

The choice of fitting equations in critical evaluation of solubility data in binary mixtures MCl-H₂O

Roger Cohen-Adad

Université Lyon I, Laboratoire de Physico-chimie minérale 2,
L.A. CNRS N° 116, 69622 Villeurbanne, France

Abstract - A methodical approach to the critical evaluation of solubility, vapor pressure and density data of saturated solutions is proposed. If appropriate fitting equations are chosen, this approach allows the extrapolation of solubility, vapor pressure and density curves and the deduction of such missing data as phase change enthalpies, heat capacities, metastable equilibria, double saturation points, etc. The choice is difficult, since fitting equations must obey several conditions, and assumptions must be made concerning the interactions between solvent and solute and their variation with concentration and temperature. Some examples of critical evaluations are examined for binary systems MCl-H₂O.

INTRODUCTION

The main purpose of the Solubility Data Project of the International Union of Pure and Applied Chemistry is the collection of solubility data, the selection of best values, evaluation of errors and calculation of solubilities for rounded values of temperature. However, the needs of users are much more extensive and it is necessary, when possible, to define the nature and stoichiometry of solid phases in equilibrium with liquid, to determine solubility in the whole range of stability of solid phase, to state precisely the experimental conditions for the measurements: temperature, composition, vapor pressure of saturated solution (particularly, at the standard boiling point), to evaluate density in order to convert volume units into mass units, to deduce missing data (enthalpies, entropies of phase change, activity coefficients, metastable equilibria...). Some of this information can be obtained by a rational treatment of data based on appropriate models.

In this paper, a rational method of critical evaluation for solubility data in binary mixtures MCl-H₂O is considered and the criteria for the choice for fitting equations are analysed.

TREATMENT OF DATA

The principle of the proposed method is illustrated in Fig. 1. The data are taken from three different sources: existing compilations, results taken from original papers but not previously compiled (incomplete or graphical data etc.) and thermodynamic data (phase change enthalpies, heat capacities, mixing data and excess property data).

A graphical inspection of experimental data is first performed; it is a speedy way to detect anomalies: some obviously erroneous points are eliminated (Fig. 2a); others are set aside for further inspection (Fig. 2b). The graphical inspection permits also to distinguish between sets of data belonging to very close but different solubility curves (Fig. 2c) while a mathematical treatment will lead to the mean curve.

A statistical treatment of data is then performed. Accurate physico chemical properties of phases are usually not known, so different fitting equations can be proposed in order to describe the solubility curves. For each fitting equations adjustable coefficients are calculated by an iterative method previously described by Tenu et al. (1) and summarized in the flow chart shown in Fig. 3. At each iteration, coefficients $A_n, B_n, C_n \dots$ are calculated by the

least squares method, using the experimental points selected in the previous iteration by the conditions :

$$[y_j - y(T_j)] / y(T_j) < \rho \quad (1)$$

$$[T_j - T(y_j)] / T(y_j) < \tau$$

where ρ and τ are fixed, a priori, and are the mean size of experimental uncertainty stated by the authors of data,

y_j and T_j are the coordinates of experimental point j expressed in mole fraction of salt and temperature,

$y(T_j)$, $T(y_j)$ are respectively the calculated mole fraction of salt and temperature.

