Influence of Guest Vapor-Liquid Critical Point on Hydrate Formation Conditions

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Hydrates are crystalline compounds consisting of water in a cagelike structure around smaller guest molecules, such as methane, ethane, nitrogen, and carbon dioxide. Many phase equilibria data are available for three natural gas hydrate crystal structures: structure I, structure II, and a recently discovered structure H (Lederhos et al., 1992). This note presents an interpretation of slope changes in pressure-temperature phase diagrams, with respect to hydrate crystal structure transitions.

Over small ranges of temperature, the univariant three-phase (water-hydrate-vapor) equilibrium conditions for single hydrate formers yield almost straight lines when plotted on ln P vs. $1/T$ coordinates, in accordance with the Clausius-Clapeyron equation (van der Waals and Platteeuw, 1959; Barrer, 1959; Glew, 1959). However, over wide temperature ranges, phase equilibrium data of some molecules, such as methane (Snell et al., 1961; Marshall et al., 1964), ethylene (Snell et al., 1961; Van Cleeff and Diepen, 1962), argon (Marshall et al., 1964) and xenon (Aaldjik, 1971), show substantial curvature in such plots, as shown in Figure 1.

In the case of hydrate formation, the three-phase equilibria may be written as a reaction:

$$V + L_W \rightleftharpoons H \tag{1}$$

where V, L_w, and H represent vapor, liquid water, and hydrate, respectively. For univariant equilibria the slope of a plot of ln P against $1/T$ should indicate the heat of dissociation ΔH (van der Waals and Platteeuw, 1959):

$$d \ln P/d\,(1/T) = -\Delta H/zR \tag{2}$$

where z is the gas-phase compressibility and v^g is assumed equal to $v^g + v^l - v^h$.

A complete derivation of Eq. 2 with the appropriate assumptions is given by Yamanlar et al. (1991). Equation 2 can be modified in terms of a pure-component fugacity as follows:

$$d \ln f/d\ (1/T) = -\Delta H/R \tag{3}$$

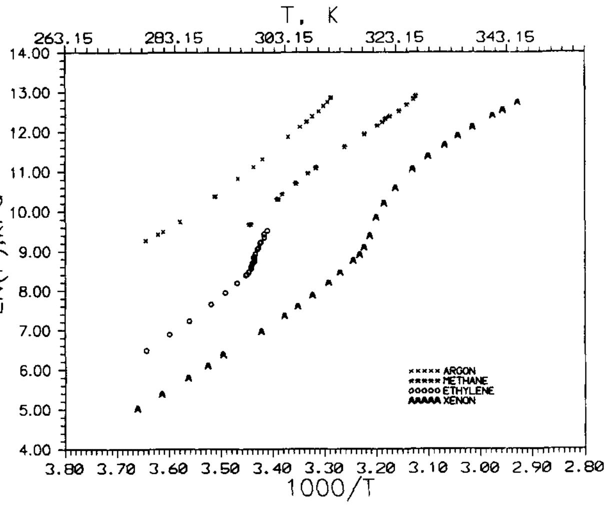

Figure 1. Three-phase (L_w-H-V) equilibrium data for pure hydrate guest gases.

The above equation suggests that a plot of ln f vs. $1/T$ would be linear, provided that the enthalpy of dissociation ($H \rightarrow L_w + V$) is constant over the region under investigation. This has been successfully done for the low-pressure xenon data of Figure 1, by Aaldjik (p. 53, 1971) whose thesis in the Dutch language is accessible to polyglots.

Five reasons commonly advanced for change in the P-T slope find their bases in Eq. 2 in the derivation of:

(1) $v^g + v^l - v^h$ is not equal to v^g as shown by Aaldjik at high pressures.

(2) Changes in gas compressibility, z

(3) Changes in heat of dissociation caused by degree of guest occupancy of hydrate cavities, indicated by Barrer (1959)

(4) Changes in heat of dissociation, as caused by heat capacity changes with temperature as suggested by Yamamuro and Suga (1989)

(5) Changes in heat of dissociation caused by a hydrate crystal structure change.

