

**J. Gmehling
U. Onken
W. Arlt**

VAPOR-LIQUID EQUILIBRIUM DATA COLLECTION

**Organic Hydroxy Compounds:
Alcohols and Phenols**



Chemistry Data Series

Vol. I, Part 2b

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Vol. I, Part 2b

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2b

Organic Hydroxy Compounds: Alcohols and Phenols

Systems with:

2-Chloroethanol	Cyclohexanol
1,2-Ethanediol	1-Hexanol
Allyl Alcohol	4-Methyl-2-pentanol
2-Propanol	2-Butoxyethanol
2-Methoxyethanol	2-Methylpentane-2,4-diol
1-Butanol	Benzyl Alcohol
2-Butanol	2-Methylphenol
tert-Butanol	3-Methylphenol
2-Methyl-1-propanol	4-Methylphenol
2-Ethoxyethanol	1-Heptanol
2,3-Butanediol	α -Phenylethanol
Diethylene Glycol	2-Ethyl-1-hexanol
Furfuryl Alcohol	1-Octanol
Cyclopentanol	1-Nonanol
Tetrahydrofurfuryl Alcohol	2-Naphthol
3-Methylbutanol	1-Decanol
1-Pentanol	5-Ethyl-2-nonanol
Phenol	

SUBJECTS OF VOLUME I

The table lists the parts of Volume I which are scheduled for publication within the next years.

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Organic Hydroxy Compounds	
Alcohols	2a
Alcohols and Phenols	2b
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PREFACE OF EDITORS

With "Alcohols and Phenols" the part 2b of the series containing hydroxy compounds is presented here.

This part covers the systems with 35 alcohols excluding methanol, ethanol, 1-propanol, which were presented in Part 2a.

Because many additional systems and data sets with hydroxy compounds have been published, it will be necessary to have at least one supplement covering hydroxy compounds.

As already pointed out in Part 2a we have given only a few necessary explanations in the "Guide to Tables" for the data presented here. Complete explanation to the matter can be taken from "General Remarks and Explanations" in Vol. I, Part 1.

Furthermore the tables of contents of the previous parts are included so that a good survey of the reading matter is ensured.

Frankfurt/Main, June 1978

Dieter Behrens
Reiner Eckermann

AUTHORS' PREFACE

With the publication of part 2 b of our vapor-liquid equilibrium data collection W. Arlt has joined us as third co-author. He has already helped us in the preparation of parts 1 and 2 a, under the name W. Posywio which he changed after his marriage. It should also be mentioned here that this part 2 b has been delayed because one of us (J. Gmehling) spent a period of time on research at Berkeley.

We should like to take this opportunity of thanking those users who have sent us vapor-liquid equilibrium data, not or not yet available to us, amongst them especially Dr. Malanowski (Polish Academy of Sciences, Warsaw). Again we would like to ask those, working on vapor-liquid equilibria, to send us pre-prints of unpublished experimental data.

Correspondence we have received from users of the VLE data collection induces us to point out again that parameter fitting of activity coefficient equations does not in all cases yield reasonable results, mainly because of two reasons: either a large scattering of experimental data or a significant deviation from non-ideal behavior such as strong association and solvation with high interaction energies. Examples of such chemical-like interactions are aldehyde-water mixtures. In such a case, activity coefficient equations with only few parameters for a binary system may lead to over-simplified results. Especially with the van Laar equation these effects may provide very erroneous results (see e. g. part 1, page XXXVI, figure 4) when the signs of the two constants are different. In this case the denominator in the van Laar expression becomes zero and the activity coefficients infinite for one composition. A check for this kind of inconsistency was not feasible for all possible cases. Therefore the parameters for the five different activity coefficient equations given in the tables should be used with judgment.

Again we would like to express our thanks to all the members of the team, who were engaged in the preparation of this part 2 b: Mrs. L. Kunzner, Mrs. U. Arlt, Miss B. Gabor, Miss G. Hennig. Thanks are also due to Dipl.-Ing. Keller, whose knowledge of the Russian language has saved us much time.

