die Fachinformation zu einer weltmarktpolitischen Aufgabe werden lassen. Der Rohstoff "Information" ist neben Boden, Arbeit und Kapital zum vierten Produktionsfaktor geworden, der mit Hilfe der Fachinformation erschlossen werden kann. Dafür stehen nebeneinander die beiden Systeme Buch und Zeitschrift sowie Informationssystem und Datenbank zur Verfügung.

Das Fachinformationsprogramm der Bundesregierung 1990 - 1994 möchte Wissenschaft und Wirtschaft zum Beschreiten dieser Wege zum Wissen der Welt anregen und sie dabei unterstützen.

Zur besseren Ausschöpfung aller zur Verfügung stehenden Informationsquellen setzt dieses neue Programm vor allem bei der Nutzungssteigerung in Hochschulen sowie in kleinen und mittleren Unternehmen an. Ein zweiter Schwerpunkt liegt auf der Bewältigung der Informationsflut. Gerade die Chemieinformation bietet ein gutes Beispiel für die Schaffung wechselseitiger Abhängigkeiten auf einem international führenden Marktsegment. Ziel ist hier der Aufbau eines integrierten Chemieinformationssystems.

In Thematik und Zielsetzung des 5. Workshops "Software-Entwicklung in der Chemie" in Oldenburg sehe ich eine bemerkenswerte Unterstützung des neuen Fachinformationsprogramms der Bundesregierung. Insbesondere wird dies deutlich bei den Schwerpunkten Fakten- und Struktur-Datenbanken, Spektroskopie, Molekülmodellierung, Reaktionsvorhersage und Synthesplanung.

Ich freue mich, daß die Gesellschaft Deutscher Chemiker der ständig wachsenden Bedeutung der Computerchemie mit der Schaffung der Fachgruppe CIC - "Chemie-Informations-Computer" Rechnung getragen hat. Ihre Workshops sind mittlerweile ein wesentliches Forum für den Erfahrungsaustausch von Wissenschaft und Industrie. Ich unterstütze diese Bestrebungen besonders durch die Förderung der Datenbanken **BEILSTEIN**, **GMELIN**, **DETERM** und der Bereiche **Reaktionen** und **Spektren** sowie des wissenschaftlich-technischen Informationsnetzes **STN International**.

Für die weitere Entwicklung dieser noch recht jungen Grenzgebiete zwischen Chemie und Informatik wünsche ich der GDCh auch weiterhin ein gutes Gelingen.

A handwritten signature in black ink, consisting of a stylized 'H' followed by a series of loops and a checkmark-like flourish.

Dr. Heinz Riesenhuber

Bundesminister für Forschung und Technologie

Foreword

The internationalization of science and industry has brought great changes to the area of technical information, so that it has de facto assumed a position of geopolitical importance. The raw material "information" has taken its position, together with land, labor and capital, as the fourth production factor and can be made accessible with the help of technical information. For this purpose two complementary systems exist:

- books and journals
- information systems and databases.

The Technical Information Program of the Federal Republic of Germany for the years 1990-1994 is intended to motivate and assist science and industry along this path to the "Knowledge of the World". So that all available information systems and sources are optimally utilized this new program is especially assigned to increasing the use of these sources in universities, in institutes of technology, and in small and medium-sized companies.

A second important point of emphasis of the program is the processing and management of the explosive increase of information. Chemical information in particular represents an example for the creation of interdependencies in a leading international field of enterprise. The goal here is the creation of an integrated chemical information system.

I see in the theme and goals of the Fifth Workshop "Software-Entwicklung in der Chemie" ("Software Development in Chemistry") in Oldenburg a remarkable support for the new technical information program of the Government of the Federal Republic of Germany. This is especially obvious from the following points of emphasis: factual and structure databases, spectroscopy, molecular modelling, prediction of reactions and synthesis planning.

I am especially pleased that with the creation of the specialized group CIC - "Chemistry-Information-Computer" the Gesellschaft Deutscher Chemiker has recognized the continually growing importance of computational chemistry. These workshops have become an essential forum for exchange of experience and information between science and industry. I support these efforts, especially through grants for the databases BEILSTEIN, GMELIN, DETHERM and the areas reactions and spectra as well as the scientific and technical information networks of STN International.

