Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Mean-Field Lattice-Gas Description of the System CO_2/H_2O

L. A. Kleintjens[a]; R. Koningsveld[a]
[a] Central Laboratory DSM Geleen, The Netherlands

To cite this Article Kleintjens, L. A. and Koningsveld, R.(1982) 'Mean-Field Lattice-Gas Description of the System CO_2/H_2O', Separation Science and Technology, 17: 1, 215 — 233
To link to this Article: DOI: 10.1080/01496398208058148
URL: http://dx.doi.org/10.1080/01496398208058148

SEPARATION SCIENCE AND TECHNOLOGY, 17(1), pp. 215-233, 1982

Mean-Field Lattice-Gas Description of the System CO_2/H_2O

L. A. KLEINTJENS and R. KONINGSVELD

CENTRAL LABORATORY DSM
GELEEN, THE NETHERLANDS

ABSTRACT

The mean-field lattice-gas model in the present form has proven to be well able to describe nearly quantitatively fluid phase behaviour of non-polar and polar pure components and mixtures over a large temperature and pressure range. In our version of the model it is assumed that all lattice sites have the same volume, independent of temperature and pressure, and that every kind of lattice site has a characteristic interacting surface area. The combinatory entropy of the system is corrected with an empirical parameter. For mixtures the same procedure can be followed and a description of fluid phase behaviour, based upon the parameters of the pure components and two binary interaction parameters, appear to come out quite reasonably.

The systems CO_2, H_2O and mixtures thereof are most commonly used in supercritical extraction. It is shown here that the lattice-gas model can quite well deal with these systems. Values of the lattice-gas parameters have been derived in the outlined manner and predict the second-type gas-gas demixing, known to occur in this system, in an essentially correct way.

INTRODUCTION

Critical phenomena in pure components and mixtures have been studied intensively since the end of the past century. Pioneering work in this field was carried out by Van der Waals and Kohnstamm (1), Bakhuis Roozeboom (2), Timmermans (3) and others. Van der

Waals in particular has already shown that phase behaviour in fluid mixtures under supercritical conditions may be quite peculiar for substances differing much in critical point (4) and he predicted gas-gas demixing (5), a phenomenon much later experimentally confirmed (6,7) in several gas mixtures.

In several fields fluid phase behaviour at supercritical conditions has become technologically important. Nowadays a number of polymers are manufactured in solvents (or monomers) under super- or near-critical conditions. A new rapidly expanding field is the extraction of valuable or toxic chemicals from raw materials by means of supercritical solvents. Review papers on PVT-phenomena in supercritical fluid mixtures have appeared, e.g., by Schneider (8-10). The most commonly used solvents are CO_2, H_2O and mixtures thereof and this paper attempts a mean-field lattice-gas description of these systems.

An obvious feature of phase transformations under near-critical conditions is the difference in density between phases and its variation with pressure and temperature. Such situations have been treated theoretically by Prigogine (11), by Flory (12), by Patterson (13) and by Simha (14).

Since we are up against large differences in density we prefer an approach which, apart from having proven its ability to cope with such situations, has the additional advantage of great simplicity. It has been outlined in principle by Guggenheim (15) and Trappeniers et al (16,17); Guggenheim developed a rigid lattice model for mixtures. One of the assumptions in his treatment is the equality of the partial specific volumes of both constituents in all fluid phases in equilibrium. This is obviously not so in a gas-liquid equilibrium. By introduction of randomly distributed vacant lattice sites Trappeniers et al circumvented this problem. The concentration of holes in the lattice can be varied between zero (rigid lattice) and 100% (absolute vacuum) and any phase-density can thus be represented.

The model is based on the hole theory of the liquid state developed by Altar (18), Cernushi and Eyring (19), Frenkel (20) and others. Much later the model was applied to pure components by Mermin (21) and by Mulholland and Rehr (22). By combining the lattice-gas treatment with Guggenheim's two-component lattice model, Trappeniers et al were able to predict qualitatively the various fluid phase equilibria. Similar versions of the model were used by other authors, i.e., to describe polymer systems (23-25), but until now quantitative descriptions of the critical phase behaviour have been very rare.

Engineering types of descriptions (26-28) usually contain a large number of adaptable parameters and have to assume mixing rules for mixture parameters. The inherent weakness of such procedures is brought out by the threefold differentiation involved in the derivation of critical conditions from free enthalpy or free energy expressions.

