Thermodynamic Behavior of Hydrogen Binary Systems with Critical Curve Divergence and Retrograde Condensation*

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Abstract
In binary systems of hydrogen and hydrocarbons, the fluid-phase thermodynamic behavior is unique in having the divergence of the critical curves to a high pressure region. The thermodynamic properties of the binary systems including hydrogen with methane, ethane, propane, and carbon dioxide were calculated from a Peng-Robinson equation of state (PR EOS). The mixing parameter of the present EOS has a functional form of temperature generalized by the critical temperatures of the hydrocarbons and carbon dioxide. Based on the corresponding states principle, the coefficients of the parameter were determined with a non-linear least squares fitting to the experimental critical points of the mixtures. The developed PR EOS shows good agreement with the experimental data of not only the critical points but also the phase equilibria. In the hydrogen binary systems, retrograde condensation is expected. The volumetric and enthalpy changes in this process were simulated for a hydrogen + carbon dioxide mixture of 0.55 mole fraction using the PR EOS at 270 K.

Key words: Hydrogen, Binary System, Phase Equilibrium, Critical Curve, Retrograde Condensation

1. Introduction
Hydrogen is expected to be a next-generation clean energy carrier. However, thermodynamic properties of hydrogen are not sufficient at high temperatures and high pressures\(^1\), and they have been measured recently\(^2\). In the coming hydrogen society, accurate thermodynamic properties of not only pure hydrogen but also hydrogen mixtures are greatly important in hydrogen production, transportation, and storage processes. For instance, the rapid filling of high-pressure hydrogen into fuel cell vehicles requires precooling at 233 K in order to avoid the temperature rise of the vessels more than 358 K due to the adiabatic compression, and the management of the dew points of impurity components is essential in the precooling process. As one of the hydrogen transportsations, it is considered to utilize existing natural gas pipelines, where hydrogen is mixed with natural gas\(^3\). Moreover, hydrogen is often used as a reducing agent for chemical reactions. Jessop et al.\(^4\) successfully enhanced the synthesis of formic acid in the reaction field where hydrogen is dissolved by supercritical carbon dioxide, and in a series of this study, the pressure was increased up to 20 MPa. Therefore, the thermodynamic properties of the...
hydrogen mixtures over a wide pressure range including the supercritical region are necessary. However, due to the inclusion of hydrogen, the thermodynamic behavior is unlike simple mixtures such as methane + ethane and methane + propane, and it is hard to be estimated. For some binary systems of hydrogen and hydrocarbons, phase equilibria and critical curves were measured, and the divergence of the critical curves to a high pressure region was observed. Generally, binary systems in the fluid phase can be classified into six types from the behavior of the critical curves according to the classification of Scott and van Konynenburg\(^{(5)}\). According to the classification, simple binary systems such as methane + ethane and methane + propane systems having a continuous critical curve are classified into Type I, and the binary systems in which the critical curve diverges to a high pressure region are classified into type III. Rowlinson and Swinton\(^{(6)}\) comprehensively explain the critical curve and phase equilibrium behavior not only for Type I and III but also the other types. Water + carbon dioxide system has been taken attention these days for carbon capture and storage, and this system is also classified into Type III\(^{(7)}\). Therefore, the critical curve behavior is of great importance to characterize the thermodynamic properties qualitatively.