For the further development of this relatively new interdisciplinary field lying between chemistry and information science I wish the GDCh much success also in the future.

Dr. Heinz Riesenhuber

The Federal Minister of Research and Technology of the Federal Republic of Germany

(translated by Dr. D. Ilten)

Preface

This book contains a great part of the contributions presented at the 5th Workshop "Software-Entwicklung in der Chemie" (Software Development in Chemistry) which took place in Oldenburg, November 1990. This annual workshop again was organized by the division "Chemistry - Information - Computer" ("Chemie - Information - Computer (CIC)" of the German Chemical Society (Gesellschaft Deutscher Chemiker (GDCh)).

The main idea of these workshops is to bring together computer users who are active in software development in the different fields of chemistry, to support interdisciplinary collaboration, to present recent software developments, to discuss actual problems in education and research, to show applications important for chemical industry and to find ways to support promising new developments.

For the first time the workshop took place in the north of Germany. The first, second and fourth meeting were held in Hochfilzen (Tyrol/Austria) and the third one in Tübingen. The proceedings of the first four workshops have also been published by Springer-Verlag. To simplify the study of the articles outside the German speaking countries and to increase their acceptance, starting with the fourth workshop, the proceedings are now published in English, although the conference language is German. The development and history of these workshops has been described in the preface of the proceedings of the 4th workshop.

Twenty seven oral and 37 poster and computer demonstrations were presented by institutions from universities, the chemical industry and other scientific bodies representing most of the important computer applications so that the participants got a good idea about what is going on in computer chemistry. The application of computers for chemical engineering, collection, interpretation and prediction of spectra, chemometrics, factual and structure data banks, expert systems, prediction of reaction paths, synthesis planning, molecular modelling and the development of graphical tools were all emphasized during this workshop. The number of participants again had to be limited to 180 as was the case the year before.

Caused by the political changes in Europe and especially because of the unification of Germany, various scientists from the former German Democratic Republic used the chance to attend this meeting. This situation, of course, enriched the meeting and gave the opportunity for scientific and private discussions not possible before and to plan or coordinate joint research activities.

Not only the poster session and computer demonstrations, but also coffee breaks, lunch or dinner with the special local dishes (e.g. Grünkohl mit Pinkel) and the cold buffet supplied sufficient time for discussions in smaller groups. Unfortunately for most of the participant who had to leave directly after the meeting, there was no time left to enjoy the city of Oldenburg and its surroundings.

The significance of this meeting is again shown by the fact, that it was organized under the patronage of the Federal Minister for Research and Technology (Bundesminister für Forschung und Technologie) Dr. H. Riesenhuber of the Federal Republic of Germany and the Minister for Science and Culture (Minister für Wissenschaft und Kultur) Helga Schuchardt from the state of Lower Saxony (Niedersachsen).

One of the highlights of the workshop was the overview on expert systems by one of the well known experts (Prof. Appelrath) in this field. Because the different topics of his lecture have already been published in various journals of computer science we refrained from publishing the manuscript in the proceedings of this workshop.

The success of such a meeting of course depends on the collaboration of many people. The scientific committee , Prof. H.-J. Appelrath, Prof. J. Brickmann, Prof. J. Gasteiger, Prof. G. Gauglitz, Dr. C. Jochum, Dr. R. Neudert, Prof. M. Otto, Dr. V. Schubert, Prof. K. Varmuza, Dr. J.H. Winter and Prof. D. Ziessow were responsible for approaching qualified scientists to deliver a contribution and for smoothing the program. The division " Chemie - Information - Computer (CIC) ", the Working Party " EDV in der Chemie " and Akademische Software-Kooperation (ASK) helped in distributing the different circulars. Various institutions and companies (ASK, BASF, Bayer, Degussa, Henkel, Krupp-Koppers, Solvay) supported the meeting. This allowed the organizers to keep the conference fee low so that interested students were also able to attend. The organizers would like to thank especially the Stipendien-Fonds des Verbandes der Chemischen Industrie for covering the travel expenses of the participants from universities of the former German Democratic Republic.