In the model we use here the only need for a mixing rule occurs when an assumption has to be made as to how the molar lattice-site volume varies with the composition in a mixture. We use the simplist possible version and assume no dependence at all.

In previous work we already showed how Trappeniers' model can be extended into a quantitative predictive description of fluid phase behaviour of non-polar (29-30) and polar systems (31) and mixtures. To achieve this, we have to accept a small number of adjustable parameters but retain the simplicity of the model. We apply the model to the system CO_2/H_2O, the solvents used in most supercritical extractions.

THEORY

The basic equations in the lattice-gas model are quite straightforward and have been published elsewhere (29-31). Here we summarize the basic assumptions and some important equations.

Pure Components

In a lattice-gas treatment a fluid pure substance is represented by a lattice composed of occupied and vacant lattice sites (holes) and can hence be viewed as a binary mixture. The only interaction to account for exists between the occupied sites and therefore the holes contribute mainly to the entropy and to the internal energy only in as much they affect the number of nearest-neighbour contacts between occupied sites. Pressure and temperature changes cause the concentration of holes to change but the volume per lattice site (v_o) is kept constant. To deal with mixtures later on in the simplest possible way with a minimum of additional assumptions, we postulate that all sites in a given system shall have the same molar volume v_o. We further assume only nearest neighbour interactions to play a role.

To derive the interaction expression for these systems, we follow a suggestion by Staverman (32), later also used by Kanig (23), and drop the rigid-lattice condition that each site will have the same number of neighbours (= lattice coordination number). Rather, we assign a characteristic interaction surface area σ_i to each kind of site i. Finally, we allow a molecule to occupy more than one lattice site, say m_i sites.

Since we aim at describing supercritical systems, the model should be valid for liquids and gases alike. In this model the only difference between a gas and a liquid is the hole concentration. A change in hole concentration however alters the number of contacts between occupied sites and hance the total internal energy. An expression for the energy (ΔE) of mixing n_o moles of holes with n_1 moles of molecules 1 each occupying m_1 sites can be derived straightforwardly (29):

$$\Delta E = -\tfrac{1}{2}\, w_{11}\sigma_o n_o \sigma_1 n_1 m_1\, (\sigma_o n_o + \sigma_1 n_1 m_1)^{-1} \qquad (1)$$

where w_{11} is the molar interaction energy per unit contact surface area involved in a 1-1 interaction. Changing to volume fractions ϕ_o and ϕ_1 of vacant and occupied sites ($\phi_o = n_o\,(n_o + n_1 m_1)^{-1} = 1 - \phi_1$) we can rewrite Eq. (1) into:

$$\Delta E/N_\phi kT = g_{11}\,(1 - \gamma_1)\,\phi_o\phi_1\,(1 - \gamma_1\phi_1)^{-1} \tag{2}$$

where $g_{11} = -\tfrac{1}{2}\, w_{11}\sigma_o/kT$, $N_\phi = n_o + n_1 m_1$, and $\gamma_1 = 1 - \sigma_1/\sigma_o$; kT has its usual meaning.

Supercritical fluids undergo large volume changes upon variations in pressure. It is therefore convenient to have an expression for the Helmholz free energy of mixing ΔF as a starting equation for other derivatives. To obtain such an expression, we follow the procedure used for strictly-regular systems (15) and add to ΔE the usual (athermal) combinatorial entropy of mixing terms. However, it is well established (33) that the athermal entropy of mixing expression above generally is not sufficient to fit experimental data. We therefore include an empirical entropy correction term of the form $\phi_o\phi_1\,\alpha$. By now the lattice has become an abstraction serving merely as a framework for convenient derivation of usable thermodynamic relations.