In addition, supercritical fluids have been attracted for chemical engineering processes as solvents, and the critical curves should be clearly specified. Nevertheless, the critical curves of mixtures are seldom calculated from equations of state (EOS) due to complexities accompanying with the thermodynamic stability calculation. Heidemann and Khalil\(^{(8)}\) and Michelsen and Heidemann\(^{(9)}\) found a useful calculation method of the critical curves of fluid mixtures from EOSs. Endo et al.\(^{(10)}\) and Sakoda and Uematsu\(^{(11)}\) developed EOSs for a Type III system of methane + hydrogen sulfide, and calculated the critical curve with this method. In the present work, for the hydrogen binary systems of methane, ethane, propane, and carbon dioxide, the thermodynamic properties were calculated by a PR EOS\(^{(12)}\). Cubic EOSs are more useful than multiparameter EOSs for the systems whose experimental data are limited. The multiparameter EOSs sometimes cause an over-fitting in the process to determine the coefficients and show physically unreasonable behavior. The mixing parameters of PR EOSs are often determined by fitting experimental phase equilibrium data, but the calculated critical curves do not ensure to represent the mixture types correctly. Quite recently, Qian et al.\(^{(13)}\) developed a PR EOS for many hydrogen binary systems, and the mixing parameter is a temperature function based on a group-contribution method. The coefficients in the parameter depending on the groups were determined using the phase equilibrium and critical point data. In the present work, the mixing parameter is formulated by a simple quadratic equation of temperature. In addition, the parameter is generalized by the critical temperatures of the hydrocarbons and carbon dioxide. The corresponding states principle was applied to the development of the mixing parameter, and the coefficients of the parameter were determined by fitting the experimental critical point data of all of the mixtures simultaneously with a non-linear least squares fitting technique. The generalization of the parameter by the critical temperatures of the pure components makes up for the lack of experimental data, and the determined parameter can be commonly used. In many phase equilibrium studies of mixtures, thermodynamic relations of temperature, pressure, and compositions are often discussed. However, density and the other derived properties such as heat capacity and enthalpy are rarely discussed. In the calculations of the derived properties from the EOS, complicated differential and integral calculations are required and the simple functional form of the mixing parameter is desirable. In the hydrogen binary systems, retrograde condensation is expected and the thermodynamic property changes in this process have not been well studied. In the retrograde condensation process, when a single-phase supercritical fluid is isothermally decompressed, a liquid phase first appears in the two phase region, and the ratio of the liquid phase increases. As the fluid is decompressed further, the ratio of the liquid phase has a maximum and then starts to decrease. Finally, the fluid becomes a single vapor phase. Using the present EOS,
the retrograde condensation was simulated for a hydrogen + carbon dioxide mixture at 270 K, and volumetric and enthalpy changes were discussed.

2. Behavior of the Hydrogen Binary Systems and Determination of the Mixing Parameter of the PR EOS

2.1 Critical Points and Phase Equilibria of the Hydrogen Binary Systems

The experimental critical point data for the hydrogen binary systems with methane, ethane, propane and carbon dioxide are shown in Fig. 1 on the pressure-temperature (P-T) diagram, and some of the experimental phase equilibrium data\(^{(14)-(17)}\) are plotted on the pressure-composition (P-x) diagram in Fig. 2. The critical curves and phase equilibria calculated from the present EOS for the hydrogen binary systems are also shown in Figs. 1 and 2. The critical curves of methane + ethane and methane + propane in Fig. 1 were calculated from the PR EOS by Endo et al.\(^{(10)}\). The critical parameters of the pure components are summarized in Table 1. For methane + ethane and methane + propane, the critical curves are described as a continuous line connecting the critical points of the two pure components, and this critical curve behavior is classified into Type I. However, for the hydrogen binary systems, the critical curves are discontinuous line. They start from the critical point of methane, ethane, propane, or carbon dioxide do not converge to that of hydrogen but diverge to the high pressure region. For hydrogen + methane, the critical curve is steeply diverges to the high pressure region at 0.65 mole fraction of hydrogen in Fig. 2. Therefore, the critical points are not unlikely to exist at mole fractions more than 0.7, which is one of the different features from Type I.

![Critical curves of the hydrogen and hydrocarbon binary systems calculated from the PR EOSs.](image-url)

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*Fig. 1* Critical curves of the hydrogen and hydrocarbon binary systems calculated from the PR EOSs.
Table 1  Critical parameters,acentric factors, and molar masses

<table>
<thead>
<tr>
<th></th>
<th>Tc / K</th>
<th>Pc / MPa</th>
<th>ρc / kg m⁻³</th>
<th>Mc / g mol⁻¹</th>
<th>ω²(24)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>33.145</td>
<td>1.2964</td>
<td>31.263a</td>
<td>2.01594</td>
<td>-0.216</td>
</tr>
<tr>
<td>Methane</td>
<td>190.564</td>
<td>4.5992</td>
<td>162.66</td>
<td>16.0428</td>
<td>0.011</td>
</tr>
<tr>
<td>Ethane</td>
<td>305.322</td>
<td>4.8722</td>
<td>206.18</td>
<td>30.06904</td>
<td>0.099</td>
</tr>
<tr>
<td>Propane</td>
<td>369.89</td>
<td>4.2512</td>
<td>44.09562</td>
<td>0.152</td>
<td></td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>304.1282</td>
<td>7.3773</td>
<td>467.6</td>
<td>44.0098</td>
<td>0.225</td>
</tr>
</tbody>
</table>

a The original value is given by mol dm⁻³, and converted to kg m⁻³ by using the molar mass.