Last but not least I must thank I. von Stuckrad, N. Grochert and J. Rarey for doing most of the work in organizing and running the workshop. Especially during the last week of preparations my whole research group - R. Böltz, A. Böning, K. Esser, T. Holderbaum, A. Koester, J. Krafczyk, B. Meents, J. Menke, T. Meyer, H.M. Polka, M. Sakuth, M. Schiller, B. Werner, G. Wienke - ran things in an exemplary way.

Furthermore I have to thank the authors who had to deliver their manuscripts in a camera-ready form and my colleagues at the university for their great understanding in spite of all the troubles especially those caused by the occupation of the large lecture room during the current semester.

I hope that all the participants enjoyed the meeting, picked up some new ideas and were able to establish new relationships to scientists working on related subjects. On this occasion I would again like to thank all the people and institutions mentioned above and all the active participants who contributed to the success of the 5th CIC-Workshop.

Jürgen Gmehling

Table of Contents

Computer Application in Chemical Engineering

J. Gmehling Development of Thermodynamic Models with a View to the Synthesis and Design of Separation Processes	1
J.R. Rarey, J. Menke, J. Gmehling DDBPC: A Program System for the Management, Correlation and Calculation of Thermodynamic Properties of Pure Components and Mixtures	15
J. Wagner, H. Knapp BDBT-BPBP-BPPT - Integrated System for Data Handling	29

Factual Databases

J. Bohlen, A. Parlow, C. Weiske, J. Gasteiger CHEMINFORM - An Integrated Production Process for the Building of a Reaction Database and the Publishing of a Printed Abstracts Service	37
M. Molnarne CHEMSAFE - A Database for Safety Characteristic Data	45

Structure and Properties

H.-G. Rohbeck Representation of Structure Description Arranged Linearly	49
W.D. Ihlenfeldt, J. Gasteiger Synthesis Planning Based upon the Similarity of Chemical Structures	59
K. Rafeiner, J. Gasteiger Calculation of Heats of Formation for Organic Radicals and Cations	69

E. Lang, Th. Förster Matching of 2D and 3D Structure Descriptions in the Cambridge Crystallographic Data Files: Outline of the Method and some Applications	77
S. Hübel, R. Franke EVAL - A New Tool to Evaluate Topological Pharmacophores	85
B. Adler, J. Will Prediction of Chemical Carcinogenicity	91
R. Grund, R. Hager, F. Herrmann, A. Kerber, R. Laue, W. Weber Groups, Graphs and Isomers	95
<u>Chemometrics</u>	
W. Werther, H. Lohninger, K. Varmuza Development of Chemometric Detectors for Gas Chromatography/Mass Spectrometry by the Use of a Linear Mapping Method	103
D. Wienke, U. Wank, M. Wagner, K. Danzer MULTIVAR, PLANEX, INTERLAB - From a Collection of Algorithms to an Expert System: Statistics Software Written from Chemists for Chemists	113
E.R. Hilf, W. Schlez, K. Kruse, A. Wullweber, U. Steenen St. Harsdorff, K. Koch, B. Nitzschmann, F. Kammer, W. Tuszyński Chemometry of Plasma Desorption Mass Spectrometry	129
G. Gauglitz Optical Sensors - Do They Require a Computer?	139
S. Ebel, H. Wätzig Validation by Automatisations: An Improved Method to Test Columns	151
H. Lohninger Classification of Mass Spectral Data Using Neural Networks	159

Molecular Modelling

P. Bleckmann, P. Breitenbach, D. Keller, F.H. Walter Calculation of Molecular Structures on Distributed Computer Systems by Use of Quantum Chemical and Vibrational Spectroscopic Methods	169
U. Sternberg, F.-Th.Koch COSMOS- A PC-Program for Molecular Modelling, Crystallography and the Prediction of Molecular Properties	183
H. Bunz, K.-H. Naumann Modelling of Physical and Chemical Processes of Polydisperse Aerosol Systems	191
H. Bögel, J. Sadowski Fast Generation of 3D-Structures with the Program MOL-CAD	199