All this leads to the following expression for the change in Helmholtz free energy upon mixing n_o moles of vacant lattice sites with n_1 moles of substance 1, each of m_1 sites:

$$\frac{\Delta F}{N_\phi\, kT} = \phi_o\,\ln\phi_o + \frac{\phi_1}{m_1}\,\ln\phi_1 + \phi_o\,\phi_1\left\{\alpha_1 + \frac{g_{11}\,(1 - \gamma_1)}{(1 - \gamma_1\phi_1)}\right\} \tag{3}$$

The concentration variable ϕ_1 (= $1 - \phi_o$) is, within the framework of the model, directly related to the density d_1 of the system. For a substance with molar mass M_1 this relation is given by:

$$d_1 = \frac{\text{total mass}}{\text{total volume}} = \frac{n_1\,M_1}{N_\phi\,v_o} = \phi_1\,M_1/v_o m_1\,. \tag{4}$$

The equation of state expression for the fluid follows conventionally from ΔF:

$$\frac{-pv_o}{kT} = \ln\phi_o + (1 - m_1^{-1})\phi_1 + \phi_1^2\left[\alpha_1 + g_{11}(1-\gamma_1)^2(1-\gamma_1\phi_1)^{-2}\right] \qquad (5)$$

By substitution of Eq. (4) this expression can be rewritten in an equation of state in measurable quantities containing 4 adjustable parameters. Three of them (v_o, g_{11}, γ) do have a physical meaning allowing their order of magnitude to be estimated; α_1 is a purely empirical correction parameter.

Van der Waals (1) already showed that parameters in an equation of state can be very well determined from the experimental gas-liquid critical point. As was shown before (29-31) expressions for the critical condition and for the spinodal* can be derived easily. Expressed in volume fractions they read:

$$\phi_o^{-1} + (m_1\phi_1)^{-1} = 2\alpha_1 + 2g_{11}(1-\gamma_1)^2(1-\gamma_1\phi_1)^{-3} \quad \text{(spinodal)} \qquad (6)$$

$$\phi_o^{-2} - m_1^{-1}\phi_1^{-2} = 6g_{11}\gamma_1(1-\gamma_1)^2(1-\gamma_1\phi_1)^{-4} \quad \text{(critical condition)} \qquad (7)$$

---

*Following Trappeniers et al (16) the spinodal for a mixture of vacant and occupied lattice sites, usually given by $(\partial p/\partial V)_{T,N_1} = 0$, is defined by:

$$\left(\frac{\partial^2 \Delta F}{\partial\phi_1^2}\right)_{V,T} \cdot \left(\frac{\partial^2 \Delta F}{\partial V^2}\right)_T - \left(\frac{\partial^2 \Delta F}{\partial\phi_1 \partial V}\right)_T^2 = 0$$

This expression can be simplified to (29): $(\partial^2\Delta F/\partial\phi_1^2)_{V,T} = 0$.

In a similar way one obtains the critical condition of such a system from $(\partial^2 p/\partial V^2)_{T,N_1} = 0$ leading to (29):

$$(\partial^3\Delta F/\partial\phi_1^3)_{V,T} = 0$$

Interactions between molecules are usually temperature dependent. Until here we assumed g_{11} to be constant, but it is better to let experimental data determine what the temperature dependence of w_{11} (and hence g_{11}) will be. For the substances considered here gas-liquid equilibrium pressure and volumes of both phases are known at several temperatures. We use some of these data to establish the temperature dependence of g_{11}.

In the present model a gas-liquid equilibrium is completely determined by the equality of the pressures and of the chemical potentials of sites 1 in both phases. The latter equality leads to (29,30):

$$\frac{1}{m_1}\ln\phi_1' + \phi_1'\left(1-\frac{1}{m_1}\right) + \phi_o'^{\,2}\left\{\alpha_1 + g_{11}(T)(1-\gamma_1)(1-\gamma_1\phi_1')^2\right\} =$$

$$\frac{1}{m_1}\ln\phi_1'' + \phi_1''\left(1-\frac{1}{m_1}\right) + \phi_o''^{\,2}\left\{\alpha_1 + g_{11}(T)(1-\gamma_1)(1-\gamma_1\phi_1'')^2\right\} \quad (8)$$

where ' and " are the phases in equilibrium.

A similar expression is obtained by substitution of Eq. (5) into the additional equilibrium condition: p' = p". With these two equations, together with Equation 5, one can calculate the compositions and thus the densities of both phases. On the other hand these equations can also be used to establish the temperature dependence of $g_{11}(T)$ and the value of v_o or m_1 from experimental phase densities at given α_1 and γ_1.

Binary Mixtures

In the present version of the lattice-gas model a binary mixture is represented by a ternary system composed of sites 1, sites 2 and a single kind of vacant lattice sites, all with the same volume per site v_o. We thus have three concentration variables (ϕ_o, ϕ_1, ϕ_2) and three kinds of interactions (1-1, 2-2, 1-2). Parameters describing the 1-1 and 2-2 interaction are obtained from data on the pure substances; only the 1-2 interaction calls for extra experimental information on the mixture.

