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VAPOR-LIQUID EQUILIBRIUM DATA COLLECTION

Aldehydes and Ketones
Ethers

DECHEMA

Chemistry Data Series

Vol. I, Parts 3 + 4

Vapor-Liquid Equilibrium Data Collection

3 + 4

Aldehydes and Ketones
Ethers

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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Aldehydes and Ketones

Systems with:

Aldehydes:

Acetaldehyde
Acrolein
Propionic Aldehyde
Crotonaldehyde
Butyraldehyde
Isobutyraldehyde
Furfural
Benzaldehyde

Ketones:

Acetone
Methyl Vinyl Ketone
2,3-Butanedione
2-Butanone
N-Methylpyrrolidone
Methyl Isopropyl Ketone
2-Pentanone
3-Pentanone
Cyclohexanone
3-Hexanone
4-Methyl-2-pentanone
1-Methyl-2-cyclohexanone
2-Heptanone
4-Heptanone

4

Ethers

Systems with:

Propylene Oxide
1,3,5-Trioxane
Dimethoxymethane
Bis(2-Chloroethyl) Ether
Tetrahydrofuran
1,4-Dioxane
Morpholine
Diethyl Ether
Dimethoxyethane
Ethyl Propyl Ether
Methyl Butyl Ether
Diisopropyl Ether
Dipropyl Ether
Ethyl Butyl Ether
Dibutyl Ether
Diethylene Glycol Butyl Ether

SUBJECTS OF VOLUME I

The table lists the parts of Volume I already published or being in preparation.

Subtitle	Vol. I, Part	
Aqueous-Organic Systems	1	published
Supplement 1	1a	in prep.
Organic Hydroxy Compounds		
Alcohols	2a	published
Alcohols and Phenols	2b	published
Supplement 1	2c	in prep.
Aldehydes, Ketones, Ethers	3/4	published
Esters and Carboxylic Acids	5	in prep.
Aliphatic Hydrocarbons	6a	in prep.
	6b	in prep.
Aromatic Hydrocarbons	7	in prep.
Halogen, Nitrogen, Sulfur and other Compounds	8	in prep.

AUTHORS' PREFACE

With this, parts 3 + 4 of our Vapor-Liquid Equilibirium Data Collection we have extended the data sheets by adding recommended parameters for those systems for which at least two data sets exist fulfilling both the point and the integral consistency test according to our standardized procedure. With these optimized parameters for the Wilson, the NRTL, and the UNIQUAC equation, it is possible to perform VLE calculations for ranges of temperature and pressure. We have thus taken up a suggestion of many users of our collection. Again we should like to point out, that parameters should be used with judgement. This applies to the recommended values of VLE parameters, too, especially when calculations are to be performed for temperatures beyond the range in which the parameters have been evaluated. Recommended values for the systems of parts 1, 2a and 2b will be given in the first supplement.

Concerning constants of the van Laar equation, these will not be listed in the tables if unreasonable values result from the optimization procedure, e.g. different signs of the two constants, as occasionally happens.

We should like to express our thanks to Dr. M. Schönberg (Hoechst AG, Frankfurt/M) for supplying vapor pressure data from his collection, and again to Dr. H. Stage (Köln-Niehl) for making available to us VLE data which were hard to obtain otherwise. Special thanks are due to Dipl.-Phys. H. Preusch (computer center of the University of Dortmund) for giving constant help so readily. On this occasion we should also like to acknowledge with gratitude the efforts of the editors, expecially of Dr. R. Eckermann. From our team the following members were engaged in the preparation of this part: Mrs. L. Kunzner, Mrs. U. Arlt, Miss B. Gabor, Dipl.-Ing. P. Grenzheuser, Miss G. Hennig, Dipl.-Ing. B. Kolbe.

Dortmund, February 1979

Ulfert Onken Jürgen Gmehling Wolfgang Arlt

University of Dortmund

PREFACE OF EDITORS

Subjects of this series are the physical and thermodynamic property data of chemical compounds and mixtures essentially for the fluid state covering PVT data, heat capacity, enthalpy, and entropy data, phase equilibrium data, transport and interfacial tension data.