Graphic Tools

H. Hayd, H. Spohn, H. Preuß Visualization Programs for Ab Initio Calculations	209
G. Apitz, Th. Brettner, S. Schönleber, J. Siebel, W. Steglich 3D-KALOTTE, Three-Dimensional Presentation of Molecular Models on IBM Compatible Computers	221
T. Cieplak The Beauty of the Graphical Structure Graph	225
N. Reuter HPGL-LOOK 3.0 - A HPGL Interpreter for Computer Displays	233

DEVELOPMENT OF THERMODYNAMIC MODELS WITH A VIEW TO THE SYNTHESIS AND DESIGN OF SEPARATION PROCESSES

J. Gmehling

Universität Oldenburg, Technische Chemie (FB9)
Postfach 2503, D-2900 Oldenburg, FRG

Abstract: The design of the different processes in chemical industry can be carried out with the help of computers by solving the resulting equations for the material and enthalpy balance. As input besides kinetic data (transport properties, reaction rate information) information about the real behavior of fluid mixtures as function of concentration, temperature and pressure is required.

For separation processes especially the reliable knowledge of the different phase equilibria (vapor-liquid equilibria (VLE), liquid-liquid equilibria (LLE), ..) in multicomponent mixtures is of great importance.

These phase equilibria can be described by using activity coefficients (g^E -models) or fugacity coefficients (equations of state) to account for the deviation from ideal behavior. Both methods do require experimental binary information. When this binary information is missing reliable group contribution methods can be used to supplement the experimental information.

In this paper different predictive methods are presented which can be applied to predict the real behavior of fluid mixtures. Furthermore the importance of the Dortmund Data Bank for the development of these methods is discussed and different important applications of these models are shown.

INTRODUCTION

Chemical plants can be roughly divided into a preparation, reaction and separation stage. Although the reactor can be regarded as the heart of a chemical plant, in most cases 60 - 90 % of the investment and operating costs are required for the different separation processes, such as rectification, extraction, absorption, ... All these processes utilize concentration differences between two different streams (phases) in countercurrent multi-stage processes for the separation of multicomponent mixtures.

While in the past a great number of laboratory and pilot plant experiments were required for the design of separation processes, today using the ideal stage concept the design can be carried out numerically by solving the balance equations (MESH equations) taking into account the phase equilibrium of the mixture to be separated. For a rectification column the balance equations are shown in Fig. 1. In real cases (large number of theoretical stages N , multicomponent systems (n components)) a large number of equations ($N (2n + 3)$) have to be solved. Nevertheless, using modern computers and algorithms the solution of such a system of equations does not cause any great problem. The accuracy of the design mainly depends on the quality of the phase equilibrium ($K_i = y_i/x_i$) and enthalpy data used.

