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RESEARCH ARTICLE

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Calculation of partial molar volume of components in supercritical ammonia synthesis system

Abstract The partial molar volumes of components in supercritical ammonia synthesis system are calculated in detail by the calculation formula of partial molar volume derived from the R-K equation of state under different conditions. The objectives are to comprehend phase behavior of components and to provide the theoretic explanation and guidance for probing novel processes of ammonia synthesis under supercritical conditions. The conditions of calculation are $H_2/N_2 = 3$, at a concentration of NH_3 in synthesis gas ranging from 2% to 15%, concentration of medium in supercritical ammonia synthesis system ranging from 20% to 50%, temperature ranging from 243 K to 699 K and pressure ranging from 0.1 MPa to 187 MPa. The results show that the ammonia synthesis system can reach supercritical state by adding a suitable supercritical medium and then controlling the reaction conditions. It is helpful for the supercritical ammonia synthesis that medium reaches supercritical state under the conditions of the corresponding total pressure and components near the normal temperature or near the critical temperature of medium or in the range of temperature of industrialized ammonia synthesis.

Keywords partial molar volume, nitrogen, hydrogen, ammonia, supercritical, medium, ammonia synthesis

1 Introduction

The investigation of the advanced technique of ammonia synthesis will have a far-reaching impact on the agriculture-based China. In spite of nearly a hundred-year history, there are still two main problems remaining in the technique. First concern is the limitation of thermodynamics in the process of synthesis, while the other is the heat transfer limitation in the synthesis tower. At present, the single-pass conversion in industry is approximately 15% to 25% due to the restriction of chemical equilibrium and the capability of catalyst. To make full use of materials, most unreacted gases have to be recycled, which is one of the factors that cause high consumption of energy. On the contrary, the energy consumption will be tremendously decreased upon the increase of single-pass conversion. On the other hand, more and more complicated equipments have to be introduced inside the synthesis tower in order to control and modulate the temperature of the catalysis bed effectively and make a better use of spaces of high-pressure reactors. In the supercritical state, fluids have the better properties in mass transfer and heat transfer because their viscosity and density are, respectively, equivalent to those of gas and liquid. Thus, studies on the application of supercritical fluid related to chemical reactions are springing up. Liu and co-workers [1] have implemented pioneering explorations in the supercritical synthesis of ammonia, where apolar fluids, such as saturated hydrocarbons, and polar fluids, such as amines, were, respectively, used as a supercritical medium under the temperature conditions ranging from 598 K to 698 K, the total system pressure of (p_t) of 10 MPa, supercritical medium partial pressure ranging from 2 MPa to 3.5 MPa, the molar ratio of hydrogen to nitrogen setting at 3 and a space velocity of 10000 h^{-1}. On the basis of experimental results, some primary knowledge has been concluded.

In this paper, the partial molar volumes of components in a supercritical ammonia synthesis system were calculated so that the phase behavior of the components and the chemical reactions in supercritical phase are better understood that actually offers the fundamentals for the ammonia synthesis in supercritical state.

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2 Calculation model

When $1 < T/T_c < 1.1$ and $1 < p/p_c < 2$, supercritical fluid exhibits its specificity prominently. Supercritical medium, however, should be introduced, because hydrogen, nitrogen and ammonia do not belong to the above category under the conditions of the industrial ammonia synthesis. Based on the transient state theory, the reaction of ammonia synthesis from hydrogen and nitrogen can be expressed by the following formula:

$$3H_2 + N_2 \rightleftharpoons M^{\neq} \rightleftharpoons 2NH_3$$

where, $M^{\neq}$ represents the activated complex of transient state. The speed-control step in ammonia synthesis is the adsorption dissociation of N_2; and the activation energy of this step is equivalent to that of the step of ammonia synthesis [2]. The parameters of a and b in R-K equations of both products and reactants are close in value as well. The supercritical medium impacts the reaction mainly by its phase behavior owing to the inertness to the reaction. Therefore, the values of a and b of activated complex can be approximately presented by those of N_2 respectively. In view that the amount of activated complex is far smaller than that of gases, activated complex can be merged with N_2 in the calculation. Suppose the supercritical fluid is regarded as the compressed gas model, the supercritical fluid can be described by the state equation. Moreover, industrial ammonia synthesis reaction is performed under the conditions of high temperature and high pressure, and the system is a compressed gas mixture of high temperature. According to the literatures [3,4], the parameters of pressure, volume and temperature of all components in supercritical phase can be correlated by R-K state equation:

$$p = \frac{RT}{V-b} - \frac{a}{T^{0.5}V(V+b)}$$

For pure substance $a = 0.42748\frac{R^2T_c^{2.5}}{p_c}$, $b = 0.08664\frac{RT_c}{p_c}$

$$\text{Mix rule} \qquad a = \left(\sum_{i=1}^{N} a_i^{0.5} y_i\right)^2, \ b = \sum_{i=1}^{N} b_i y_i \qquad (1)$$

