

## Potential of group contribution methods for the prediction of phase equilibria and excess properties of complex mixtures\*

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*Abstract:* Reliable knowledge of the thermophysical properties of pure compounds and their mixtures in the whole composition and a wide temperature and pressure range is a vital prerequisite for computer-aided synthesis, design, and optimization of chemical processes. Knowledge of the various phase equilibria is most important for the development of thermal separation processes (but also for other applications, such as the design of multiphase reactors, the prediction of the fate of a chemical in the environment, etc.).

Whereas 25 years ago, the main interest was directed to the development of predictive tools for vapor–liquid equilibria of subcritical compounds of similar size (ASOG, UNIFAC), 15 years later a proper description of the temperature dependence (excess enthalpies), the activity coefficients at infinite dilution, and solid–liquid equilibria of eutectic mixtures (including strong asymmetric systems) was achieved. After the combination with cubic equations of state [Soave–Redlich–Kwong (SRK), Peng–Robinson (PR)], the group contribution concept was extended to supercritical compounds [predictive SRK (PSRK)]. With the development of an adequate electrolyte model (LIFAC), the equation-of-state approach can even be used for systems with strong electrolytes. With the revision of the group interaction parameters, the extension of the parameter matrix (introduction of new structural groups, filling of parameter gaps), and the help of a large database (Dortmund Data Bank), the predicted results of group contribution methods were significantly improved and the range of applicability greatly extended. Furthermore, still-existing problems with the group contribution approach (proximity effects, etc.) were reduced.

With the help of a volume-translated PR equation of state and application of temperature-dependent and improved mixing rules, the remaining weaknesses of group contribution equations of state (such as poor results for liquid densities, excess enthalpies, and the problems with asymmetric systems) were minimized.

### INTRODUCTION

A classical chemical plant can be roughly divided in a preparation, reaction, and separation step. Although the reactor can be considered as the heart or core of the chemical plant, often 60–80 % of the total costs are caused by the separation step, where the various thermal separation processes (in particular distillation processes) are applied to obtain the products with the desired purity, to recycle the unconverted reactants, and to remove the undesired side-products.

Different aspects have to be considered during the synthesis of separation processes. First, the engineer has to decide which separation processes should be used. Then, he or she has to find out if sep-

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\*Plenary lecture presented at the 17<sup>th</sup> IUPAC Conference on Chemical Thermodynamics (ICCT), Rostock, Germany, 28 July–2 August 2002. Other presentations are published in this issue, pp. 859–936.

aration problems occur. In the case of distillation, these are azeotropic points. To understand the separation process, knowledge of residual curves and boundary lines is quite helpful. In the case of a separation problem in the form of an azeotropic point, the engineer has to find an alternative way (vacuum, pressure, or pressure swing distillation) without the use of an entrainer, or has to select suitable solvents for the separation of the considered system (e.g., by azeotropic or extractive distillation). Furthermore, the engineer has to determine the number of theoretical stages or the height of the packing of the separation column, and, additionally, he or she has to choose the optimal separation sequence. To treat the different aspects mentioned before, a reliable knowledge of the phase equilibrium behavior as  $f(T, P, x_i)$  for multicomponent systems is required.

However, phase equilibria are not only important for the design of separation processes, but also for other applications, such as the design of biphasic reactors or the estimation of the fate of a persistent chemical in the environment.

Therefore, the typical question asked by the chemical engineer is: "What is the composition and pressure in phase  $\beta$ , when this phase is in equilibrium with phase  $\alpha$  with given composition and temperature?", whereby often multicomponent systems with nonpolar, polar, supercritical compounds and electrolytes have to be considered. For the ethanol/water/sodium chloride/ $\text{CO}_2$  system, the problem is shown in Fig. 1. The following questions may arise:

- How strong sodium chloride influences the solubility of  $\text{CO}_2$  in the ethanol/water system?
- Can carbon dioxide be used for the separation of ethanol and water by supercritical extraction?
- Does the ethanol/water system still show azeotropic behavior in the presence of sodium chloride?

Of course, the phase equilibria as function of temperature, pressure, and composition can be measured. However, measurements of multicomponent systems are very time-consuming. For example, the measurement of a 10-component system in 10 mol % steps at only atmospheric pressure would last approximately 37 years [1].

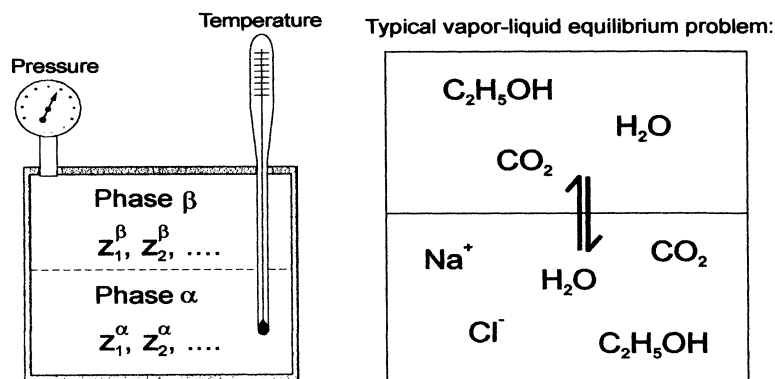


Fig. 1 Typical question asked by the chemical engineer.