Dortmund, June 1978

Ulfert Onken, Jürgen Gmehling, Wolfgang Arlt

GUIDE TO TABLES

1. Order of Succession of Systems of Data Sets.

- 1.1 In this part binary, ternary and quaternary systems with methanol, ethanol and 1-propanol respectively are given.
- 1.2 Within this class of mixtures all binary systems are given first, followed by ternary and quaternary systems.
So binary systems with ethanol follow binary systems with methanol, ternary systems with methanol follow binary systems with 1-propanol, etc.
- 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.

2. Antoine Vapor Pressure Equation

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

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

with $[p_i^0]$ vapor pressure of pure component i in mm Hg
 t temperature in degrees Celsius ($^{\circ}\text{C}$)

The Antoine constants A, B, and C are given with respective temperature regions (in $^{\circ}\text{C}$).

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. Constants 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 are given 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

<i>Symbol</i>	<i>Meaning</i>
P MM HG	pressure in mm Hg
T DEG C	temperature in °C (degrees Celsius)
X1 (X2...)	liquid mole fraction x_1 ($x_2...$)
Y1 (Y2...)	vapor mole fraction y_1 ($y_2...$)

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]
<p>+</p> <p>(consistent)</p>	$\overline{\Delta y} \leq 0,01$ ¹⁾	<p>isothermal data: $D \leq 10\%$ ²⁾</p> <p>isobaric data: $(D-J) \leq 10\%$ ³⁾</p> <p>exception: for nearly ideal systems with $0.95 < \gamma < 1.10$ (for all γ_i) method 2 is not employed, but character + is given.</p>
<p>–</p> <p>(not consistent)</p>	$\overline{\Delta y} > 0.01$ ¹⁾	<p>either a)</p> <p>isothermal data: $D > 10\%$ ²⁾</p> <p>isobaric data: $(D-J) > 10\%$ ³⁾</p> <p>or b)</p> <p>maximum deviation in $\ln \frac{\gamma_1}{\gamma_2}$ between 3rd order interpolation polynomial and experimental data point > 1.17 fold mean deviation</p>
<p>blank</p> <p>(no result)</p>	<p>calculation does not converge</p>	<p>a) less than 5 data points in the set</p> <p>b) interpolation polynomial does not intersect x-axis ⁴⁾</p>
<p>1) $\overline{\Delta y}$</p> <p>$\Delta y = y_{\text{exp}} - y_{\text{calc}}$</p>	<p>mean deviation in vapor mole fraction y</p>	<p>3) $J = 150 \cdot \frac{ \Delta T_{\text{max}} }{T_{\text{min}}} [\%]$</p>
<p>2) D</p> <p>$= \frac{ A' - B' }{A' + B'} \cdot 100 [\%]$</p>	<p>$= \frac{ A' - B' }{A' + B'} \cdot 100 [\%]$</p>	<p>4) this may happen, when all data points are within a small range of composition near one of the pure compounds.</p>

Table 2 Notation of Constants of Activity Coefficient Equations

Type of Equation	Notation of Constants in Data Sheet		
	A12	A21	ALPHA12
Margules [6], eq.(28) ¹⁾	A_{12}	A_{21}	
Van Laar [7], eq.(29) ¹⁾	A_{12}	A_{21}	
Wilson [8], eq. (30) ¹⁾	$(\lambda_{12} - \lambda_{11})$	$(\lambda_{12} - \lambda_{22})$	
NRTL [9], eq. (31) ¹⁾	$(g_{12} - g_{22})$	$(g_{21} - g_{11})$	α_{12}
UNIQUAC [10], eqs. (32) to (35) ¹⁾	$(u_{12} - u_{22})$	$(u_{21} - u_{11})$	
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. 1) Refer to Volume I, Part 1, General Remarks and Explanations.			

5.2 Calculated data

<i>Symbol</i>	<i>Meaning</i>
DIFF P	$P = P_{\text{exp}} - P_{\text{calc}}$
DIFF T	$T = T_{\text{exp}} - T_{\text{calc}}$
DIFF Y1	$y_1 = y_{1,\text{exp}} - y_{1,\text{calc}}$
DIFF Y2	$y_2 = y_{2,\text{exp}} - y_{2,\text{calc}}$

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

MAX. DEVIATION maximum absolute deviation

Results of calculations with activity coefficient equations are usually tabulated 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. $y_{1,\text{calc}} = y_{1,\text{exp}} - \Delta y_1$.

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 \circ) connected by a straight line.

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