The main purpose is to provide chemists and engineers with data for process design and development. For computer based calculations in process design appropriate correlation methods and accurate data must be used. These are only in some cases available in the open literature. For that reason the most urgent requirement regarding the publication of data is to offer classified and critically evaluated data, thus giving an impression which of them are reliable or not. This will be the goal of the series.

DECHEMA gives the opportunity to authors especially from universities to publish not only their theoretical results, but also their measured or compiled data, most often a large amount, that would otherwise never have been published.

The work of Dr. Gmehling, Prof. Onken and Dipl.-Chem. Arlt on vapor-liquid equilibria which was supported by the Federal Ministry of Research and Technology and DECHEMA has been very fruitful; in particular, it led to an extension of the UNIFAC method. The authors have produced what is probably the largest collection of vapor-liquid equilibrium data that is today available with evaluation programs and experimental data.

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

Frankfurt/Main, February 1979

Dieter Behrens
Reiner Eckermann

GUIDE TO TABLES

1. Order of Succession of Systems of Data Sets.

1.1 In this part binary and ternary systems with aldehydes, ketones, and ethers are given.

1.2 Within each class of mixtures all binary systems are given first, followed by ternary systems.

1.3 The sequence of systems is based on the empirical formula convention used in the index of Chemical Abstracts, which means arranging the compounds according to increasing C and H, with the remaining elements in alphabetical order: Br, Cl, F, I, N, O, S. Compounds with identical empirical formula are arranged alphabetically according to their names.

1.4 Order of succession for different data sets for a given system (a set of data points, taken from one original paper, which have been measured varying the composition at constant temperature or pressure, is referred to as a data set):

1. Name of first author in alphabetical order,
2. isothermal data sets, with increasing temperature,
3. isobaric data sets, with increasing pressure,
4. recommended values (see section 7).

2. Antoine Vapor Pressure Equation

The Antoine vapor pressure equation is used in the following form:

$$\log[p_i^0] = A - \frac{B}{t + C} \qquad (70)$$

with $[p_i^0]$ vapor pressure of pure component i in mm Hg
t temperature in degrees Celsius (° C)

The Antoine constants A, B, and C are given with respective temperature regions (in ° C).

3. Consistency Tests

Method 1: Point test of Van Ness et al. [5] in the version of Fredenslund et al. [1].

Method 2: Integral or area test of Redlich - Kister [4] and Herington [2, 3].

Meaning of symbols (see also **Table 1**):

+	consistent
–	not consistent
blank	no result

For more detailed information see sections 2.3 (p. XXII to XXIX) and 4.2 (p. XXXVIII to XLIII) of General Remarks and Explanations in Part 1 of this volume.

4. Parameters of Activity Coefficient Equations

Parameters for the following equations are given:

Margules, eq. (28)
van Laar, eq. (29)
Wilson, eqs. (30) and (36)
NRTL, eqs. (31) and (37)
UNIQUAC, eqs. (32) to (35) and (38) to (40)

Equations and parameters are given in **Tables 2** to **4** and in Tables 1 to 4 of General Remarks and Explanations, (p. XVI to XXI), Part 1.

For ternary systems, only Wilson, NRTL, and UNIQUAC parameters are given; for systems with more than three components no parameters of activity coefficient equations are given.

For notation of constants of activity coefficient equations see **Table 2.**

Wilson, NRTL, and UNIQUAC parameters are given in cal/mol with the gas constant $R = 1.98721$ cal/mol K and the temperature T in K.

Data for the pure liquid components, which are required for the Wilson equation (molar volume V_i^L) and UNIQUAC equation (volume parameter r_i and area parameter q_i), are given in Appendix A.

5. Vapor — Liquid Equilibrium Data

5.1 Experimental data

Symbol	*Meaning*
P MM HG	pressure in mm Hg
T DEG C	temperature in °C (degrees Celsius)
X1 (X2 . . .)	liquid mole fraction x_1 (x_1 . . .)
Y1 (Y2 . . .)	vapor mole fraction y_2 (y_2 . . .)