Fig. 2  Phase equilibria and critical curves of the hydrogen binary systems. (A) Hydrogen + methane, (B) Hydrogen + ethane, (C) Hydrogen + propane, (D) Hydrogen + carbon dioxide.

2.2 Determination of the Mixing Parameter of the PR EOS

The PR EOS (12) is expressed by Eq. 1 and the mixing rules from Eq. 2 to 4 were adopted in the present work.

\[
P = \frac{RT}{v - b} - \frac{a \alpha}{v^2 + 2bv - b^2}
\]

\[
a \alpha = \sum x_i x_j (a \alpha)_{ij}
\]

\[
b = \sum x_i b_i
\]

\[
(a \alpha)_{ij} = (1 - k_i) [(a \alpha)_j (a \alpha)]^{1/2}
\]

where, \(P\) is the pressure, \(T\) is the temperature, \(v\) is the molar volume, \(R\) is the universal gas...
constant \((8.314472 \text{ J mol}^{-1} \text{ K}^{-1})(25)\), and \(x\) is the mole fraction. \(a\) and \(b\) denote the constants and \(k_{ij}\) is the mixing parameter between the two components. The subscript, \(i\), denotes a component. The critical parameters and acentric factors of the pure components required in the PR EOS are summarized in Table 1 with their molar masses. The mixing parameter, \(k_{ij}\), is formulated as a temperature function expressed by Eq. 5.

\[
k_{ij} = n_0 + n_1 T_r + n_2 T_r^2
\]  

(5)

where \(n_0, n_1, \text{ and } n_2\) are the coefficients. \(T_r = T / T_{C,i}\) and \(T_{C,i}\) is the critical temperature of the less volatile components (methane, ethane, propane, and carbon dioxide). \(k_{ij}\) is generalized by the critical temperatures, and Eq. 5 is commonly used for the hydrogen binary systems with methane, ethane, propane, and carbon dioxide. \(k_{ij}\) is of great importance to characterize the mixture type, and the critical curve behavior changes depending on \(k_{ij}\).

The mixing parameter is often determined from comparisons with phase equilibrium data. In the present work, from the point of view of the corresponding states principle, the coefficients of \(n_0, n_1, \text{ and } n_2\) were fitted to the experimental critical point data. Generally, the corresponding states principle based on the critical points for mixtures to cubic type EOSs such as PR EOS is hardly applied because the determination of the critical points for mixtures from the gibbs free energy(26) are very complicated, and the parameters in the EOSs are not analytically derived from the critical points unlike pure fluids. Therefore, the applicability of the corresponding states principle to the PR EOS for the Type III mixtures has not been well studied, but this attempt is of very importance for the development of EOSs for multicomponent systems, which have usually few reliable experimental data sets, in the future. The coefficients in Eq. 5 were determined by a non-linear least squares fitting technique to minimize the \(SS\) expressed by Eq. 6.

\[
SS = \sum_{k=1}^{K} w_k^2 (T_{r,\text{EXP},k} - T_{r,\text{CAL},k})^2 + \sum_{l=1}^{L} w_l^2 (P_{r,\text{EXP},l} - P_{r,\text{CAL},l})^2
\]  

(6)

\[
w_k = \frac{1}{\left| \frac{\partial (T_{r,\text{EXP},k})}{\partial x_{f}} \right|}
\]  

(7)

\[
w_l = \frac{1}{\left| \frac{\partial (P_{r,\text{EXP},l})}{\partial x_{f}} \right|}
\]  