## THERMODYNAMIC FUNDAMENTALS

Because of the time required, thermodynamic models are desired, which allow the calculation of the phase equilibrium behavior of multicomponent systems using only a limited number of experimental data. Following Gibbs and Lewis, phase equilibria exist when the components show the same chemical potentials or fugacities in the different phases:

$$\mu_i^\alpha = \mu_i^\beta \quad (1)$$

$$f_i^\alpha = f_i^\beta \quad (2)$$

But these relations are not very helpful. The connection to the measurable quantities  $T$ ,  $P$ , and composition in the liquid and vapor phase is needed to be able to calculate the required K-factors or separation factors for the different separation processes. Therefore, auxiliary quantities such as activity and fugacity coefficients have been introduced. With the help of these quantities, two different approaches are obtained. The resulting equations for vapor–liquid equilibria (VLE) are the following [2]:

$$\text{approach A: } x_i \phi_i^L = y_i \phi_i^V \quad (3)$$

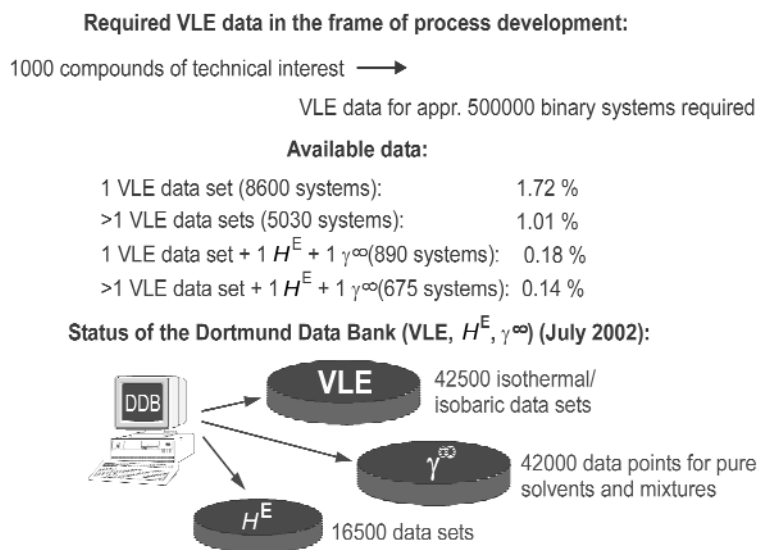
$$\text{approach B: } x_i \gamma_i P_i^s \approx y_i P \quad (4)$$

In approach A, the fugacity coefficients in the liquid and vapor phase are needed, which can be calculated using an equation of state and reliable mixing rules. In approach B, besides a  $G^E$  model, vapor pressure data are required. When the advantages and disadvantages of the different approaches are compared, approach A shows various important advantages over approach B, for example:

- the same auxiliary quantities are used to describe the real behavior in the liquid and vapor phase, and
- no problems arise with supercritical compounds, since no standard fugacity is required.

At the same time, densities, enthalpies (including heats of vaporization), and heat capacities as a function of temperature, pressure, and composition can be calculated for both phases, which are required as additional information in the gamma- $\phi$  approach.

But both approaches allow the calculation of multicomponent systems using only binary information. Unfortunately, the required binary data are often missing. When one assumes that 1000 compounds are of technical interest, phase equilibrium information for about 500 000 binary systems are required (see Fig. 2). Although the Dortmund Data Bank (DDB) contains more than 42 000 VLE data sets up to now, VLE data are available for only 8600 systems. This means that only one VLE data set is available for 1.72 % of the required systems. When only consistent VLE data are accepted, or when more than one VLE data is desired, the percentage goes down to approximately 1 %. When, besides



**Fig. 2** Overview about the available experimental thermodynamic data (VLE,  $\gamma^\infty$ ,  $H^E$ ) for process development.

VLE, information about the dilute range and the temperature dependence in the form of  $\gamma^\infty$  and  $H^E$  should also be used to fit the required model parameters, the percentage of the available systems goes down to even less than 0.2 %, although in the DDB, approximately 42 000  $\gamma^\infty$  values and 16 500  $H^E$  data sets are stored [3]. Since the assumption of ideal behavior can be very erroneous and measurements are very time-consuming, reliable predictive models are required.

## GROUP CONTRIBUTION METHODS (UNIFAC, MODIFIED UNIFAC)

The first predictive model (regular solution theory) with a wide range of applicability was developed by Scatchard and Hildebrand [4]. But the regular solution theory can only be applied for nonpolar systems. To be able to handle all kinds of systems, we started in 1973 at the University of Dortmund with the development of a group contribution method. In group contribution methods, it is assumed that the mixture does not consist of molecules, but of functional groups. By a thermodynamic cycle, it can be shown that the required activity coefficients can be calculated when only the interaction parameters between the functional groups are known. The advantage of group contribution methods is that the number of functional groups is much smaller than the number of possible molecules.

First of all, our idea was to work on the further development of the ASOG method [5], which was developed at Shell. Later on, we decided to work on the further development of the UNIFAC method, which was published in 1975 [6]. In the UNIFAC method, the activity coefficients are calculated from a combinatorial and a residual part. Whereas the combinatorial part takes into account the size and form of the molecule, the residual part considers the enthalpic interactions.

At this time, because of the importance of distillation processes, it was the goal to develop a group method for the prediction of VLE. Therefore, only VLE data stored in the DDB were used to fit the required UNIFAC group interaction parameters. This was done in collaboration with the group of Prof. Aa. Fredenslund (Lyngby/Denmark). Because of the reliable results obtained for VLE, and the large range of applicability, the method was directly integrated in the different process simulators [7]. However, in spite of the reliable results for VLE, UNIFAC also shows a few weaknesses, e.g., unsatisfying results are obtained for:

- activity coefficients at infinite dilution,
- heats of mixing (this means the temperature dependence of the activity coefficients following the Gibbs–Helmholtz relation), and
- asymmetric systems.

These weaknesses are not surprising since, with the VLE data used to fit the required group interaction parameters, no information from the very dilute range, the temperature dependence (heats of mixing) and very asymmetric systems is used, since VLE data are usually only measured between 5 and 95 mol % for symmetric or slightly asymmetric systems.

To improve the situation, a modified UNIFAC method was developed [8]. The main differences compared to original UNIFAC are:

- an empirically modified combinatorial part is introduced;
- temperature-dependent group interaction parameters are used; and
- additional main groups (e.g., for cyclic alkanes, formic acid, etc.) were added.