According to Snell et al. (1961), marked curvature of the ln P vs. $1/T$ curve indicates a change in hydrate structure,

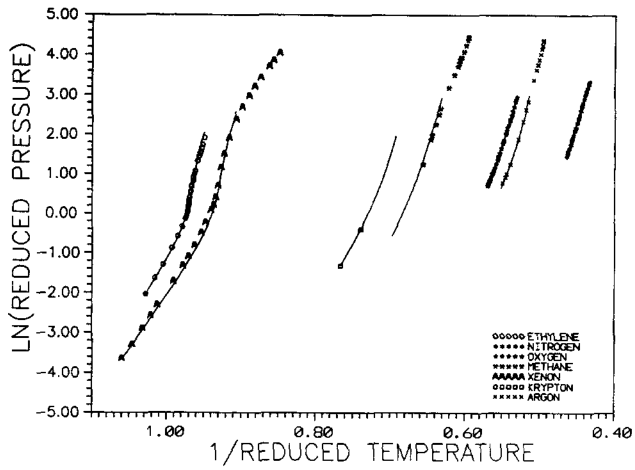

Figure 2. Three-phase (L_w-H-V) equilibrium data and predictions for pure hydrate guest gases on reduced coordinates.

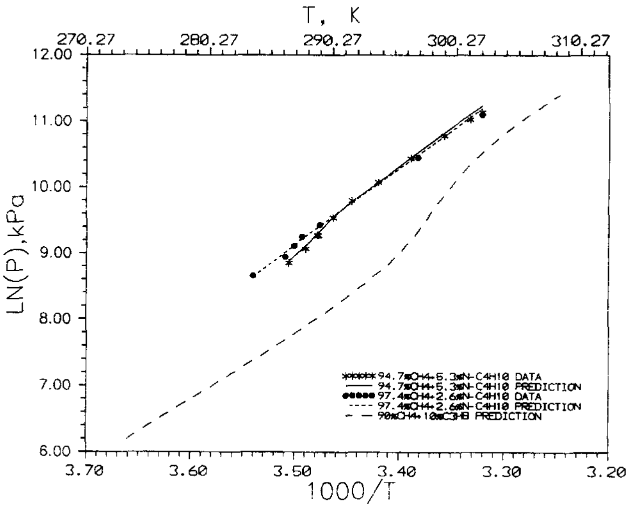

Figure 3. Three-phase (L_w-H-V) equilibrium data and predictions for mixtures.

caused by a change in the number of water molecules associated with the guest molecule in the solid. Marshall et al. (1964) proposed that the change in slope was caused by hydrate structural changes analogous to those in ice at high pressures. According to Marshall et al., these slope changes are not abrupt in the case of hydrates, because the compressibility of the gas has a masking effect on the pressure-temperature curve.

Hafemann and Miller (1969) and Majid et al. (1969) show that the slope of the three-phase line for cyclopropane changes abruptly at points of structural transition [structure I(*s*I) → structure II(*s*II)]. Holder and Hand (1982) show that abrupt changes in slope occur for ethane-propane mixtures, when *s*I changes to *s*II.

The Gibbs phase rule provides a check to the curvature hypotheses by Snell et al. and Marshall et al. The phase rule indicates that the transition between two hydrate phases (say *s*I and *s*II, coexisting with both a vapor phase and an aqueous phase) is invariant [$F = C - \Phi + 2 = 0$] for either a single hydrate former or a hydrate of a fixed gas composition. The transition must exist at a single temperature, not over a range of temperatures.

Critical Point Proximity

We suggest that the reasons for the above slope changes may be due to changes around the critical point, both for pure components as indicated in somewhat obscure Dutch references (van Cleeff and Diepen, 1962; Aaldijk, 1971) and for mixtures of gases shown for the first time here.