When a medium is introduced into the synthesis gas, the calculation formula of partial molar volume is deduced as follows:

$$\begin{aligned}\frac{V_i}{RT} = &\left[\frac{1}{V} - \frac{1}{V-b} - \frac{b_i}{(V-b)^2}\right.\\ &+ \left(\frac{2\sqrt{aa_i}}{bRT^{1.5}} - \frac{ab_i}{b^2RT^{1.5}}\right)\left(\frac{1}{V} - \frac{1}{V+b}\right)\\ &\left.+ \frac{ab_i}{bRT^{1.5}(V-b)^2}\right] \cdot \left[\frac{-RT}{(V-b)^2} + \frac{a(2V+b)}{T^{0.5}V^2(V+b)^2}\right]^{-1}\\ &- \frac{1}{V}\left[\frac{-RT}{(V-b)^2} + \frac{a(2V+b)}{T^{0.5}V^2(V+b)^2}\right]^{-1} \qquad (2)\end{aligned}$$

3 Results and discussion

The parameters of some relevant substances are listed in Table 1 and the partial molar volumes of components in a supercritical ammonia synthesis system are calculated from formula (2).

Table 1 Critical constants and parameters of R-K equation of state

substance	T_c/K	p_c/MPa	a	$b \times 10^3$
hydrogen	33	1.29	0.1430	0.0184
nitrogen	126.2	3.4	1.5549	0.0267
ammonia	405.6	11.28	8.6790	0.0259
n-heptane	540.3	2.74	74.2436	0.1441
n-tridecane	676.0	1.68	208.9359	0.2898
aniline	698.8	5.31	71.8201	0.0948

3.1 Calculation of components' partial molar volumes in a normal industrial ammonia synthesis system

Figure 1 shows the variation relationship between V_i and p_t (V_i-p_t plot) at 648 K, in which the industrial ammonia synthesis system consists of $H_2/N_2/NH_3 = 3/1/0.35$ ($H_2/N_2 = 3$, single-pass conversion = 15%, $C_A = 8\%$). From Fig. 1, it is evident that the molar volume of gas is 1000 times of the one of liquid. Meanwhile, at $T = 648$ K and $p = 0.1$ MPa, the molar volume of gas is 100 times of that at $T = 649$ K and $p = 11$ MPa. The normal industrial ammonia synthesis gas system is in the state of "compressed gas" of high temperature.

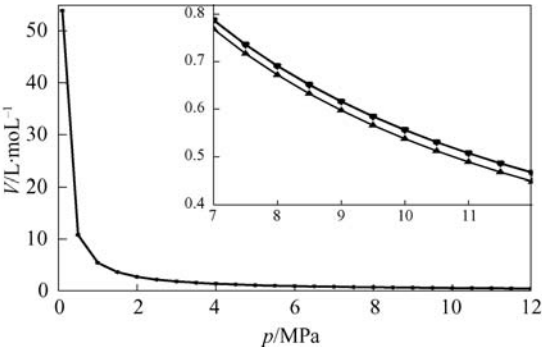


Fig. 1 Partial molar volume of components and molar volume of synthesis gas without supercritical medium
$H_2/N_2 = 3$; $C_A = 8\%$; $T = 648$ K; ■ H_2; ● N_2; ▲ NH_3; ▼ molar volume

3.2 Calculation of partial molar volumes of components in a supercritical ammonia synthesis system under different conditions

3.2.1 Under the condition of fixed components

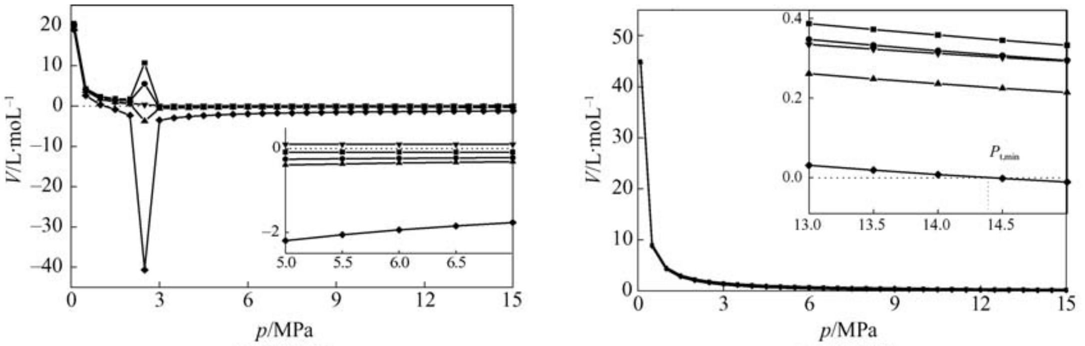
Figure 2 displays the V_i-p_t plot of supercritical ammonia synthesis system using *n*-heptane as medium at various temperatures. This system consists of $H_2/N_2/NH_3$/medium = 3/1/0.35/1.86 ($H_2/N_2 = 3$, $C_A = 8\%$, medium concentration = 30%).