The Helmholtz free energy expression for a mixture can be derived in a similar way as for a pure substance (29) and reads:

$$\frac{\Delta F}{N_\phi RT} = \phi_o \ln\phi_o + \frac{\phi 1}{m_1} \ln\phi_1 + \frac{\phi 2}{m_2} \ln\phi_2 + \phi_o \phi_1 \left\{ \alpha_1 + g_{11}(1-\gamma_1)q^{-1} \right\}$$
$$+ \phi_o\phi_2 \left\{ \alpha_2 + g_{22}(1-\gamma_2)q^{-1} \right\} + \phi_1 \phi_2 \left\{ \alpha_{12} + g_{12}(1-\gamma_2)q^{-1} \right\}$$
$$- g'_{01} \phi_{01} \phi_1 - g'_{02} \phi_{02} \phi_2 \qquad (9)$$

where $N_\phi = n_o + n_1m_1 + n_2m_2$, $q = 1 - \gamma_1\phi_1 - \gamma_2\phi_2$. The last two terms of Eq. (9) arise from ΔF standing for the change in free energy of mixing system I (= constituent 1 + holes) with system II (constituent 2 + holes) where the compositions ϕ_{01} and ϕ_{02} of systems I and II are independent of the composition in the mixture.

These two terms do not concern us since they do not show up in spinodal and critical conditions and cancel in gas-liquid equilibrium expressions. It is worthwhile to compare Eq. (9)(mixture) with the corresponding expression (5) for the single substances i. The values of α_i, g_{ii}, γ_i, m_i occurring in Eq. (9) are not affected by the mixing, the latter process being expressed in α_{12} and g_{12} only, with no new γ value being needed.

The simplicity of Eq. (9) obviously arises from the simple model assumptions which need to be justified by the applicability of the procedure.

The pressure expression for a mixture reads:

$$-\frac{pv_o}{kT} = \ln\phi_o + (1 - \frac{1}{m_1})\phi_1 + (1 - \frac{1}{m_2})\phi_2 + (\alpha_1\phi_1 + \alpha_2\phi_2)(\phi_1 + \phi_2)$$
$$+ \left\{ g_{11}(1 - \gamma_1)\phi_1 + g_{22}(1 - \gamma_2)\phi_2 \right\} (q - \phi_o)q^{-2}$$
$$- \left\{ \alpha_{12} + g_{12}(1 - \gamma_2)q^{-2} \right\} \phi_1\phi_2 . \qquad (10)$$

Expressions for chemical potentials, spinodal and critical condition can be derived from Eq. (9) and are listed in Ref. 29. The volume fractions ϕ_o, ϕ_1 and ϕ_2 are convenient variables the introduction of which involves the simplicity of the final equations. In experimental practice, however, one has to do, e.g., with the two mole fractions in a binary system. They are related to the 'model' volume fractions by:

$$x_2 = 1 - x_1 = (1 + \phi_1 m_2/\phi_2 m_1)^{-1} \qquad (11)$$

This expression allows a return to physically relevant variables at any moment in the calculation.

APPLICATION OF THE MODEL TO CO_2/H_2O

In Fig. 1a, b it is shown that both pure CO_2 and H_2O can be described fairly well by the model over quite a temperature and pressure range. In the derivation of the parameters we used the experimental gas-liquid critical point and some gas-liquid equilibrium densities, at given pressures and temperatures, as reported in literature (34). Since we postulated that v_o should be the same for all sites in the mixtures, the derivation of the parameters of both H_2O and CO_2 was carried out for the same, arbitrarily chosen value of v_o = 25 cm^3/mole. The procedure for the calculation of the parameters is as follows. For an estimated value of m_1 the critical point is fitted with Eqs. (5), (6), and (7) leading to values for α_1, γ_1 and $g_{11_{crit}}$. The temperature dependence of g_{11} is obtained from some equilibrium densities using Eqs. (5) and (8) for both phases. Assuming g_{11} to have to show the usual linear dependence on T^{-1}, we repeat the calculation varying m_1 until the best achievable fulfillment of this condition is reached. The values of the parameters so obtained are given in Table 1.