Further insight into the gradual slope changes is obtained via a plot showing proximity of hydrate equilibrium data to the vapor-liquid critical points of the hydrate formers. A semilogarithmic plot of reduced pressure vs. reciprocal reduced temperature is shown in Figure 2 for several gases which are hydrate guest molecules. The solid lines are predictions by the modified statistical thermodynamics model of van der Waals and Platteeuw (1959), and the symbols represent data. From the figure, it is clear that as the critical point ($T_r = P_r = 1.0$) is approached (such as for C_2H_4 and Xe), the hydrate formation curves exhibit a gradual change in slope. On the other hand, nitrogen L_w-H-V data, which are far from the N_2 critical temperature, do not show any apparent change in slope in Figure 2.

Extension to Mixtures

The above analysis can be extended to three-phase hydrate formation data for gas mixtures. The data by McLeod and Campbell (1961) for methane + *n*-butane mixtures (Figure 3) exhibit a change in slope, which leads to a crossover of two constant composition three-phase curves. This phenomenon is very unusual when the hydrate structure is constant and has caused some mistaken discount of the data. Prediction with the van der Waals and Platteeuw model (1959) indicates no structural change from *s*II over this region. Additionally, in contrast to observations at the higher temperatures of the plot, intuition suggests that mixtures of a higher *n*-butane composition should form at lower pressures for a given temperature.

When the $CH_4 + n\text{-}C_4H_{10}$ data are plotted with reduced coordinates in Figure 4, however, the two lines of Figure 3 separate and the crossover is not observed. For such calculations,

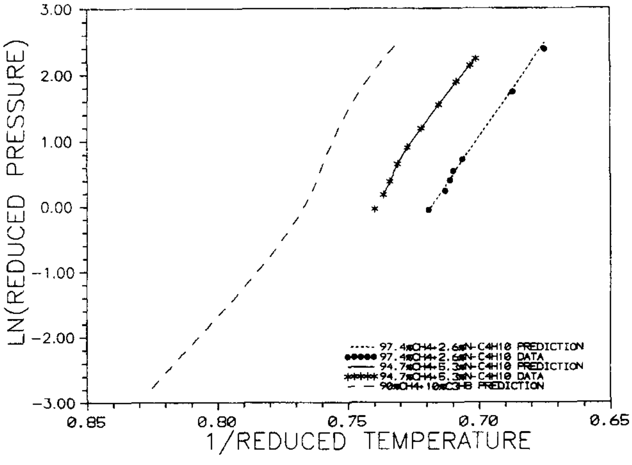

Figure 4. Three-phase (L_w-H-V) equilibrium data and predictions for mixtures on reduced coordinates.

the mixture critical temperature and pressure may be determined using the Li method (1971). The mixture containing 97.4% CH_4 is far removed from its critical point and exhibits linear behavior, while the mixture containing 94.7% CH_4 is somewhat closer to the critical and therefore curved. In addition to the behavior of the $CH_4 + n\text{-}C_4H_{10}$ data, it is interesting to note that the three-phase predictions for other common mixtures, like 90% CH_4 + 10% C_3H_8 (shown in Figure 4), demonstrate curvature close to the mixture critical point. If the curvature is observed in hydrate-phase equilibria data, plotting the data on reduced coordinates might be considered as an evaluation tool.

Conclusions

1) The proximity of the three-phase equilibrium to the guest critical point can cause substantial and continuous changes in the slope of the univariant, three-phase (L_w-H-V) ln P vs. $1/T$ hydrate formation line.

2) This continuous change in slope observed both for pure components and mixtures is not due to structural change.

3) Such a change in slope can lead to crossover for lines of constant composition, three-phase ln P vs. $1/T$ data.

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Notation

C = number of independent components
f = fugacity
F = number of intrinsic degrees of freedom
H = hydrate phase
ΔH = heat of dissociation
Lw = liquid water
P = pressure
Pr = reduced pressure
R = universal gas constant
T = temperature
Tr = reduced temperature
v^g = molar volume of vapor
v^h = molar volume of hydrate
v^l = molar volume of water
V = vapor phase
z = compressibility factor

Greek letter

Φ = number of Phases

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