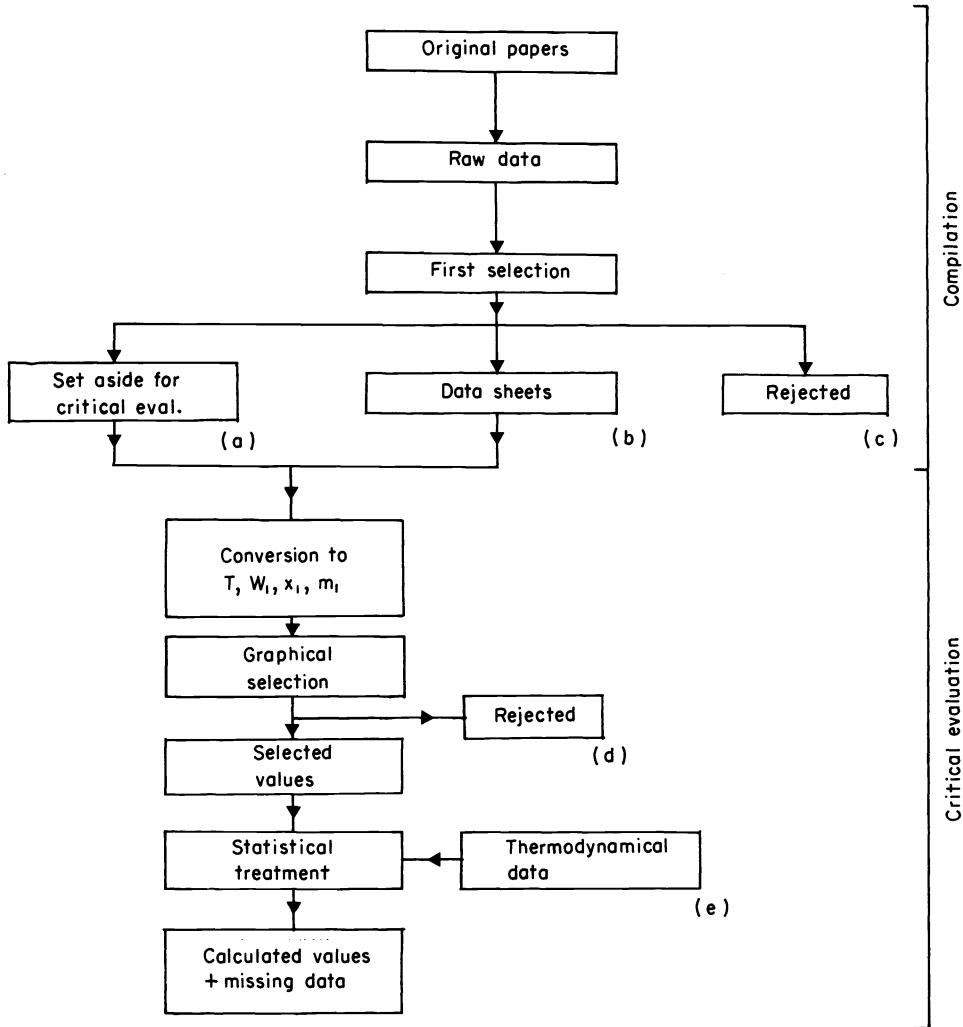


Fig. 1. Treatment of data

- (a) Incomplete data, graphical results etc.
- (b) Solubility data, density and vapor pressure of saturated solutions
- (c) Previously published or taken in existing compilation
- (d) Rejected or set aside for further inspection
- (e) Phase change enthalpies, specific heats etc.

The calculation is stopped when steady values are obtained for the coefficients. The results for different possible fitting equations are then compared. The fitting equation which lead to the most complete utilisation of the data will be considered as the best. This choice is a very subjective one and may be called into question, if new data are published.

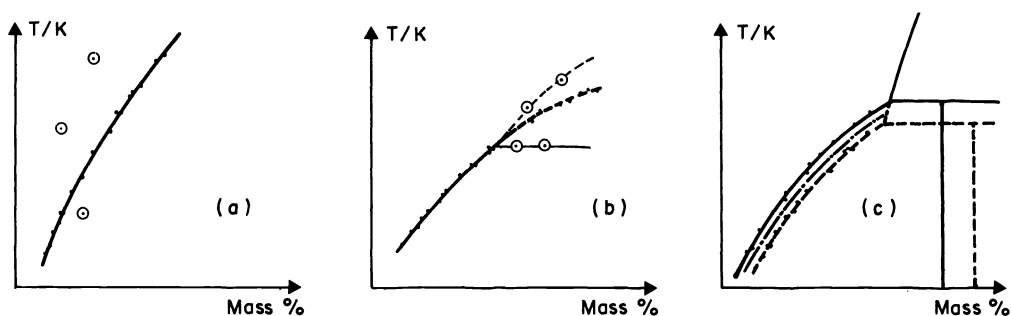


Fig. 2. Graphical selection

- (a) obviously erroneous points
- (b) anomalous data selected for further inspection
- (c) mean curve (treatment of data without graphical analysis)