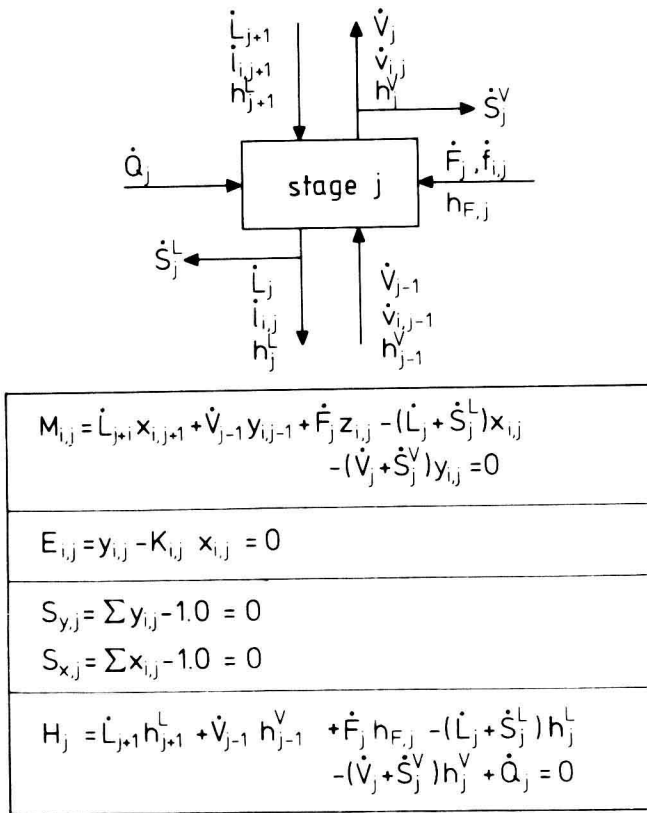


Fig. 1 MESH Equations

PHASE EQUILIBRIUM

For the description of the phase equilibria today modern thermodynamic models are available. Starting from the isofugacity criterion:

$$f_i^\alpha = f_i^\beta$$

the different phase equilibria can be described by using activity or fugacity coefficients to account for the real behavior of the different phases (1). For vapor-liquid equilibria it can be distinguished between two different methods. One method only requires fugacity coefficients φ_i for the liquid (L) and the vapor (V) phase:

$$x_i \varphi_i^L = y_i \varphi_i^V$$

whereby the required fugacity coefficients can be derived from the PVTx(y)-behavior e.g. by using cubic equations of state such as the Soave-Redlich-Kwong or Peng-Robinson equation of state.

Another method (γ - φ -approach) employs activity coefficients to describe the real behavior in the liquid and fugacity coefficients for the vapor phase, whereby for compounds which do

not associate strongly at moderate pressures often the following simplified relation can be used:

$$x_i \gamma_i P_i^S = y_i P$$

For the calculation of activity coefficients in multicomponent systems different g^E -models (e.g. Wilson, NRTL, UNIQUAC) are available.

Both methods have different advantages and disadvantages. They have in common that phase equilibria of multicomponent mixtures can be calculated using binary data alone. This is most important since nearly no data are available for multicomponent systems. But for fitting the required binary parameters reliable phase equilibrium information for the whole concentration and a large temperature range is required. Using equations of state there is the great advantage that besides the phase equilibrium different other pure component and mixture properties can be calculated (densities, vapor pressures, thermodynamic properties such as enthalpies, entropies, .. of the different phases, heat of vaporization, ..) and that this method also can be used to handle supercritical compounds.

For actual problems often at least a part of the required binary data is missing. This means that in many cases the methods mentioned above cannot directly be applied. To overcome these problems the missing binary data have to be measured or ideal behavior has to be assumed. Since the measurement of phase equilibrium data is very time consuming and the assumption of ideal behavior can lead to very erroneous results it would be most desirable to apply a reliable predictive method.

DORTMUND DATA BANK

For the development of reliable methods covering a large range of applicability most of the published phase equilibrium information should be available in a computer readable form. This was the reason that with the intention to employ the vast store of published VLE data for the development of predictive methods for vapor-liquid equilibria the Dortmund Data Bank (DDB) was started in 1973 at the University of Dortmund. Today the DDB represents the largest computerized data bank for thermodynamic mixture properties. The stored data are available in printed form (2 - 5), by an online service provided by FIZ Chemie and DECHEMA and are used in form of an inhouse version by a number of different chemical companies.

The present status of the Dortmund Data Bank is shown in Table 1. From Table 1 it can be seen that beside pure component data for appr. 2500 components data on vapor-liquid equilibria, liquid-liquid equilibria, heats of mixing, excess heat capacities, gas solubilities and activity coefficients at infinite dilution are stored. Furthermore work was started on a data bank for azeotropic data. In the future the started data banks with solubility data of solids and VLE data for electrolyte systems should be extended and furthermore thermodynamic information on polymer systems should be included in the Dortmund Data Bank. To complete the available phase equilibrium information also VLE data of low boiling substances which were kindly given to us by Prof. Knapp (Berlin/FRG) were integrated in the Dortmund Data Bank. The Dortmund Data Bank with the stored pure component properties and the comprehensive mixture data is the ideal tool for fitting reliable model parameters for g^E -models or equations of state and for the development of group contribution methods. So for the development of reliable group contribution methods with a broad range of applicability nearly all available information covering a large temperature and the whole concentration range for a variety of compounds very different in size can be used. Furthermore nearly no input for

the selection of the desired systems, the consistency tests and the parameter fit is needed since all the required informations (vapor pressure data, critical data, structural information) from the different programs are automatically called from DA-files. This means that the user only has to specify the structural groups which have to be fitted. Today the development of a reliable generally applicable predictive method would not be possible without the use of this kind of data bank.