The required temperature-dependent group interaction parameters are fitted simultaneously to all reliable phase equilibrium [VLE,  $\gamma^\infty$ , azeotropic data, solid–liquid equilibria (SLE) of eutectic systems, liquid–liquid equilibria (LLE)] and excess property data ( $H^E$ ,  $C_p^E$ ). To be able to do this job, the DDB was largely extended. The contribution of the different thermodynamic properties can be summarized as follows. VLE and azeotropic data deliver the required information about the composition dependence of the activity coefficients. Activity coefficients at infinite dilution measured with the help of

gas–liquid chromatography, different ebulliometer techniques or gas stripping methods provide the required information about the real behavior in the dilute range. At the same time, the data measured by gas–liquid chromatography deliver the information about the real behavior of asymmetric systems. With the help of heats of mixing data, the most important information about the temperature dependence is available. Unfortunately, most  $H^E$  data have been measured around room temperature. To improve the situation, two isothermal flow calorimeters are used in our laboratory to obtain heats of mixing data at 90 and 140 °C. Up to now, more than 600 data sets have been measured for the systematic further development of modified UNIFAC. The  $H^E$  data measured at high temperature (140 °C), together with the SLE data of eutectic systems, are of special importance as supporting data at high and low temperature, for fitting reliable temperature-dependent group interaction parameters. For fitting the parameters, weighting factors are used for the different contributions to the objective function.

For this job, besides a comprehensive data bank with mixture data and pure component properties (vapor pressures, heats of fusion, melting temperature, critical data, etc.), a sophisticated software package is required for the selection of the suitable data, examination of the quality of the data (e.g., with the help of consistency tests), the simultaneous fit of temperature-dependent parameters and a thorough examination of the results. For fitting the group interaction parameters for one group combination, often more than 3000 data points are used.

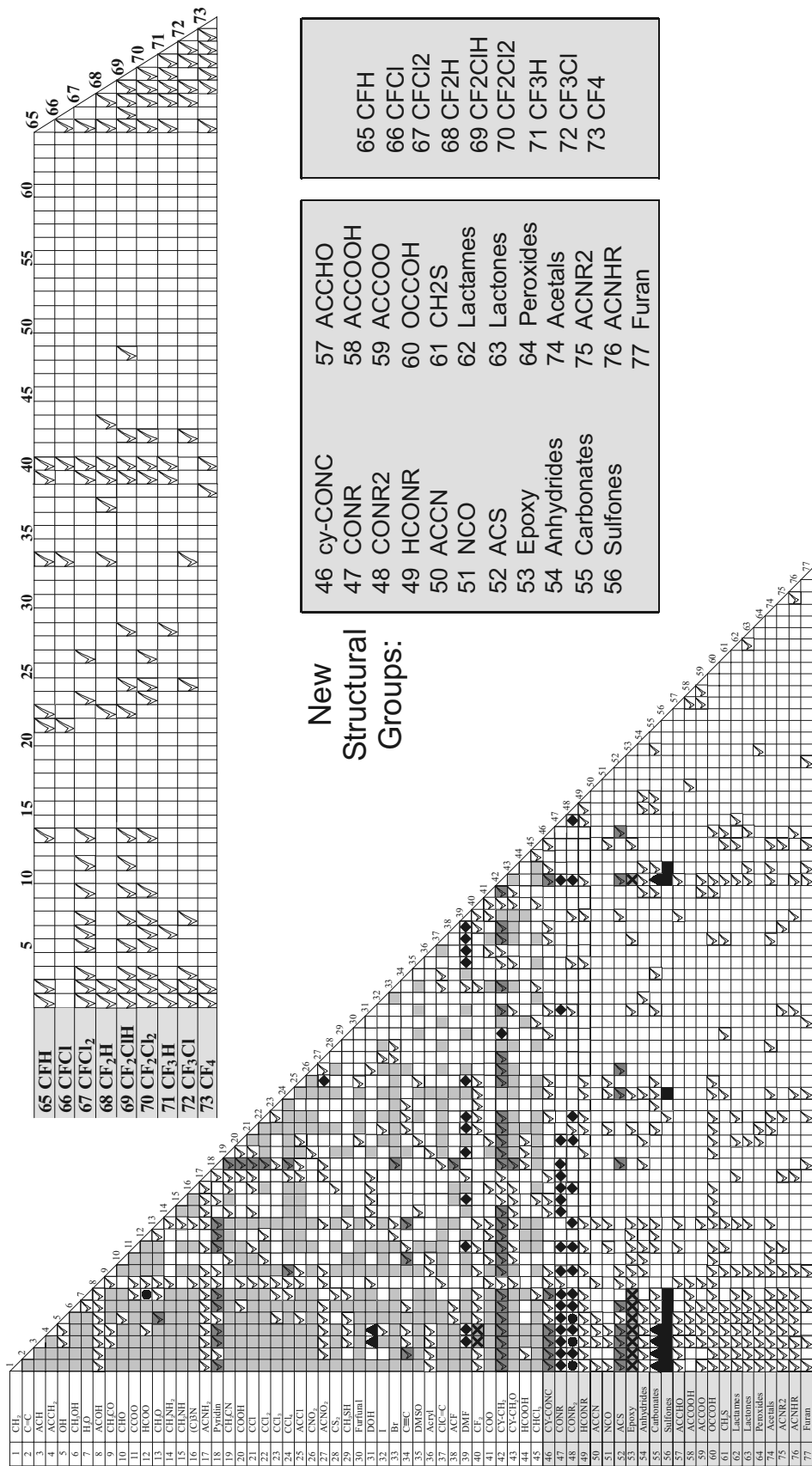
Most important for the application of group contribution methods for the synthesis and design of separation processes is a comprehensive parameter matrix with reliable parameters. The present status of modified UNIFAC is shown in Fig. 3. Today, parameters are available for 77 main groups. In the last years, new main groups were introduced for the different types of amides, isocyanates, epoxides, anhydrides, peroxides, carbonates, various sulfur compounds, and also chlorofluorohydrocarbons (refrigerants). A great part of the group interaction parameters have been published [9]. The further extension (i.e., the filling of gaps in the parameter matrix or the introduction of new main groups) is carried out within the UNIFAC consortium. The current status of the parameter matrix is always available via the Internet [10].