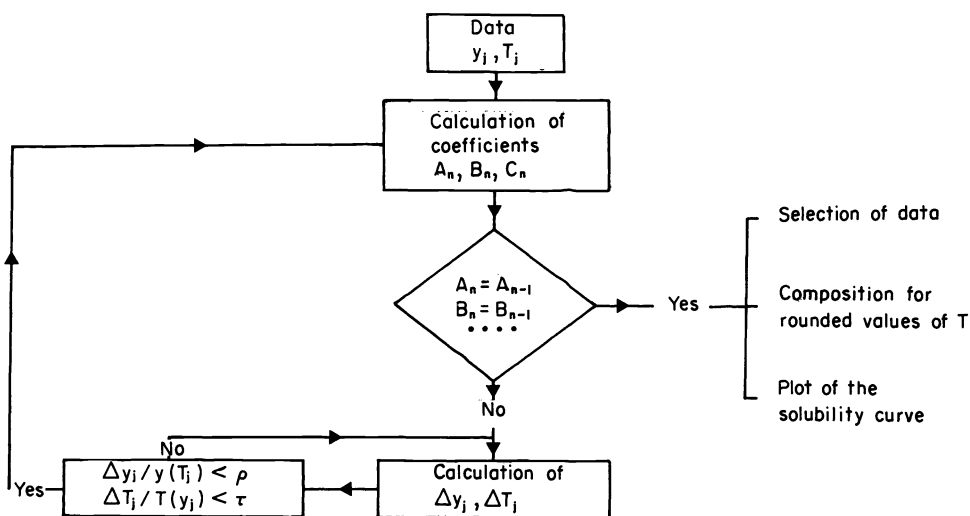


Fig. 3. Treatment of data for each fitting equation

CHOICE OF MODELS

The different fitting equations are based on models which must take in account all available data (activity coefficients, phase change enthalpies, heat capacities, mixing or excess data, etc.) and never be in contradiction with thermodynamic laws. In the particular case of binary systems $\text{MCl-H}_2\text{O}$, the models must comply with the following constraints :

- the aqueous solution is a strong electrolyte,
- the solid phases (ice, salt, hydrates) are stoichiometric,
- each phase is in equilibrium and any two phases are in mutual equilibrium :

$$\sum_i \nu_i \mu_i^\alpha = 0 \quad ; \quad \mu_i^\alpha = \mu_i^\beta \quad ; \quad d\mu_i^\alpha = d\mu_i^\beta \quad (2)$$

where μ_i^α = chemical potential of component i in phase α
 ν_i = stoichiometric coefficient of i in solid phase

- Raoult's and Stortzenbaker's laws for the limiting slopes of the liquidus and solidus must be satisfied :

$$\lim_{x \rightarrow 0 \text{ or } x \rightarrow 1} |dx^\beta/dT - dx^\alpha/dT| = \lim_{x \rightarrow 0 \text{ or } x \rightarrow 1} [\Delta H_m / (RT^2)] \quad (3)$$

where x = mole fraction of salt

- Gibbs-Konovalov's relation is satisfied at stable or metastable congruent melting points,
- activities are consistent with the Gibbs-Duhem relation

$$s_m dT + \sum_i x_i d\mu_i = 0 \quad (P \text{ constant}) \quad (4)$$

- the variation of phase change enthalpy follows Kirchhoff's law.