Pure Component Properties:

for appr. 2500 compounds

References for each type of data XXX:

XXX = VLE, LLE, HE, ACT, GLE, CPE, AZD, SLE, ELE
appr. 7600 references

Data on Mixtures:

	Number of Isotherms or Isobars
Vapor-Liquid Equilibria (VLE)	14000
Liquid-Liquid Equilibria (LLE)	3400
Heats of Mixing (HE)	7400
Activity Coefficients at Infinite Dilution (ACT)	27000 values
Gas Solubilities (GLE)	5200
Excess Heat Capacities (CPE)	560
Azeotropic Data (AZD)	10000 values
Solid-Liquid Equilibria (SLE)	300
VLE of Electrolyte Systems (ELE)	120

integrated:

VLE of Low Boiling Substances (HPV)	2800
-------------------------------------	------

Table 1 Current Status of the Dortmund Data Bank (DDB)

DEVELOPMENT OF PREDICTIVE METHODS

As already planned in 1973 the VLE data stored in the Dortmund Data Bank were used for the development or further development of different predictive methods. For the prediction of pure component properties the application of group contribution methods has been proved to be most successful. The same concept can be used for mixture properties. In these group contribution methods it is assumed that the mixture does not consist of molecules but of functional groups. In these methods the activity coefficient γ_i is calculated

from a combinatorial ($\ln \gamma_i^C$) and a residual part ($\ln \gamma_i^R$):

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R$$

The equation used for the residual part follows from the solution of groups concept:

$$\ln \gamma_i^R = \sum_k \nu_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)})$$

whereby for the calculation of the group activity coefficients in the mixture ($\ln \Gamma_k$) and in the pure compounds ($\ln \Gamma_k^{(i)}$) group interaction parameters are required. These can be fitted using experimental phase equilibrium data. The great advantage of this procedure is that the number of different functional groups is much smaller than the number of different possible compounds.

Different group contribution methods were suggested in literature. From these methods the UNIFAC method found the greatest acceptance in chemical industry because of the reliable results produced and the large range of applicability. Today there is the tendency towards a further development of the UNIFAC method and to combine it with equations of state to be able to take advantage of the extensive potentials of equations of state.

UNIFAC

The work on UNIFAC (6) was performed in close collaboration between our group and the group of Prof. Fredenslund (Lyngby/Denmark). In the UNIFAC method besides the relative van der Waals properties for the combinatorial part group interaction parameters are required to calculate the residual part. These parameters were fitted using only the VLE data stored in the Dortmund Data Bank.

In the present form the UNIFAC method (7) contains the parameters for 50 different structural groups (main groups) (see Fig. 2) where the fitted parameters are characterized by the black squares and the data gaps by the open squares. Because of the reliable results produced for VLE as well as its wide area of application the UNIFAC method has become an important tool in chemical industry and is used worldwide in the different process simulators. Results of the UNIFAC method were published in a large number of papers. Fig. 3 shows the results for different binary systems of alcohols and aromatics. It can be seen that there is good agreement between the experimental and predicted values. The agreement shown in Fig. 3 is typical also for other kinds of systems.

MODIFIED UNIFAC

In spite of its popularity also some weaknesses of the UNIFAC method are well known. For example the combinatorial part of the model equation leads to negative deviations from Raoult's law which are too large when molecules very different in size are considered. Furthermore only qualitative agreement was obtained for heats of mixing data and activity coefficients at infinite dilution.