The progress obtained when going from UNIFAC to modified UNIFAC can be recognized from a comparison of the results for 2200 consistent VLE data sets. Using the UNIQUAC equation for the correlation, a mean deviation of 0.0058 for the vapor-phase mole fraction was obtained. Whereas with the original UNIFAC method, a mean deviation of 0.0141 is obtained, with the modified UNIFAC a mean deviation of 0.0088 of the vapor-phase mole fraction is achieved. This means that the deviation compared to the deviation obtained by a correlation of the VLE data with the UNIQUAC model was improved by nearly a factor of 3 from 0.0083 to 0.003. Similar improvements are also obtained for the predicted temperatures and pressures for VLE, excess enthalpies, and activity coefficients at infinite dilution.

Typical results for VLE, excess enthalpies, SLE, activity coefficients at infinite dilution, and azeotropic data for systems of aromatics with alcohols are shown in Figs. 4 and 5.

Whereas Fig. 4 presents results for the ethanol/benzene system, Fig. 5 compares the predicted and experimental results for benzene and naphthalene with various alcohols. In the case of SLE, additionally, the results (assuming ideal behavior) are shown by the dashed lines. The improvement when taking into account the real behavior is obvious. Of course, the same group interaction parameters are applied for all the predictions. As can be seen, in all cases good agreement is obtained for the different phase equilibria and excess properties although a wide temperature range (–100 to 160 °C) is covered. This means that the correct description of the temperature dependence (excess enthalpies) ensures a safe extrapolation to low or high temperatures.

new or revised parameters for refrigerants



New Structural Groups:

- 65 CFH
- 66 CFCI
- 67 CFCI2
- 68 CF2H
- 69 CF2CIH
- 70 CF2CI2
- 71 CF3H
- 72 CF3CI
- 73 CF4

- 46 cy-CONC
- 47 CONR
- 48 CONR2
- 49 HCONR
- 50 ACCN
- 51 NCO
- 52 ACS
- 53 Epoxy
- 54 Anhydrides
- 55 Carbonates
- 56 Sulfones
- 57 ACCHO
- 58 ACCOOH
- 59 ACCOO
- 60 OCCOH
- 61 CH2S
- 62 Lactames
- 63 Lactones
- 64 Peroxides
- 74 Acetals
- 75 ACNR2
- 76 ACNHR
- 77 Furan

- published parameters I  
Gmehling, J., Li, J., Schiller, M.,  
*Ind. Eng. Chem. Res.*, **32**, 178 (1993).
- ▨ published parameters II  
Gmehling, J., Lohmann, J., Jakob, A., Li, J., Joh, R.,  
*Ind. Eng. Chem. Res.*, **37**, 4876 (1998).
- ⊗ published parameters III  
Lohmann, J., Joh, R., Gmehling, J.,  
*Ind. Eng. Chem. Res.*, **40**, 957 (2001).
- ▲ published parameters IV  
Lohmann, J., Gmehling, J.,  
*J. Chem. Eng. Jpn.*, **34**, 43 (2001).
- published parameters V  
Wittig, R., Lohmann, J., Joh, R., Horstmann, S.,  
Gmehling, J., *Ind. Eng. Chem. Res.*, **40**, 5831 (2001).
- ◆ published parameters VI  
Gmehling, J., Wittig, R., Lohmann, J., Joh, R.,  
*Ind. Eng. Chem. Res.*, **41**, 1678 (2002).
- published parameters VII  
Wittig, R., Lohmann, J., Gmehling, J.,  
*AIChE J.*, **49**, 530 (2003)
- ▨ new or revised parameters  
Currently only available for the  
members of the UNIFAC-consortium
- no parameters  
available

Fig. 3 Present status of the modified UNIFAC method.

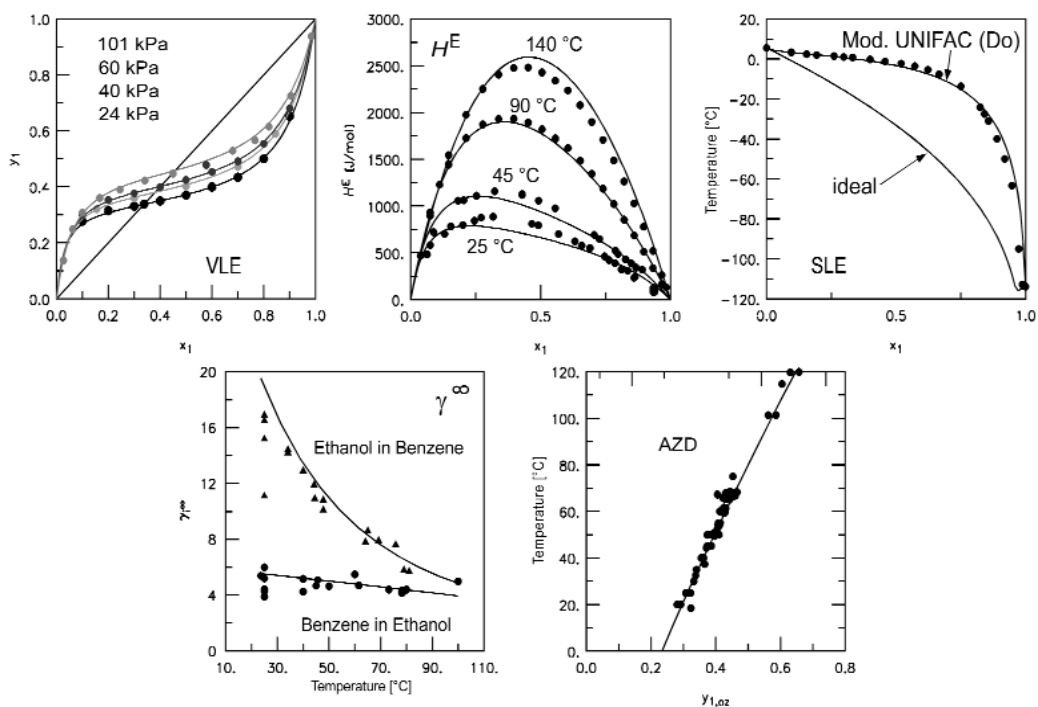


Fig. 4 Predicted and experimental results for the ethanol/benzene system.