In expressing the chemical potentials as functions of the activities of the constituents of the system, the liquidus curve can be written in the form :

$$Y - Y_0 = U - U_0 \quad (5)$$

Y is a function of activities expressed in different ways, according to the nature of the solid phase :

$$\text{ice} \quad : \quad Y = \ln (a_2) \quad (6)$$

$$\text{salt} \quad : \quad Y = \ln (a_M \cdot a_{\text{Cl}}) \quad (7)$$

$$\text{hydrate } \text{MCl} \cdot n\text{H}_2\text{O} \quad : \quad Y = \ln (a_M \cdot a_{\text{Cl}} \cdot a_2^n) \quad (8)$$

where a_2 is the activity of solvent and n the stoichiometric coefficient of water in hydrate.

The subscript o concerns the coordinates of a particular point of the solubility curve taken as limit of integration (usually the congruent melting point of solid phase).

U is a function of temperature :

$$U = \int [\Delta H_m / (RT^2)] dT \quad (9)$$

It may be written in most cases :

$$U - U_0 = A (1/T - 1/T_0) + B \ln(T/T_0) + C (T - T_0) \quad (10)$$

where A, B, C are, according to the case under consideration, deduced from thermodynamical data ($\Delta H_m, \Delta C_m$) for the pure components or considered as adjustable coefficients.

In the same way, the vapor pressures of saturated solutions are constrained by the liquid \rightleftharpoons vapor and solid \rightleftharpoons liquid equilibrium conditions. According to the nature of the solid phase, one of the equations (6), (7) or (8) is satisfied and, at the same time :

$$p = p^0 a_2 \quad (11)$$

p^0 is the vapor pressure of pure water at the temperature of the system.

ACTIVITY OF SOLUTIONS

In order to derive an appropriate expression for activities, the experimental solubility curve is compared, when possible, to the liquidus curve obtained in the ideal approximation : ($f_i = 1$, $a_2 = 1 - x_1$, $a_M = a_{Cl} = x_1$, $x_1 =$ mole fraction of MCl in solution).

For instance, the solubility curves of ice in solutions of NH_4Cl , $CsCl$ and $LiCl$ are shown in Fig. 4. A comparison with ideal solubility curve of ice in alkali chloride solution shows that two different situations are observed.

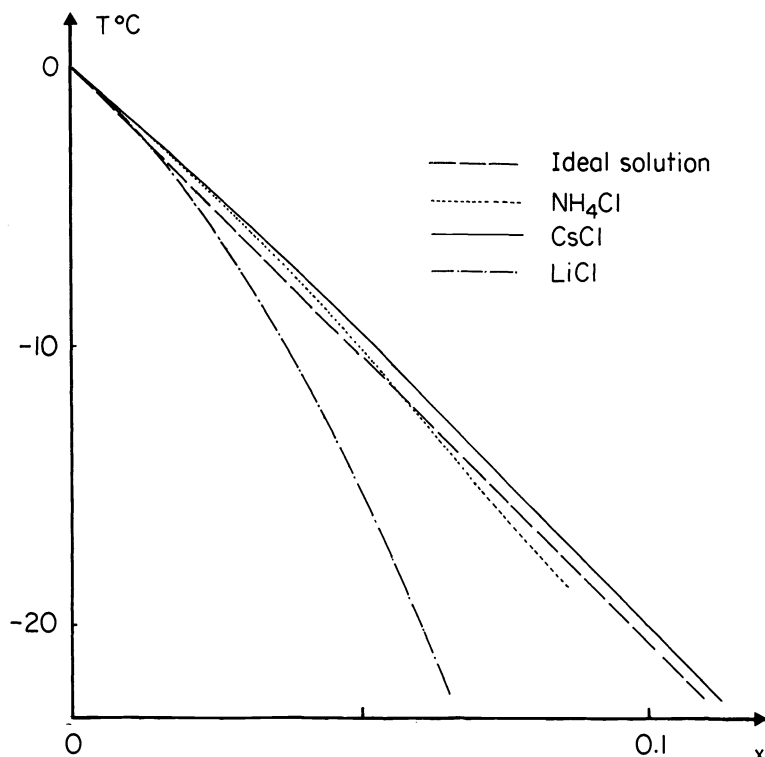


Fig. 4. Solubility of ice in solutions of alkali chloride

* With NH_4Cl or $CsCl$, the experimental curve is very close to the calculated ideal one. The interactions between solute and solvent are assumed to be weak and are expressed through rational activity coefficients f_i :