(8)

where, \(P_r = P / P_{C,i}\) and \(P_{C,i}\) is the critical pressure of the less volatile components. The subscript EXP and CAL are the experimental data and calculated value from the EOS, respectively. By using the reduced temperature, \(T_r\), and pressure, \(P_r\), all of the experimental critical points, which are summarized in Table 2, were simultaneously used in the fitting procedure. \(w\) denotes the weight and calculated by Eqs. 7 and 8 using the derivatives with respect to the mole fraction, \(x\). This novel parameter fitting was developed based on the critical point and phase equilibrium calculation program by Endo et al.(10), where the calculations are executed according to the method by Heidemann and Khalil(8) for the critical points and Michelsen(27) for the phase equilibria. Figure 3 shows the experimental critical temperatures and pressures reduced by the critical parameters of the less volatile components. As mentioned above, the Type III critical curve is a discontinuous line due to the critical divergence and the Type III mixtures have no critical points at certain mole fractions. In a preliminary fitting, the EOS has no critical points at 0.680 and 0.675 mole fractions of hydrogen + methane and the data were omitted from the fitting process. The critical points at extremely high pressures above 200 MPa were also not used for the fitting.
Table 2 Experimental critical points of the hydrogen binary systems

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Composition range</th>
<th>Temperature range / K</th>
<th>Pressure range / MPa</th>
<th>Number of points</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen + methane</td>
<td>0.22 – 0.68</td>
<td>92 – 180</td>
<td>9 – 141</td>
<td>10</td>
<td>Tsang et al. (14)</td>
</tr>
<tr>
<td>Hydrogen + ethane</td>
<td>0.42 – 0.80</td>
<td>145 – 280</td>
<td>22 – 563</td>
<td>11</td>
<td>Heintz and Streett (15)</td>
</tr>
<tr>
<td>Hydrogen + propane</td>
<td>0.11 – 0.67</td>
<td>310 – 566</td>
<td>7 – 55</td>
<td>14</td>
<td>Burriss et al. (16)</td>
</tr>
<tr>
<td>Hydrogen + carbon dioxide</td>
<td>0.27 – 0.64</td>
<td>235 – 290</td>
<td>21 – 192</td>
<td>8</td>
<td>Tsang and Streett (17)</td>
</tr>
</tbody>
</table>

Finally, the coefficients, \( n_0, n_1, \) and \( n_2 \), in Eq. 5 were determined as \(-0.138790, 0.0457219, \) and \(0.218793\), respectively. In Fig. 3, the calculated critical temperatures and pressures are in good agreement with the experimental data. The calculated phase equilibria are shown in Fig. 2. The phase equilibrium data were not used for the fitting. Nevertheless, the calculated phase equilibria show good agreement with the experimental data except for high pressures.

Fig. 3 Reduced critical temperatures and pressures of the hydrogen binary systems calculated from the present EOS with the experimental data. (A) Reduced critical temperature, (B) Reduced critical pressure.

3. Simulation of a Retrograde Condensation Process in the Hydrogen and Carbon Dioxide System

In the hydrogen binary systems, retrograde condensation is expected. In the present work, volumetric and enthalpy changes in the retrograde condensation process were simulated by using the developed EOS. Figure 4(A) shows the phase equilibrium diagram at 270 K for the hydrogen and carbon dioxide system. The composition of the critical point at 270 K is 0.49 mole fraction of hydrogen, and in this simulation, two mixtures of 0.3 and 0.55 mole fraction are isothermally decompressed from 50 MPa. Assuming that each mixture is filled in a vessel whose volume is \( V_{vsl} \) at 270 K and 50 MPa as an initial condition, the pressure is decreased by continuously removing the mass in the vessel with a rate of \( M_{rv} = 0.01 \times V_{vsl} \times (T = 270 K, P = 50 MPa) \) mol s\(^{-1}\), which is 1 % of the initial mass per second. In the vapor-liquid equilibrium, the compositions in the vapor phase and liquid phase are different as shown in Fig. 4, and then, the composition of the removed mass was ideally regarded to be the same as the initial composition. The simulation procedure is summarized below.

1. Calculate the initial mass in the vessel at 270 K and 50 MPa from the density by the
2. Remove the mass, $M_{\text{rmv}}$, from the vessel, and calculate the density and pressure in the vessel.

3. If the pressure is larger than the phase boundary at the higher pressure side, which is corresponding to A for 0.3 mole fraction and E for 0.55 mole fraction in Fig. 4(A), repeat the procedure 2.

4. If the pressure is lower than the phase boundary at the higher pressure side, calculate the phase equilibrium, and determine the pressure and volumes of the vapor and liquid phases.