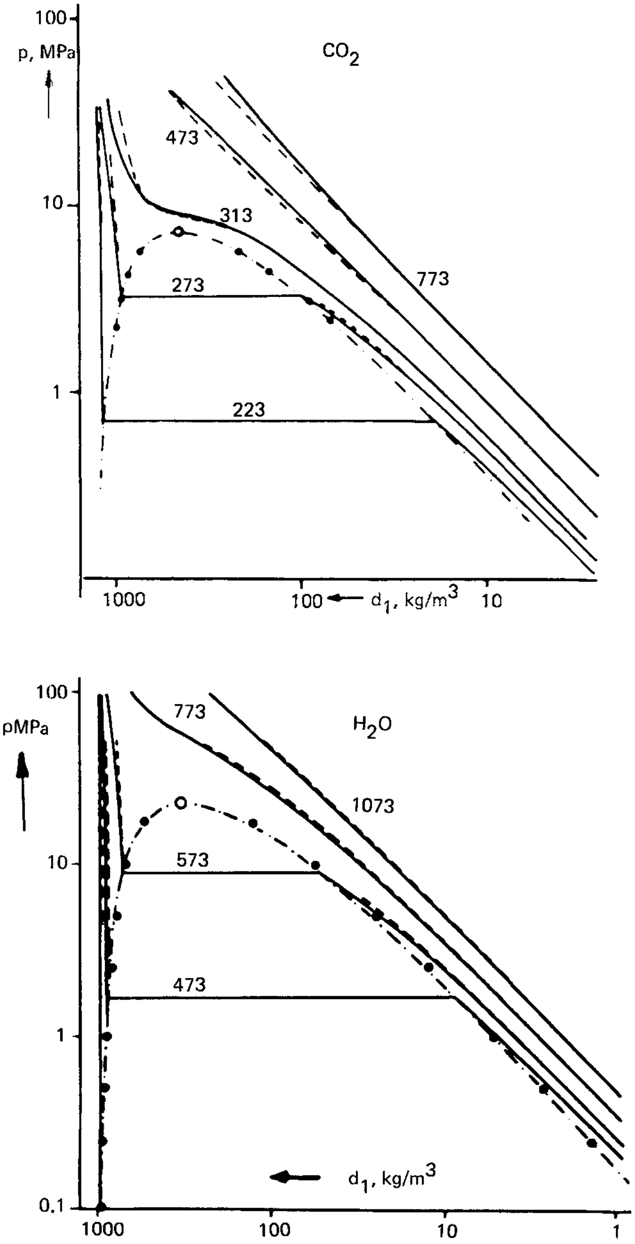
100
p, MPa
10
1
CO$_2$
473
313
273
223
773
1000
100
d$_1$, kg/m^3
10
100
pMPa
10
1
0.1
H$_2$O
773
1073
573
473
d$_1$, kg/m^3
1000
100
10
1

TABLE 1

Values of the Interaction Parameters

	CO_2	H_2O	Mixture
α	1.1401	1.5467	0.92
γ	-1.6368	-2.469	-
g	$-1.1199 + 468.25/T$	$-0.5473+297.1/T+3x10^5/T^2$	$-56.8626+56.8x10^3/T-$ $-129x10^5/T^2$
m	1.25	0.72	-
v_o	25	25	25

Better agreement between data and description than the present one can be achieved by a simultaneous fitting of all existing experimental PVT-data of a system. This involves a more sophisticated computer program which is now being developed. All calculations shown in this paper were carried out on a desk-computer (HP 9830).

Having determined the values of the parameters of the pure constituents of a mixture, we can now try to describe the PVT-behaviour of the mixture itself. As was shown for polyethylene/ethylene and CH_4/CO_2 such a description can be obtained with parameters derived from binary critical points (29). To this end the binary mixture expressions for spinodal and critical condition analogous to Eqs. (6) and (7) are used.

Experimental binary critical points and gas-liquid equilibrium densities at given temperature and pressure for the system CO_2/H_2O

FIGURE 1. PVT-diagrams for indicated temperatures (in K) for CO_2 (a) and H_2O (b).

