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VAPOR-LIQUID EQUILIBRIUM DATA COLLECTION

Aqueous-Organic Systems

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Vapor-Liquid Equilibrium Data Collection

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Tables and diagrams of data for binary and multicomponent mixtures up to moderate pressures. Constants of correlation equations for computer use.

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PREFACE OF EDITORS

Thermophysical property data are needed for the designing of process units. In designing process units, one cannot rely on the data found in the literature alone: for example, one can seldom find data for mixtures. What one needs in modern plant design is the exactest possible advance computation of material data.

This was why the DECHEMA Engineering Data Committee recommended the establishment of a data bank for chemical engineering in 1973. Work on the Dechema Data Service (DSD) began during the same year. This data centre is to collect and store all thermophysical data of substances that are relevant to chemical engineering; above all, it must be able to evaluate them and carry out computations for planned applications.

In the meantime, the necessary programs have been purchased or are being developed. A program system for the computation of thermophysical data, the Thermophysical Properties Program Package of Messrs. Uhde of Dortmund, was first installed at the DECHEMA to compute the pure substance and mixture data on request of users. The introduction of the data analysis system (SDA) fulfilled the requisites to evaluating data and obtaining basic data. A data storage system that will accommodate any desired data and data quantities and the corresponding programs (data retrieval system, SDR) is being developed.

Since the beginning of 1977, the Dechema Data Bank and Service has formed part of the newly-established Technical Information Centre — Chemistry in Frankfurt which is sponsored by the Federal German Government.

It was soon found that the existing data computation methods were inadequate for many cases. The DECHEMA therefore invited the users of the data system to establish a development group which has been concerning itself with the development of new computation methods for thermophysical property data since then. A study entitled "Stoffdaten" which the DECHEMA Engineering Data Committee prepared on request of the Federal Minister for Research and Technology analyzes the data situation, particularly from the viewpoint of advance computation of thermophysical properties, and makes recommendations for future developments. This study will serve as the basis for all future development work.

We intend to publish the measured data, data evaluations and other data collections resulting from the development of methods as generally-available information in the DECHEMA Chemistry Data Series, which is published at irregular intervals.

The above-mentioned development work concentrates on computation methods for phase equilibria, in particular, vapor-liquid equilibria. In this field, the work of Prof. Onken and Dr. Gmehling in Dortmund which was supported by the DECHEMA has been very fruitful; in particular, it led to an extension of the UNIFAC method, which is at present being integrated into the data compiler. Prof. Onken and Dr. Gmehling have produced what is probably the largest collection of vapor-liquid equilibrium data that is today available with evaluation programs and experimental data — for direct retrieval by means of computers. This is also part of the DECHEMA Data Service and can be used by subscribers.

We present the evaluation of this material in several parts of the first volume of the new series. We hope that this gives particularly the users an instrument that will allow them to solve their problems consideralby more easily and quickly than before.

Frankfurt/Main, March 1977

Dieter Behrens
Reiner Eckermann

AUTHORS' PREFACE

Vapor-liquid equilibria form the basis of various kinds of chemical engineering calculations. In particular this is true for the design of certain separation processes, such as distillation and condensation. For the large number of computations of this kind vapor-liquid equilibrium data for the systems to be handled are required. Unfortunately experimental data are very often either incomplete or totally lacking. In principle the appropriate measurements are not too difficult to perform, but it can be very time-consuming to carry them out, especially for multicomponent systems, if values for numerous data points have to be obtained. With the existence of equations representing multicomponent liquid mixtures with binary parameters only, such as Wilson, NRTL and UNIQUAC, the amount of experimental work necessary to describe multicomponent systems has been reduced considerably; even so, equilibrium measurements often are not feasible because of lack of time, for instance, when process alternatives have to be evaluated, as happens in process development and in preliminary design. In those cases the missing binary parameters must be predicted. Regardless of the method employed for prediction, the results will be the more reliable, the more data for related systems have been used.

It was the intention of the senior author, when he took the Chair of Industrial Chemistry B at the new University of Dortmund in 1971 to employ the vast store of vapor-liquid equilibrium data published in literature for the prediction of binary parameters of liquid mixtures. The realisation of this plan became possible only when the junior author joined the group in 1973. A computerized compilation of binary and multicomponent vapor-liquid equilibria, now called Dortmund Data Bank (DDB), was started for the purpose of testing and developing prediction methods. At the suggestion of many colleagues and of DECHEMA and GVC we are now making this collection of VLE-data available to others. This has only been possible with the help of DECHEMA. In order to limit the price of this VLE-data collection, the print-out of DDB is used as basis for reproduction.