5. Remove the mass, $M_{\text{rmv}}$, from the vessel, and repeat the procedure 4 until the pressure reaches the phase boundary at the lower pressure side, which is corresponding to C for 0.3 mole fraction and G for 0.55 mole fraction in Fig. 4(A).

6. If the pressure is lower than the phase boundary at lower pressure side, the mixture is the vapor phase, and execute the procedure 2 until the pressure becomes 0.1 MPa.

Fig. 4 Phase equilibrium and volumetric changes at a retrograde condensation in the hydrogen + carbon dioxide system at 270 K. (A) Equilibrium pressure, (B) Equilibrium density, (C) Equilibrium enthalpy, (D) Volume ratio of the liquid phase in the vessel.

The phase equilibrium behaviors of the density and enthalpy depending on the composition are shown in Figs. 4(B) and (C), and the volumetric change in the vessel is shown in Fig. 4(D). The ideal-gas isobaric heat capacities of hydrogen and carbon dioxide required for the enthalpy calculation were referred from the EOSs by Leachman et al.\cite{18} and Span et al.\cite{22}, respectively. The mixture of 0.3 mole fraction is decompressed, and the mixture crosses the phase boundary at 38 MPa, which is A in Fig. 4(A). The vapor phase indicated by B appears, and below this pressure the mixture exists in the vapor-liquid equilibrium. When the pressure is further decreased, the liquid phase changes along the bubble-point curve and the vapor phase changes along the dew-point curve. After the pressure reaches 5.5 MPa, the mixture becomes the vapor phase. In Fig. 4(B), the density in the vapor-liquid equilibrium is shown. As the pressure is decreased, the density in the liquid phase increases and that in
the vapor phase decreases. In this case, the volume ratio of the liquid phase in the vessel is monotonically decreased as shown in Fig. 4(D). This behavior in the vessel is similar to that of pure component fluids.

On the other hand, in the same decompression process for the 0.55 mole fraction, on the phase boundary at 48 MPa, the appearing phase has larger density (F in Fig. 4(B)) than the initial phase (E). Therefore, the initial density behaves like the vapor phase rather than the liquid phase. In addition, the volume ratio of the liquid phase in the vessel increases as shown in Fig. 4(D), nevertheless the pressure decreases, and at 38 MPa, the volume ratio has a maximum up to 16 %. As the pressure is decreased further, the volume of the liquid phase starts to decrease. Finally, the liquid phase disappears and only vapor phase exists.

Figure 4(C) shows the enthalpy behavior along the phase equilibrium at 270 K in the $h$-$x$ diagram, which has been seldom described. When a mixture of 0.3 mole fraction becomes in the two phase region at A in Fig. 4(C), the appearing vapor phase has larger enthalpy than the liquid phase, which is indicated by B. As the mixture is decompressed, the enthalpies of the liquid phase and the vapor phase change along the bubble-point curve and dew-point curve, respectively, as the same as the phase equilibrium behavior in Fig. 4(A). However, for a mixture of 0.55 mole fraction, in the retrograde condensation process, the appearing liquid phase accompanying with the decompression has smaller enthalpy than the vapor phase, which is indicated by F in Fig. 4(C). That is different behavior from pure fluids and simple mixtures. In hydrogen industries, safety control of hydrogen is of great importance. On the assumption that vessels containing hydrogen mixtures have cracks and they leaks from the vessels, change in the thermodynamic behavior of the mixtures should be understood in advance. The enthalpy is essential for the estimation of the change in temperature of the mixtures. In the retrograde condensation process, it should be taken in consideration that the liquid phase having smaller enthalpy appears for the estimation of temperature.

4. Conclusions

The generalized mixing parameters of the PR EOS for the hydrogen binary systems with methane, ethane, propane, and carbon dioxide were developed by fitting the experimental critical point data based on the corresponding states principle. The EOS represents the critical curve divergence and show good agreement with the phase equilibrium data. By using the EOS, the retrograde condensation process was simulated for a hydrogen + carbon dioxide mixture of 0.55 mole fraction at 270 K. The volume ratio of the liquid phase in the vessel increases although the pressure decreases, and at 38 MPa, the ratio has a maximum up to 16 %.

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