Experimental data (34)
----- smoothed isotherms
● gas-liquid coexistence
o critical point

Calculated
——— isotherms
-·-·- gas-liquid coexistence

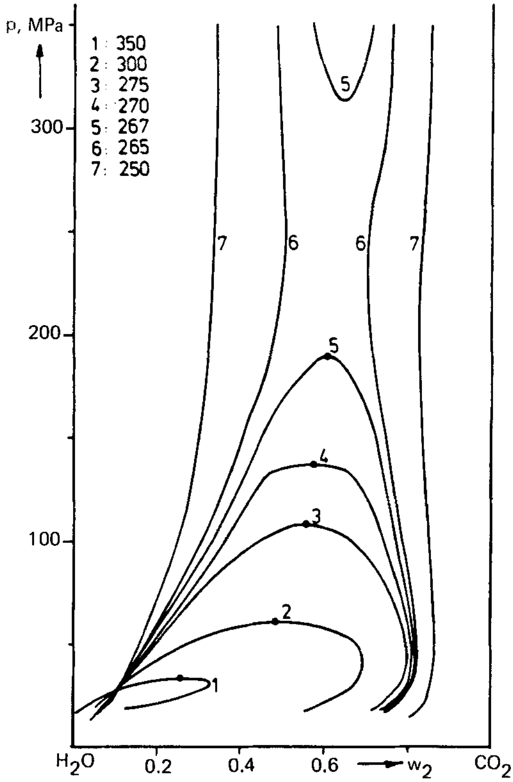

FIGURE 2. Curves of the experimental compositions of the gas-liquid equilibrium (at low pressure, curves 1-5) and the gas-gas equilibrium (at high pressure, curve 5) at the indicated temperatures (34) for the system CO_2/H_2O; ● critical points. At 266°C the critical points of the gas-liquid and the gas-gas equilibrium region coincide, to form at lower temperatures a continuous demixing region up to very high pressures (curves 6 and 7).

are reported in the literature (34). Fig. 2 shows some of the existing data. The system shows gas-liquid equilibria but also gas-gas equilibria of the second type (35) at high pressures and temperatures around the critical temperature of water. We use only some critical points of the gas-liquid equilibrium range of

CO_2/H_2O to derive the values of the two binary interaction parameters α_{12} and $g_{12}(T)$. From the critical pressure, temperature and composition is it quite straightforward to calculate the critical composition in lattice site volume fractions and the two binary parameters at that temperature using Eqs. (10) and (11) and the expressions for spinodal and critical conditions of a mixture. The values of α_{12} and g_{12} were determined at three different critical temperatures (and of course also different pressures and compositions). The value of g_{12} proved to be temperature dependent; α_{12} was hardly affected by temperature. The values of g_{12} and α_{12} are given in Table 1.

Having derived the values of the binary interaction parameters, we can calculate the complete ternary phase diagram with the derived

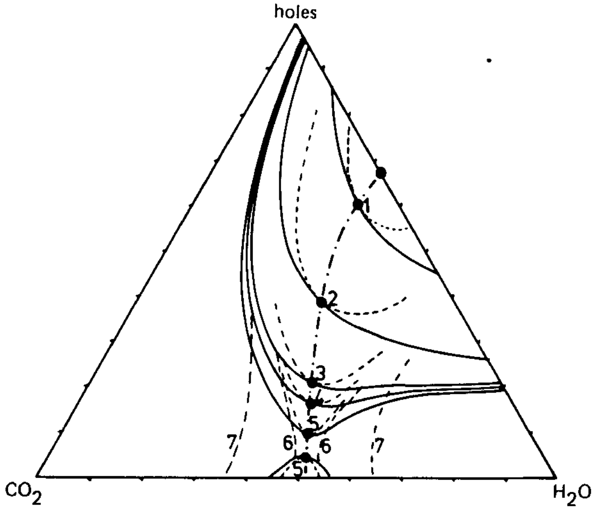

FIGURE 3. Calculated ternary lattice gas representation of gas-liquid and gas-gas equilibria for the system H_2O/CO_2. Temperatures are as indicated in Fig. 2.