Table 1 Thermodynamic Consistency Tests

Character in the table	**Method 1** Van Ness et al. [5] and Fredenslund et al. [1]	**Method 2** Redlich-Kister [4] and Herington [2,3]
+ (consistent)	$\overline{\Delta y} \leqslant 0{,}01$ 1)	isothermal data: $D \leqslant 10\%$ 2) isobaric data: $(D\text{–}J) \leqslant 10\%$ 3) exception: for nearly ideal systems with $0.95 < \gamma < 1.10$ (for all γ_i) method 2 is not employed, but character + is given.
– (not consistent)	$\overline{\Delta y} > 0.01$ 1)	either a) isothermal data: $D > 10\%$ 2) isobaric data: $(D\text{–}J) > 10\%$ 3) or b) maximum deviation in $\ln \frac{\gamma_1}{\gamma_2}$ between 3rd order interpolation polynomial and experimental data point > 1.17 fold mean deviation
blank (no result)	calculation does not converge	a) less than 5 data points in the set b) interpolation polynomial does not intersect x-axis 4)

1) $\overline{\Delta y}$ mean deviation in vapor mole fraction y
$\Delta y = y_{exp} - y_{calc}$

2) $D = \frac{|A' - B'|}{A' + B'} \cdot 100\ [\%]$

3) $J = 150 \cdot \frac{|\Delta T_{max}|}{T_{min}}\ [\%]$

4) this may happen, when all data points are within a small range of composition near one of the pure compounds.

Table 2 Activity Coefficient Equations for Binary Systems and Notation of Parameters*)

Type of Equation	Parameters	$\ln \gamma_1 =$ $\ln \gamma_2 =$		Notation of Parameters in Data Sheet
Margules [6]	A_{12}	$\left[A_{12} + 2(A_{21} - A_{12})\, x_1\right] x_2^2$	(28a)	A 12
	A_{21}	$\left[A_{21} + 2(A_{12} - A_{21})\, x_2\right] x_1^2$	(28b)	A 21
van Laar [7]	A_{12}	$A_{12} \left(\frac{A_{21} x_2}{A_{12} x_1 + A_{21} x_2}\right)^2$	(29a)	A 12
	A_{21}	$A_{21} \left(\frac{A_{12} x_1}{A_{12} x_1 + A_{21} x_2}\right)^2$	(29b)	A 21
Wilson [8]	$\lambda_{12} - \lambda_{11}$ 1)	$-\ln (x_1 + \Lambda_{12} x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2}\right)$	(30a)	A 12
	$\lambda_{21} - \lambda_{22}$	$-\ln (x_2 + \Lambda_{21} x_1) - x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2}\right)$	(30b)	A 21
NRTL [9]	$g_{12} - g_{22}$ 2)	$x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}}\right)^2 + \left(\frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2}\right)\right]$	(31a)	A 12
	$g_{21} - g_{11}$			A 21
(continued)	α_{12}	$x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}}\right)^2 + \left(\frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2}\right)\right]$	(31b)	ALPHA 12

Table 2 (continued)

Type of Equation	Parameters	$\ln\gamma_1 =$ $\ln\gamma_2 =$		Notation of Parameters in Data Sheet
UNIQUAC [10]	$u_{12} - u_{22}$ 3)	$\ln\gamma_1^C + \ln\gamma_1^R$ 3)	(32a)	A 12
	$u_{21} - u_{11}$	$\ln\gamma_2^C + \ln\gamma_2^R$	(32b)	A 21

1) $\Lambda_{12} = \frac{V_2^L}{V_1^L} \exp - \frac{\lambda_{12} - \lambda_{11}}{RT}$ $\quad\quad$ $\Lambda_{21} = \frac{V_1^L}{V_2^L} \exp - \frac{\lambda_{21} - \lambda_{22}}{RT}$

V_i^L molar volume of pure liquid component i. For values of V_i^L see Appendix A.