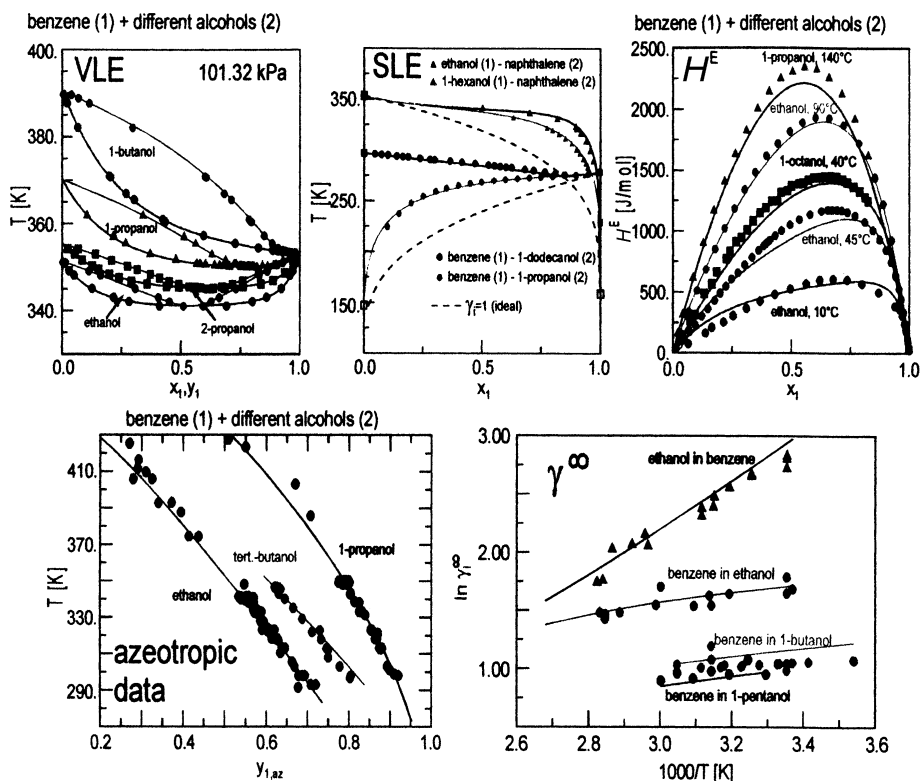


Fig. 5 Predicted and experimental results for systems of aromatics (benzene, naphthalene) with various alcohols.

## PREDICTIVE SOAVE-REDLICH-KWONG EQUATION OF STATE

As can be recognized from the results shown before, modified UNIFAC is a very powerful predictive model for the synthesis, design, and optimization of chemical processes, in particular separation processes. However, modified UNIFAC is a  $G^E$  model. This means that it cannot handle supercritical compounds. For supercritical compounds, the equation-of-state approach has to be used. Of course, an equation of state is required, which is able to describe the  $PVT$  behavior of the vapor and the liquid phase. The first equation of state for both phases was developed by van der Waals. With only two parameters,  $a$  and  $b$ , the van der Waals equation of state is able to describe the different observed phenomena, such as condensation, evaporation, the two-phase region, and the critical behavior.

Today, improved cubic equations of state such as the Soave-Redlich-Kwong (SRK) equation or the Peng-Robinson (PR) equation are used. But, until 1979, the application of the equations-of-state approach was limited to nonpolar or slightly polar compounds, in particular, caused by the empirical quadratic mixing rules used. Huron and Vidal [11] combined the advantages of  $G^E$  models and equations of state by introducing more sophisticated so-called  $G^E$  mixing rules. With the application of original UNIFAC for the prediction of the required  $G^E$  values, a predictive group contribution equation of state was developed [12]. While the approach of Huron and Vidal uses infinite pressure, in the group contribution equation of state (PSRK) developed atmospheric pressure is used as the reference state. For the parameter  $b$  in both approaches, linear mixing rules are used. Using PSRK and the already available UNIFAC parameters, the range of applicability was directly extended to supercritical conditions. At the same time, with the equation-of-state approach the behavior of systems with supercritical gases can be handled. To use PSRK for process synthesis and design, a large matrix with reliable parameters is desirable. Therefore, 30 gases were added as new main groups, and the parameters were fitted to VLE data of low boiling substances and gas solubilities stored in the DDB [13].

A few years ago, the application of PSRK was even extended to systems with strong electrolytes by using the LIFAC method [14] instead of the original UNIFAC method. In the LIFAC method, the middle- and long-range interactions of the electrolytes are taken into account by the Debye-Hückel and a modified Pitzer term [15,16]. The extended model now also allows the prediction of salting in and salting out effect of strong electrolytes on VLE and gas solubilities. In Fig. 6, the influence of sodium nitrate on the solubility of carbon dioxide in water for different salt concentrations at 40 and 100 °C is shown. As can be seen, not only the composition, but also the temperature dependence for this ternary system is described with the required accuracy.