Since our work on prediction methods is aimed at non-electrolyte systems, this data collection is restricted mainly to mixtures of organic compounds, but does include water. Within this scope all VLE-data up to pressures of 15 bars have been collected from the available literature (handbooks, tables, scientific journals, etc.) and filed on magnetic tape. The printed edition of our data compilation will comprise all available data published up to 1975. Besides experimentally determined data points from the literature, values calculated by the following correlation equations are included in the tables: Margules, van Laar, Wilson, NRTL, UNIQUAC. The parameters for these equations are also tabulated, as are the constants of the Antoine vapor pressure equation for the pure compounds.

Wherever possible, the tables of data are accompanied by an equilibrium diagram from which the type of system can be perceived at first glance. The reliability of data is indicated by results of two different thermodynamic consistency tests. Parameter adjustment of the correlation equations has been achieved by the Nelder-Mead optimizing method. Deviations between measured and calculated data points and the resulting mean of absolute deviations give an idea of the quality of fit. Such values must be used with judgment, however. If for example for one set of data the mean deviations for two correlation equations are different, but both well below experimental error, this does not mean that the equation with the smaller deviation is necessarily the better one for all purposes. We can, of course, not give general recommendations here as to which correlation equation should be used; this has rather to be left to the judgment of the individual user, the optimal choice depending on the actual problem. In those cases, however, where some of the binary parameters in a multicomponent system are not available from experiment, but can be predicted by the UNIFAC-method, the obvious procedure will be to use the UNIQUAC-equation, since UNIFAC uses the same form of concentration dependence for the activity coefficient.

More detailed information on scope and most profitable use of our data collection is given under the heading "General Remarks and Explanations" at the beginning of Part 1, where also arrangement and organization of the tables are described.

We expect to add new data to our data bank as they appear and we plan to publish these data as supplements in the future. Therefore we are calling upon all workers in the field of vapor-liquid equilibrium to send us separate prints of new papers on their experimental results. We shall also be grateful to each user of the data collection who will notify us of mistakes or omissions in the tables.

The preparation of these tables would not have been possible without the valuable aid of many persons. As regards the data bank we should like to mention gratefully in particular Dr. H. Stage (Köln-Niehl); from his collection of separate prints we received many papers, which were hard to obtain otherwise. Dr. M. Schönberg (Hoechst AG, Abt. Angewandte Physik) supplied a large number of pure component data on vapor pressures (including Antoine constants) and densities, which is gratefully acknowledged here. Dr. A. Fredenslund (Danish Technical University, Lyngby) has contributed a computer program for his version of the point test of thermodynamic consistency by H.C. Van Ness; from this and also from the discussions with him this compilation has benefited. Prof. Dr. H. C. Van Ness (Rensselaer Polytechnic Institute, Troy, New York) kindly reviewed the manuscript of the "General Remarks and Explanations". The edition of the data collection was much helped by the efforts of Dr. R. Eckermann (DECHEMA, Frankfurt/M), for which he deserves special thanks. We also

thank Prof. Dr.-Ing. A. Mersmann (T. U. Munich), who as chairman of the committee of GVC (Gesellschaft für Verfahrenstechnik und Chemie-Ingenieurwesen im VDI) on separation processes promoted this edition.

Special thanks are due to Dipl.-Math. E. Edelhoff, chief of the computer center of the University of Dortmund, and to his staff for their co-operation and effective assistance regarding both data bank and the print-out; without their help neither would have been possible. Here we should also like to mention all members of our team who were engaged in this work: first of all Dipl.-Chem. W. Posywio, who did a considerable part of the programming for parameter fitting, plotting, etc., then Mrs. L. Kunzner for carefully checking data, Dipl.-Chem. H.W. Schulte and cand.-ing. M. Soeparno; all of them have contributed diligence and enthusiasm.

Finally we should like to express our thanks to all colleagues who have promoted this project by giving advice, information, and encouragement. In this respect we are indebted especially to Prof. Dr. J. M. Prausnitz for inspiring discussions and for writing a separate preface.

Dortmund, March 1977

Ulfert Onken Jürgen Gmehling
University of Dortmund

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2. QUATERNARY SYSTEMS