λ_{ij} interaction energy between components i and j $\lambda_{ij} = \lambda_{ji}$

2) $\tau_{12} = \frac{g_{12} - g_{22}}{RT}$ $\quad\quad$ $\tau_{21} = \frac{g_{21} - g_{11}}{RT}$

$G_{12} = \exp(-\alpha_{12}\tau_{12})$ $\quad\quad$ $G_{21} = \exp(-\alpha_{21}\tau_{21})$

g_{ij} parameter for interaction between components i and j; $g_{ij} = g_{ji}$

α_{ij} nonrandomness parameter; $\alpha_{ij} = \alpha_{ji}$

3) for detailed equations see table 4

*) Wilson, NRTL, and UNIQUAC parameters are given in cal/mol with the gas constant R = 1.98721 cal/mol K and the temperature T in K.

Table 3 Activity Coefficient Equations for Multicomponent Systems

Type of Equation	Parameters	$\ln \gamma_i =$
Wilson [8] *)	$\Lambda_{ij} = \frac{V_j^L}{V_i^L} \exp - \left[\frac{(\lambda_{ij} - \lambda_{ii})}{RT}\right]$ 1) $\Lambda_{ii} = \Lambda_{jj} = 1$	$-\ln\left(\sum_{j=1}^{m} x_j \Lambda_{ij}\right) + 1 - \sum_{k=1}^{m} \frac{x_k \Lambda_{ki}}{\sum_{j=1}^{m} x_j \Lambda_{kj}}$ 1) (36)
NRTL [9]	$\tau_{ji} = \frac{(g_{ji} - g_{ii})}{RT}$ 2) $G_{ji} = \exp(-\alpha_{ji}\tau_{ji})$ $\tau_{ii} = \tau_{jj} = 0$ $G_{ii} = G_{jj} = 1$	$\frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{m} G_{li} x_l} + \sum_{j=1}^{m} \frac{x_j G_{ij}}{\sum_{l=1}^{m} G_{lj} x_l} \left(\tau_{ij} - \frac{\sum_{n=1}^{m} x_n \tau_{nj} G_{nj}}{\sum_{l=1}^{m} G_{lj} x_l}\right)$ (37)
UNIQuAC [10] *) (continued)	$\tau_{ji} = \exp - \left(\frac{u_{ji} - u_{ii}}{RT}\right)$ 3)	$\ln \gamma_i^C + \ln \gamma_i^R$ 3) (38)

Table 3 (continued)

	$\tau_{ii} = \tau_{jj} = 1$	$\ln \gamma_i^C = \ln \frac{\varphi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\vartheta_i}{\varphi_i} + l_i - \frac{\varphi_i}{x_i} \sum_j x_j l_j$ (39) $\ln \gamma_i^R = q_i \left[1 - \ln \left(\sum_{j=1}^{m} \vartheta_j \tau_{ji} \right) - \sum_{j=1}^{m} \frac{\vartheta_j \tau_{ij}}{\sum_{k=1}^{m} \vartheta_k \tau_{kj}} \right]$ (40) $l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \qquad z = 10$ (35)

1) explanation of symbols see footnote 1 of table 2
2) explanation of symbols see footnote 2 of table 2
3) explanation of symbols see table 4

*) For values of V_i^L, r_i and q_i see Appendix A

Table 4 UNIQUAC Activity Coefficient Equations [10] for Binary Systems

$$\ln \gamma_1 = \ln \gamma_1^C + \ln \gamma_1^R \tag{32a}$$

$$\ln \gamma_1^C = \ln \frac{\varphi_1}{x_1} + \frac{z}{2}\, q_1 \ln \frac{\vartheta_1}{\varphi_1} + \varphi_2 \left(l_1 - \frac{r_1}{r_2}\, l_2 \right) \tag{33a}$$

$$\ln \gamma_1^R = -q_1 \ln (\vartheta_1 + \vartheta_2 \tau_{21}) + \vartheta_2 q_1 \left(\frac{\tau_{21}}{\vartheta_1 + \vartheta_2 \tau_{21}} - \frac{\tau_{12}}{\vartheta_1 \tau_{12} + \vartheta_2} \right) \tag{34a}$$