$$f_M = a_M \cdot (1 + x_1) / x_1 ; f_{Cl} = a_{Cl} \cdot (1 + x_1) / x_1 \quad (12)$$

$$f_2 = a_2 (1 + x_1) / (1 - x_1) \quad (13)$$

Eq. 12 and 13 do not distinguish between free and bound solvent. For dilute solution, f_M and f_{Cl} are expressed by the Debye-Hückel relation.

For concentrated solutions several semi-empirical equations for activity coefficients of salt have been proposed (Refs. 2-24). They apply in particular cases and definite ranges of concentration. Most of them were derived for isothermal conditions so an additional hypothesis is necessary, concerning the variation of the activity coefficients with temperature.

These considerations led us to search for more simple expressions and two relations have been found suitable for the critical evaluation of data :

Solubility curve of salt or hydrate. $\ln(f_i)$ is expressed by (Ref. 25) :

$$\ln(f_i) = a_i/T + b_i \ln(T) + c_i T + d_i \quad (14)$$

Solubility curve of ice. The activity of water has the form :

$$\ln(f_2) = [x/(1+x)]^{3/2} \varphi(xT) \quad (15)$$

Instead of using for $\varphi(xT)$ the relation of Margules which leads to an alternating series, we have preferred to express $\varphi(xT)$ in the following way :

$$\varphi(xT) = (a' + b'z + c'z^2 + d'z^3 + \dots) / T \quad (16)$$

where a' , b' , c' , d' are adjustable coefficients and $z = \ln[x_1/(1+x_1)]$.

* With LiCl a large deviation from ideality is observed due to the solvation of ions. A good representation of solubility curve of ice is obtained if we assume that the mean number of moles of water bound to an ion varies slowly with the concentration of ions. Then :

$$\begin{aligned} x_{Cl} &= x_1 / [1 - (E-1)x_1 - Fx_1^2] \\ x_2 &= [1 - (1+E)x_1 - Fx_1^2] / [1 - (E-1)x_1 - Fx_1^2] \end{aligned} \quad (17)$$

where E and F are adjustable coefficients.

APPLICATION TO CRITICAL EVALUATION OF THE CsCl-H₂O SYSTEM

Few data are available for critical evaluation of the binary system CsCl-H₂O (Table 1) and the numerical values are essentially centred on two ranges of temperature : between 0 and -10°C for the solubility of ice, and between 0 and 120°C for the solubility of CsCl, cubic).

TABLE 1. Available data on binary system CsCl-H₂O

| T°C | Available data | Solid phase |
|--------|---|----------------|
| 0 | ΔH , ΔC | ice |
| 0, -10 | composition of solution | ice |
| 0, 120 | (solution composition, density, vapor pressure | CsCl, cubic |
| 400 | vapor pressure | |
| 450 | vapor pressure | |
| 472 | transition point | cubic + f.c.c. |
| 500 | vapor pressure | CsCl, f.c.c. |
| 638 | vapor pressure | CsCl, f.c.c. |
| 645 | ΔH , ΔC , melting point | CsCl, f.c.c. |

In order to draw the phase diagram of the system, the solubility curve of the high temperature, face centered cubic form CsCl has first been calculated in the ideal approximation and the composition of the transition point has been deduced. The solubility curve of CsCl cubic is represented by eq. 5 where Y and U are expressed by eq. 7, 10 and 14 ; the transition point is taken as a point of the liquidus curve and the coefficients of fitting equation are evaluated by a two parameters linear regression.