----- spinodals
-·-·- critical line
——— gas-liquid and gas-gas coexistence

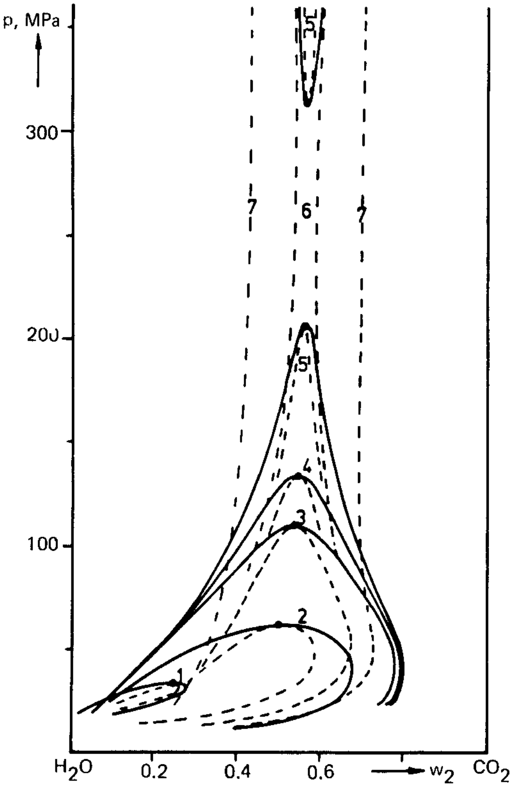

FIGURE 4. Phase diagram of the system CO_2/H_2O, derived from the calculated lattice-gas representation (Fig. 3). The calculated behaviour is in good agreement with the experimental findings (Fig. 2). The gas-gas demixing region is predicted within experimental error. For simplicity only spinodal curves are shown at temperatures 6 and 7. Temperatures are as indicated in Fig. 2.

——— gas-liquid and gas-gas equilibrium compositions
----- spinodals
● critical points

expressions for the critical line and the spinodal. The compositions of the coexisting phases are calculated with the expressions for the equality in chemical potentials in both phases for CO_2 and for H_2O together with the relation derived from p' = p" and with Eq. (10).

Figure 3 shows some 'ternary' lattice-gas representations of CO_2/H_2O mixtures in the pressure and temperature ranges of 0-4000 bar and 250-350°C. It is seen that the calculation based on critical liquid-gas data predicts gas-gas equilibrium of the second kind to occur. This prediction turns out to be in surprisingly good agreement with the experimental data. A quite similar situation was encountered with the system CH_4/H_2O (31).

The ternary lattice-gas representation of the phase behaviour can be converted into the usual binary P-x_2 or T-x_2 diagrams with Eq. (11). Fig. 4 shows the P-w_2 (mass fraction) plot for CO_2/H_2O obtained from Fig. 3. To be comparable with Fig. 2 we converted the mole fraction into the mass fraction w_2 in the usual way. Although the calculated phase-diagram does not completely fit the experimental findings, one may say that the agreement is quite satisfactory, especially because only three experimental points of the phase diagram were used as information. Better agreement can doubtless be achieved upon fitting all existing PVT-data of the mixture. For the moment the objective was to illustrate that even with a simple model, scarce information, and simple computer facilities an essentially correct description and prediction of PVT-behaviour of binary fluid systems is obtainable.

DISCUSSION

In the past, several variants of the lattice-gas model have been applied but complete quantitative agreement between description and experiment has rarely, if at all, been achieved--particularly in the gas-liquid critical region. We believe that there are two important reasons why we come closer to a quantitative treatment:

i) we use identical v_o-values for all sites in a mixture and thus avoid detailed mixing rules for v_o that may lead to greatly uncertain terms in higher derivatives of the free energy with respect to the composition of the mixture. Of course, our assumption can be viewed as a special form of a mixing rule.

ii) the introduction of characteristic interacting contact surface areas leads to a versatile expression for the internal energy of mixing.

In the present treatment the mathematical expressions are quite simple and also allow calculation of values for the adjustable parameters in cases where only scarce data are available. The most suitable data are critical data and, in addition, some liquid-gas equilibrium densities or compositions. Sometimes critical data are not available, e.g., because the system decomposes before reaching critical conditions. Then more non-critical data, like liquid density as a function of pressure and temperature, may serve to determine the parameters in Eq. (3). We have recently found this approach to work quite well with a substance like molten polyethylene, yielding parameter values that could be used successfully to predict lower critical phase behaviour of polyethylene in solvents like ethylene and n-paraffins (30,36).

One point of further research exists with an investigation of other thermodynamic data (specific heat, heat of vaporization, excess volume) as a basis to calculate adjustable parameters.