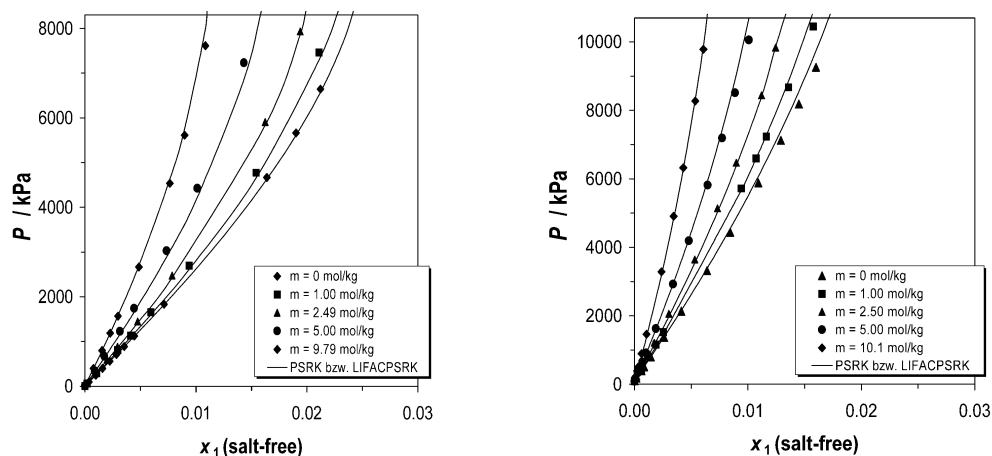


Fig. 6 Experimental and predicted (PSRK + LIFAC) results for the system  $\text{CO}_2$  (1) –  $\text{H}_2\text{O}$  (2) –  $\text{NaNO}_3$  (3).



## UNIVERSAL GROUP CONTRIBUTION EQUATION OF STATE

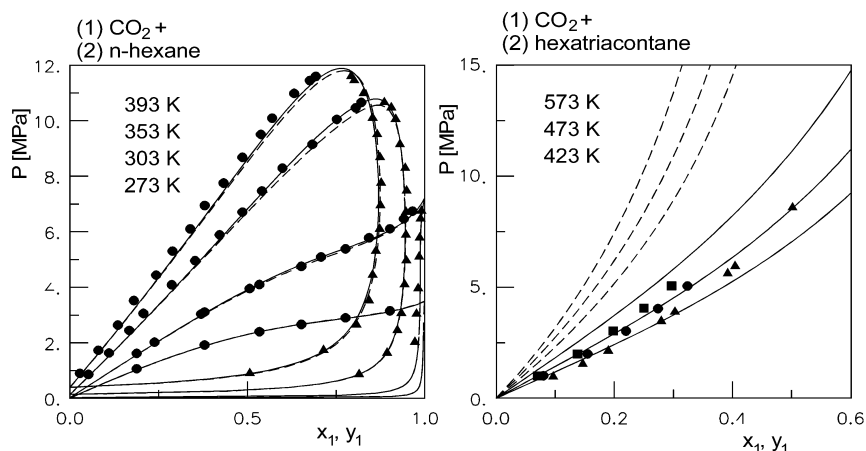
The PSRK model [12,13,15,16] provides reliable predictions of VLE and gas solubilities. Therefore, the PSRK model was implemented in the different process simulators and is well accepted as a predictive thermodynamic model for the synthesis and design of the different processes in the chemical, gas processing, and petroleum industries. But also the group contribution equation of state PSRK shows a few weaknesses. Because the SRK equation of state is used in PSRK, poor results are calculated for liquid densities of the pure compounds and the mixtures. Furthermore, because of the use of original UNIFAC, and the limited database used to fit the parameters, poor results are obtained for activity coefficients at infinite dilution, heats of mixing, and very asymmetric systems. In his thesis, Jens Ahlers [17] developed a generalized group contribution equation of state. In this model, most of the weaknesses of PSRK were removed. The main differences compared to PSRK are summarized in Table 1.

**Table 1** Main differences between the new group contribution equation of state and the PSRK model.

Model	PSRK	New equation of state
Equation of state	Soave–Redlich–Kwong	Volume-translated
Peng–Robinson $\alpha$ -Function	Mathias–Copeman $T > T_r$ : generalized SRK- $\alpha$ -function	Exponential $\alpha$ -function of Twu $T > T_r$ : generalized Twu function
a mixing rule	PSRK mixing rule: $\frac{a}{bRT} = \sum_i x_i \cdot \frac{a_{ii}}{b_i RT} + \frac{1}{A} \left( \frac{g^E}{RT} + \sum_i x_i \ln \frac{b}{b_i} \right)$ $A = -0.64663$	New mixing rule of Chen: $\frac{a}{b} = \sum_i x_i \cdot \frac{a_{ii}}{b_i} + \frac{g^{E,R}}{A}$ $A = -0.53087$
b combination and b mixing rule	$b = \sum_i x_i \cdot b_i$	$b_{ij}^{3/4} = (b_i^{3/4} + b_j^{3/4}) / 2$ $b = \sum_i \sum_j x_i \cdot x_j \cdot b_{ij}$
$G^E$ information	1. Temperature-independent orig. UNIFAC parameters 2. Temperature-dependent PSRK parameters (fitted to VLE and GLE data)	Mod. UNIFAC with temperature-dependent group interaction parameters
Database	VLE, GLE	VLE, GLE, $H^E$ ( $\gamma^\infty$ , SLE)