The determination of the solubility curve of ice has been performed with ten different models in order to compare the various approaches. Most of them lead to very good interpolation results but are unable to represent correctly the solubility curve out side the range where experiments have been done (Fig. 5). To evaluate the quality of the fitting equations, the coordinates of the eutectic point ($x = 0.1126$, $t/^\circ\text{C} = -22.3$) have been determined by thermal analysis and by drawing a Tammann diagram (Ref. 26). The best approach for the solubility curve of ice is obtained by calculation of $\ln(f_2)$ using Eq. 13.

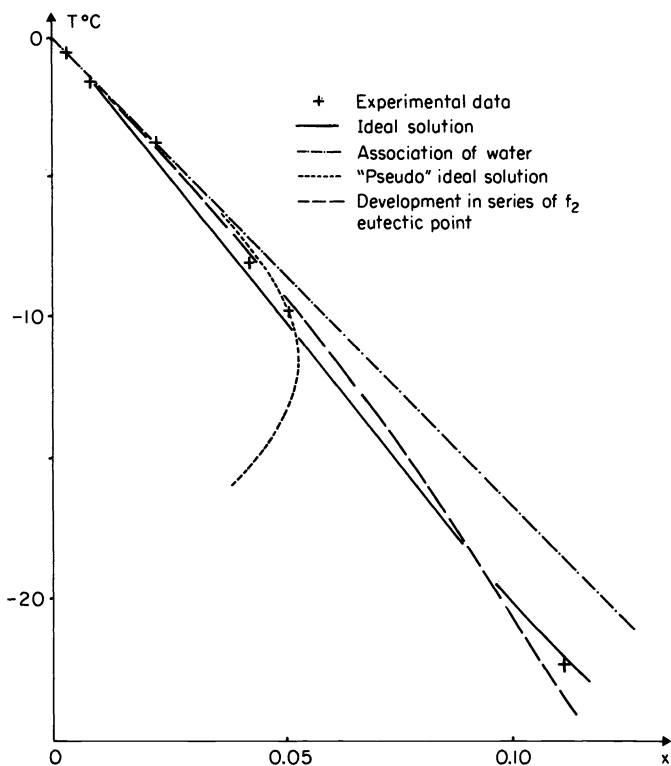


Fig. 5 Solubility of ice in aqueous solution of CsCl
Comparison of various fitting equations

Finally the solubility and vapor pressure curves have been drawn for the whole range of concentrations (Figs. 6 and 7). The agreement between experimental and calculated data is very good. Nevertheless, the results must be considered tentative in the extrapolated regions.