Therefore work was started on the development of a modified UNIFAC method (8). The main differences compared to original UNIFAC are a modification of the combinatorial part, the introduction of temperature dependent parameters and the use of a larger data base (VLE, h^E , γ^∞ , (LLE)) to fit the required group interaction parameters whereby often more than 1000 data points and molecules very different in size are used to fit the parameters for one group combination. A similar mod. UNIFAC model was also developed by the group of Prof.

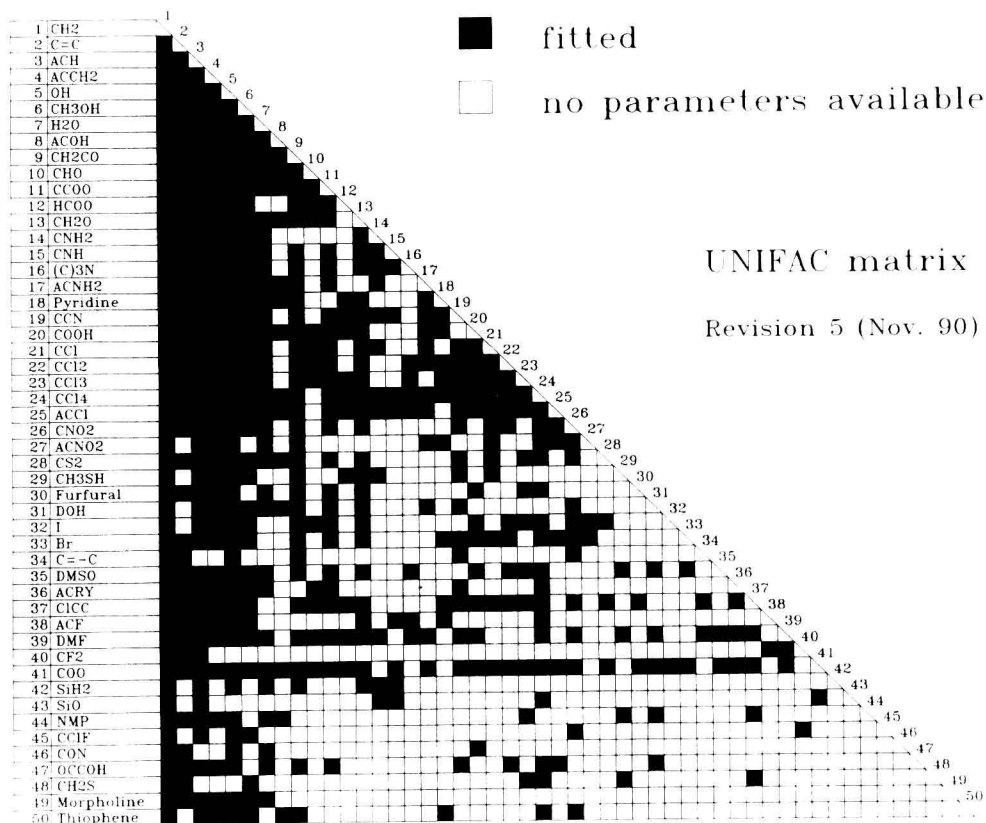


Fig. 2 Present Status of the UNIFAC Matrix

Fredenslund in Lyngby/Denmark (9). Both modified versions allow a much better description of the real behavior than the original version. But the number of fitted group interaction parameters is still limited when compared with the original UNIFAC method. One reason is that there are a lot of experimental data gaps especially for heats of mixing and activity coefficients at infinite dilution required for fitting the group interaction parameters for the modified UNIFAC method. But experimental and development work is in progress to complete the mod. UNIFAC matrix. A comparison of the predictive capability of the different UNIFAC methods and the ASOG method is given in (10). Results of the original and the modified form of the UNIFAC model are shown in Fig. 4. It shows the predicted and experimental results for heats of mixing and the liquid-liquid equilibrium (LLE) of the system butanone-2-water as a function of temperature. It can be seen that for this system with an upper and lower critical solution temperature there is good agreement between the experimental and predicted data in the case of mod. UNIFAC. The original UNIFAC method is not able to describe this behavior. But this is not surprising since no h^E -data for fitting the