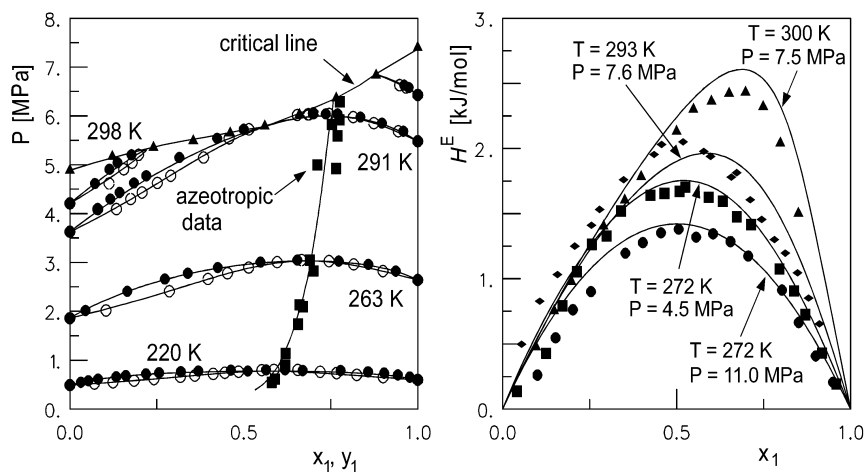
A better description of liquid densities is achieved by using a volume-translated PR (Peneloux [18]) instead of the SRK equation of state, which is used in the PSRK model. The translation parameter  $c$  can either be determined by the difference of the experimental and calculated liquid density at a reduced temperature  $T_r = 0.7$ , or calculated with the help of a generalized Racket equation using critical data. For the representation of the  $\alpha$ -function, instead of the Mathias–Copeman expression [19], the function introduced by Twu [20] and, based on the ideas of Chen [21], an improved  $G^E$  mixing rule is used. Furthermore, the prediction of asymmetric systems is improved by using a quadratic b mixing rule with a modified combination rule. And, of particular importance, instead of constant group interaction parameters as in original UNIFAC, temperature-dependent group interaction parameters as in modified UNIFAC are used in the new group contribution equation of state, which are fitted simultaneously to VLE, GLE, SLE,  $\gamma^\infty$ , and  $H^E$  data covering a large temperature and pressure range.

The results obtained for the different pure component properties and various phase equilibria of the new group contribution equation of state are very promising [17,22–24]. In Fig. 7, the predicted VLE results for the systems of CO<sub>2</sub> with hexane and hexatriacontane using PSRK and the new group contribution equation of state are presented.



**Fig. 7** Experimental and predicted VLE data for the CO<sub>2</sub>-*n*-hexane and CO<sub>2</sub>-hexatriacontane systems: - - - PSRK, — new group contribution equation of state.

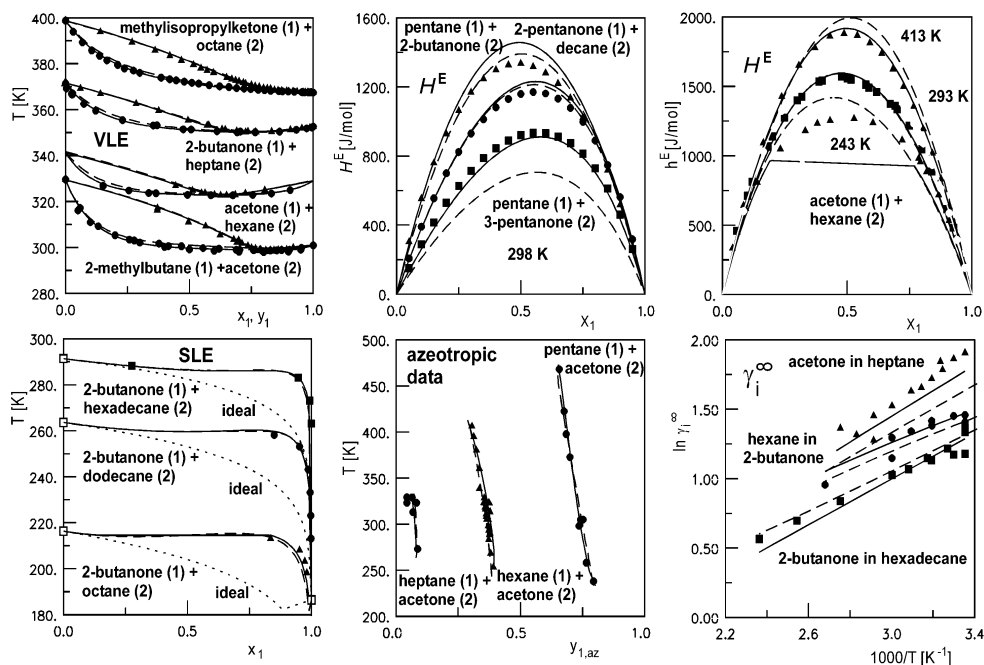
Whereas similar results are obtained for the slightly asymmetric system CO<sub>2</sub>-*n*-hexane, because of the improved mixing rule for the co-volume *b*, much better results are achieved for the strong asymmetric system CO<sub>2</sub>/hexatriacontane with the new group contribution equation of state. Using the same parameters, VLE, azeotropic data, critical data and excess enthalpies for the CO<sub>2</sub>/ethane system were predicted. A comparison of the predicted and experimental results is shown in Fig. 8. Whereas on the left-hand side, a comparison of the predicted and experimental VLE, azeotropic, and critical data for the system CO<sub>2</sub>/ethane is shown, on the right-hand side, excess enthalpies for the same system are presented. It can be seen that a nearly perfect description of the VLE, azeotropic, and the critical line is obtained. Furthermore, with the new group contribution equation of state, not only the temperature, but also the pressure dependence of the excess enthalpies is described correctly. Perhaps it has to be men-



**Fig. 8** Experimental and predicted VLE and excess enthalpy data for the CO<sub>2</sub>/ethane system.

tioned again that, for all the predictions (VLE, azeotropic data, critical line,  $H^E$ ) shown in Figs. 7–8, the same parameters were used to describe the interactions between  $\text{CO}_2$  and alkanes.

The next example (Fig. 9) shows the results of the new group contribution equation of state for different VLE, SLE, azeotropic data, activity coefficients at infinite dilution, and excess enthalpies for various alkane–ketone systems.



**Fig. 9** Experimental and predicted phase equilibrium data and excess enthalpies for alkanes with ketones predicted using modified UNIFAC, respectively, the new group contribution equation of state; — modified UNIFAC, - - - new group contribution equation of state.