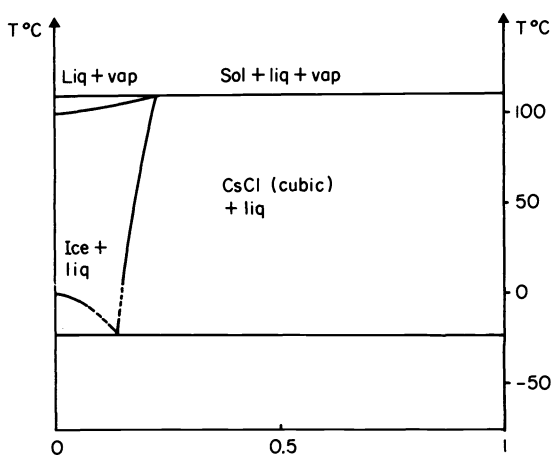


Fig. 6. CsCl-H₂O phase diagram under atmospheric pressure

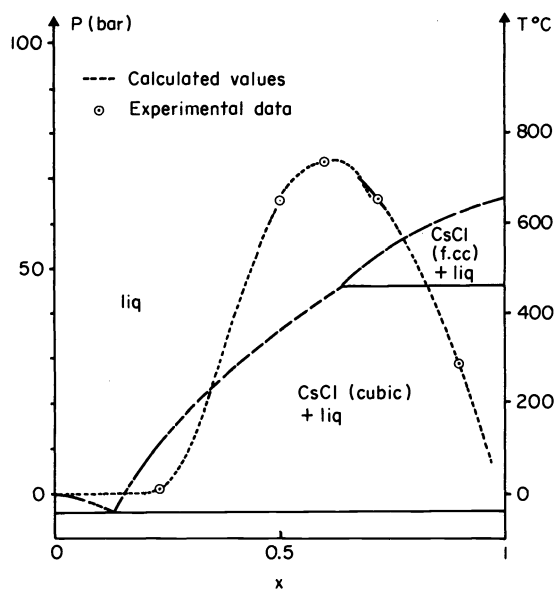


Fig. 7. CsCl-H₂O solubilities and vapor pressure of saturated solution

CONCLUSIONS

In the binary system CsCl-H₂O a great number of missing data may be obtained by a rational treatment of available data.

Nonetheless, the method is still somewhat subjective and the results depend on the choice of fitting equations.

REFERENCES

1. R. Tenu, J.J. Counioux and R. Cohen-Adad, 8th International CODATA Conference, Jachanka, Poland (1982) (not yet published)
2. E.A. Guggenheim and J.C. Turgeon, Trans. Farad. Soc. **51**, 747-61 (1955)
3. R.A. Robinson and R.H. Stokes, Electrolyte Solutions, Butterworths, London, 2nd Ed., 222-60 (1970)
4. R.H. Stokes and R.A. Robinson, J. Solut. Chem. **2**, 173-91 (1973)
5. G. Scatchard, Chem. Rev. **19**, 309-27 (1936)
6. K.S. Pitzer, J. Phys. Chem. **77**, 268-77 (1978)
7. J.G. Kirkwood and J.C. Poirier, J. Phys. Chem. **58**, 591-6 (1954)
8. E. Glueckauf, Proc. Roy. Soc. A310, 449-62 (1969)
9. M.H. Lietzke, R.W. Stoughton and R.M. Fuoss, Proc. Nat. Acad. Sci. **59**, 39-45 (1968)
10. Mitra in J. Braunstein, Ionic interactions, Academic Press, **I** (1971)
11. L.A. Bromley, J. Am. Inst. Chem. Eng. **19**, 313-20 (1973)
12. L.A. Bromley, J. Chem. Thermodynamics, **4**, 669-73 (1972)
13. H.P. Meissner and C.L. Kusik, J. Am. Inst. Chem. Eng. **18**, 294-8 (1972)
14. H.P. Meissner and J.W. Tester, Ind. Eng. Chem. Proces. Des. Develop. **11**, 128-33 (1972)
15. H.P. Meissner, C.L. Kusik and J.W. Tester, J. Am. Inst. Chem. Eng. **18**, 661-2 (1972)
16. H.P. Meissner and C.L. Kusik, Ind. Eng. Proces. Des. Develop. **12**, 205-8 (1973)
17. R. Haase, H. Naas and H. Thumm, Z. Physik. Chem. N.F., **37**, 210-29 (1963)
18. R. Haase, H. Naas and K.H. Ducker, Z. Physik. Chem. N.F., **39**, 383 (1963)
19. R. Haase, Ang. Chem. **77**, 517-29 (1965)
20. H.A. Correa and J.H. Vera, Can. J. Chem. Eng. **53**, 204-10 (1975)
21. R. Vega and J.H. Vera, Can. J. Chem. Eng. **54**, 245-8 (1976)
22. E. Hala, J. Pick, V. Frjed and O. Vilim, Vapour-liquid equilibrium, Pergamon Press, 2nd Ed. 144-55 (1967)
23. E. Hala, Proc. Inst. Symp. Distillation, Brighton (1969)
24. J.L. Cruz and H. Renon, C.R. Acad. Sci. Paris, **282**, série C, 477-80 (1976)
25. J.J. Counioux and R. Tenu, J. Chim. Phys. **78**, 815-21 (1981)
26. E.H. Merrachi, unpublished