SYMBOLS

ΔE = Energy of mixing

ΔF = Helmholtz free energy of mixing

R = Gas constant

T = Temperature

V = Volume

g_{ij} = i - j interaction parameter

k = Boltzmann's constant

m_i = Number of lattice sites in molecule i

n_i = Number of moles i

p = Pressure

x_i = Mole fraction of i

w_{ij} = i - j molar interaction energy per unit contact surface area

v_o = Volume per lattice site

α = Empirical entropy correction

γ_i = $(1 - \sigma_i/\sigma_o)$, parameter

σ_i = Characteristic interaction surface area of sites i

ϕ_i = Volume fraction of sites i

REFERENCES

1. J.D. van der Waals and Ph. Kohnstamm, Lehrbuch der Thermodynamik, Vol. II, Leipzig, 1912.
2. H.W. Bakhuis Roozeboom, Die heterogene Gleichgewichte vom Standpunkte der Phasenlehre, Vol. III, Braunschweig, 1913.
3. J. Timmermans, J. Chim. Phys. Phys. Chim. Biol., 20, 491 (1923).
4. J.D. van der Waals, Kontinuität, I and II, Barth, Leipzig, 1899.
5. J.D. van der Waals, Zittingsverslag Kon. Acad. v. Wetensch., Amsterdam, 1894. (see J. de Boer, Physica, 73, 1 (1974))
6. I.R. Krichevskii, Acta Physicochim. URSS, 12, 480 (1940).
7. J.A. Schouten, Ph.D. Thesis, Amsterdam (1969).
8. G. Schneider, Ber. Bunsenges. Phys. Chem., 70, 497 (1966).
9. G. Schneider, Adv. Chem. Phys. XVII (1970).
10. G. Schneider, Chem. Thermodyn., 2, 105 (1978).
11. I. Prigogine, Molecular Theory of Solutions, North Holland Press, Amsterdam, 1957.
12. P.J. Flory, J. Am. Chem. Soc., 86, 3507; 3515 (1964).
13. D. Patterson, J. Polym. Sci., C16, 3379 (1968).

14. V.S. Nada and R. Simha, J. Chem. Phys., 41, 3870 (1964) and J. Phys. Chem., 68, 3158 (1964).

15. E.A. Guggenheim, Mixtures, Clarendon Press, Oxford, 1952.

16. N.J. Trappeniers, J.A. Schouten, and C.A. Ten Seldam, Chem. Phys. Lett., 5, 541 (1970).

17. J.A. Schouten, C.A. Ten Seldam, and N.J. Trappeniers, Physica (Amsterdam), 73, 556 (1974).

18. J. Altar, J. Chem. Phys., 5, 577 (1937).

19. F. Cernushi and H. Eyring, J. Chem. Phys., 7, 547 (1939).

20. J. Frenkel, Kinetic Theory of Liquids, Dover Publ., New York, 1947.

21. N.D. Mermin, Phys. Rev. Lett., 26, 957 (1971).

22. G.W. Mulholland and J.J. Rehr, J. Chem. Phys., 60, 1297 (1974).

23. G. Kanig, Kolloid Z.Z. Polym., 190, 1 (1963); 233, 829 (1969).

24. J.T. Bartis and C.K. Hall, Physica (Amsterdam), 78, 1 (1974).

25. I.C. Sanchez and R.H. Lacombe, J. Phys. Chem., 80, 2352; 2568 (1976).

26. O. Redlich and J.N.S. Kwong, Chem. Rev., 44, 233 (1949).

27. D.Y. Peng and D.B. Robinson, Ind. Eng. Chem. Fundam., 15, 59 (1976).

28. T.F. Anderson and J.M. Prausnitz, Ind. Eng. Chem. Process Des. Dev., 19, 1 (1980).

29. L.A. Kleintjens, Ph.D. Thesis, Essex UK (1979).

30. L.A. Kleintjens and R. Koningsveld, Colloid Polym. Sci., 258, 711 (1980).

31. L.A. Kleintjens and R. Koningsveld, J. Electrochem. Soc., 127, 2352 (1980).

32. A.J. Staverman, Recl. Trav. Chim. Pays Bas, 56, 885 (1937).

33. G. Rehage, D. Möller, and O. Ernst, Makromol. Chem., 88, 232 (1965).

34. e.g. collected in: Landolt-Börnstein, 'Zahlenwerte und Funktionen'.

35. G.M. Schneider, Extraction with Supercritical Gases, Verlag Chemie, Weinheim, 1980.

36. L.A. Kleintjens and R. Koningsveld, to be published.

Received by editor October, 1980