$$\ln \gamma_2 = \ln \gamma_2^C + \ln \gamma_2^R \tag{32b}$$

$$\ln \gamma_2^C = \ln \frac{\varphi_2}{x_2} + \frac{z}{2}\, q_2 \ln \frac{\vartheta_2}{\varphi_2} + \varphi_1 \left(l_2 - \frac{r_2}{r_1}\, l_1 \right) \tag{33b}$$

$$\ln \gamma_2^R = -q_2 \ln (\vartheta_1 \tau_{12} + \vartheta_2) + \vartheta_1 q_2 \left(\frac{\tau_{12}}{\vartheta_1 \tau_{12} + \vartheta_2} - \frac{\tau_{21}}{\vartheta_1 + \vartheta_2 \tau_{21}} \right) \tag{34b}$$

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \qquad z = 10 \tag{35}$$

Symbols

l_i	see equation (35)
q_i	area parameter of component i *)
r_i	volume parameter of component i *)
u_{ij}	Parameter of interaction between components i and j; $u_{ij} = u_{ji}$
z	coordination number
γ_i^C	combinatorial part of activity coefficient of component i
γ_i^R	residual part of activity coefficient of component i
$\vartheta_i = \dfrac{q_i x_i}{\sum_j q_j x_j}$	area fraction of component i
$\varphi_i = \dfrac{r_i x_i}{\sum_j r_j x_j}$	volume fraction of component i
τ_{ij}	see Table 3

*) For values of r_i and q_i see Appendix A

5.2 Calculated data

Symbol	*Meaning*
DIFF P	$P = P_{exp} - P_{calc}$
DIFF T	$T = T_{exp} - T_{calc}$
DIFF Y1	$y_1 = y_{1,exp} - y_{1,calc}$
DIFF Y2	$y_2 = y_{2,exp} - y_{2,calc}$

MEAN DEVIATION e.g. for T: $\Delta T = \frac{1}{n}\sum_{n} |\Delta T|$

MAX. DEVIATION maximum absolute deviation

Results of calculations with activity coefficient equations are usually tabluated as the difference of experimental value minus calculated value. Calculated vapor mole fractions are given directly only for isothermal P-x data and isobaric T-x data. In all other cases the calculated values are obtained by subtracting the tabulated difference from the experimental value, e.g. $y_{1,calc} = y_{1,exp} - \Delta y_1$.

6. Equilibrium Diagrams

6.1 Binary Systems

x - y diagrams show data points and equilibrium line calculated by activity coefficient equation yielding the lowest mean deviation Δy_1. The type of this equation is printed on the diagram, together with the values for the activity coefficients at infinite dilution γ_1^∞ and γ_2^∞ (for equations see Table 3 of General Remarks and Explanations, p. XIX of Part 1).

In the case of limited liquid miscibility, calculated solubilities (which may be different from experimental values!), are inserted into the equilibrium line as small circles connected by a horizontal line.

6.2 Ternary Systems

Triangular diagrams show experimental data points with equilibrium composition of vapor (sign ✻) and liquid (sign ○) connected by a straight line.

7. Recommended Values

Additionally, for systems with at least two data sets fulfilling both the point and the integral test for thermodynamic consistency (method 1 and 2, see section 3), so-called recommended values are given for the constants of the Wilson, NRTL, and UNIQUAC equation. In the evaluation of these parameters for a given system, only those data sets were used which showed consistency with both tests. Regardless of the number of data points per set, the same weight was attributed to each data set in the optimization procedure and one set of Antoine constants has been used.

With the sum of squared relative deviations of activity coefficients as objective function, parameter sets are obtained which can be supposed to produce the "best" representation of vapor-liquid equilibrium within the temperature resp. pressure range which is covered by the sets of experimental data used.

For systems for which the evaluation has been possible, the recommended values are given at the end of the system on a separate page. Besides recommended parameters for the Wilson, NRTL, and UNIQUAC equation, there are listed the data sets used in the optimization by citing the references together with corresponding temperature or pressure.