Instead of PSRK, modified UNIFAC is applied for the comparison. Again, it can be seen that, with the new group contribution equation of state, similar good results are obtained for the different phase equilibria and excess enthalpies as obtained with modified UNIFAC. This means that, in the near future, the new group contribution equation of state can replace not only PSRK, but also modified UNIFAC. But, up to now, the available parameter matrix of the new group contribution equation of state is still limited. For a wide range of applicability, the parameter matrix has to be largely extended, with the help of a comprehensive factual database. At the same time, it is planned to extend the range of applicability to very asymmetric systems (i.e., systems with polymers).

## APPLICATIONS

The possibility of predicting the real behavior of multicomponent systems opens a wide field of applications of industrial interest. With the chance of predicting the various phase equilibria, thermodynamic models are, for example, ideal tools for the synthesis, design, and optimization of separation processes. But thermodynamic models can also be applied for other applications of industrial interest.

Since a lot of results for pure component properties, phase equilibria, and excess properties have already been presented in different publications [17,22–24] and in this paper, in the final example, the results for the calculation of the chemical equilibrium for the ammonia synthesis should be discussed.

The chemical equilibrium constant  $K$  for a given temperature can be calculated with the help of tabulated thermodynamic standard properties (Gibbs energies and enthalpies of formation, heat capacities in the reference state). But fugacities instead of partial pressures have to be used for the thermodynamic equilibrium constant  $K$ . This means the real behavior has to be taken into account to be able to calculate the equilibrium composition. For gas-phase reactions, this is usually done by the equilibrium constant  $K_\phi$ . With the help of  $K_\phi$ , one is able to calculate  $K_p$ , which is required to calculate the chemical equilibrium conversion as function of pressure and composition. On the right-hand side of Fig. 10, the experimental and predicted  $K_p$ s for different equations of state (PSRK, new group contribution equation of state VTPR, SRK with correlated binary parameters, ideal gas law) are given. It can be seen that, using PSRK or the new GCEOS, much better results are predicted than are obtained with the help of the SRK equation of state [2] using fitted binary parameters. Of course, using the ideal gas law, no influence of the real behavior on the chemical equilibrium conversion can be observed ( $K_\phi = 1$ ).

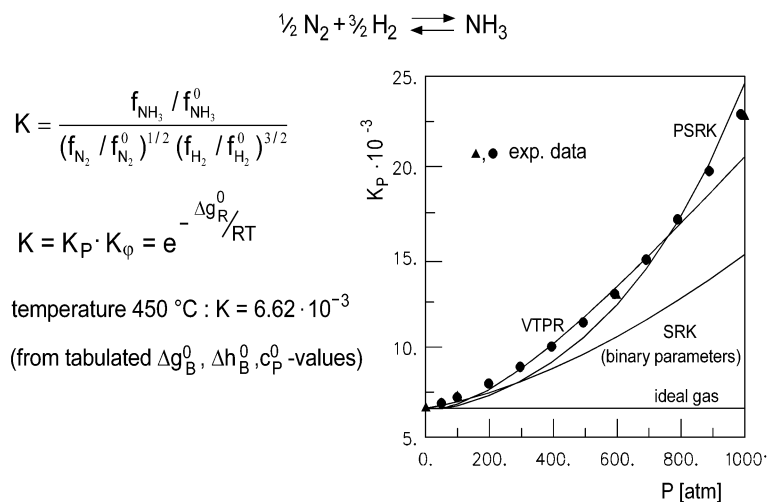


Fig. 10 Experimental [25] and predicted equilibrium constants  $K_p$  for the ammonia synthesis at 450 °C.

## CONCLUSIONS

In the last 30 years, great progress has been achieved in the field of predictive thermodynamic models. Whereas at the beginning, the main objective was the prediction of VLE using group contribution methods ( $G^E$  models), today powerful group contribution equations of state (e.g., PSRK) can be applied to predict the required pure component properties, such as densities, enthalpies (including enthalpies of vaporization), heat capacities for the different phases at given conditions (temperature, pressure, composition), the various phase equilibria and excess properties for nonpolar, polar, and supercritical compounds, and strong electrolytes. Owing to the wide range of applicability and the reliable results, group contribution equations of state are ideal tools for the synthesis, design, and optimization of chemical plants (in particular, separation processes).

The remaining weaknesses of PSRK were minimized using a volume-translated PR equation of state with modified mixing rules for the parameters  $a$  and  $b$  and temperature-dependent parameters, which are fitted simultaneously to reliable phase equilibrium data and excess properties. Using this ap-

proach, reliable liquid densities for the pure compounds and mixtures are obtained, and the model can be applied reliably to very asymmetric systems.

From all the promising results obtained up to now, it can be concluded that the new group contribution equation of state is an important step in the right direction. Therefore, it can be expected that models like modified UNIFAC or PSRK can be replaced completely by the new group contribution equation of state. But up to now, the range of applicability is limited, since the matrix of the new group contribution equation of state is quite small. Therefore, in a planned research project, the further development of the new group contribution equation of state and the extension of the existing parameter table with the help of the DDB is planned. Furthermore, the effects of strong electrolytes (similar as in PSRK) should be taken into account, and the results for polymer systems should be carefully examined.

## LIST OF SYMBOLS AND ABBREVIATIONS

a, b	parameters in equations of state
$C_p$	heat capacity at given pressure
$f_i$	fugacity of component $i$
$G$	Gibbs energy
GLE	gas–liquid equilibrium
$H$	enthalpy
LLE	liquid–liquid equilibrium
$P$	total pressure
$P_i^s$	vapor pressure
SLE	solid–liquid equilibrium
VLE	vapor–liquid equilibrium
$x_i$	mole fraction of component $i$ in the liquid phase
$y_i$	mole fraction of component $i$ in the vapor phase

## Greek symbols

$\alpha, \beta$	different phases
$\mu_i$	chemical potential of component $i$
$\gamma_i$	activity coefficient of component $i$
$\phi_i$	fugacity coefficient of component $i$

## Superscripts

L	liquid phase
V	vapor phase
E	excess property
$\infty$	at infinite dilution

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