Figure 2(a) demonstrates the relations between V_i and p_t at normal temperature. Influenced by the supercritical medium, each V_i is negative at $p_t > 3$ MPa, suggesting all components conglomerate to some extent. When $T = 245$ K, $p_t = 25$ MPa, the V_i of *n*-heptane shows a negative maximum of -40.7 L·mol^{-1}. The V_i of ammonia has a smaller negative value. The values of V_i of nitrogen and hydrogen are positive. These data reveal the fact that there are pronounced differences in the accumulating states of gas and fluid. However, the normal catalyst can not show its activity at this degree of temperature and pressure, which is far from enough for the best conditions of normal ammonia synthesis.

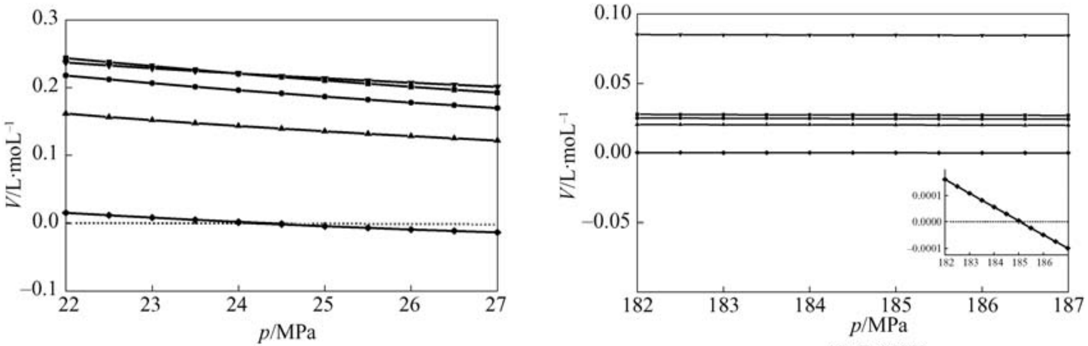
With the appropriate total pressure, the V_i of medium shows a smaller negative value around the medium supercritical temperature (demonstrated in Fig. 2(b)).

At the lowest total pressure of $p_{t,\ min}$ where the partial molar volumes of medium are negative, the actual partial pressure of medium is greater than its supercritical pressure. In this case, the supercritical liquid can be described by the state equation of the actual gas as follows:

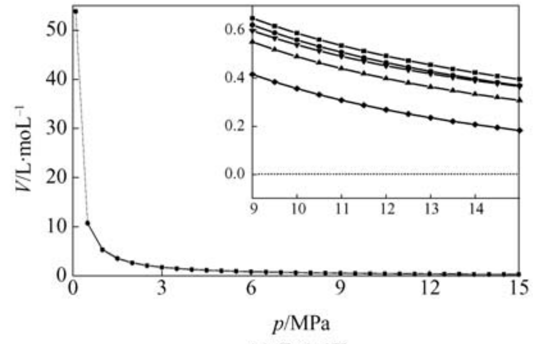
$$pV = nZRT$$



(a) T=243K (b) T=540K



(c) T=598K (d) T=698K



(e) T=648K

Fig. 2 Effect of temperature on the partial molar volume of components and molar volume of mixture $H_2/N_2 = 3$; $C_A = 8\%$; $C_M = 30\%$; *n*-heptane as medium; ■ H_2; ● N_2; ▲ NH_3; ▼ molar volume; ◆ medium

Then

$$\rho = \frac{pM}{ZRT}$$

In above formulas, Z represents compressed factor, M is molar mass of molecule.

At the supercritical point

$$\rho_{\mathrm{c}} = \frac{p_{\mathrm{c}}M}{Z_{\mathrm{c}}RT_{\mathrm{C}}}$$

If

$$D = \frac{\rho}{\rho_{\mathrm{c}}} = \frac{p}{p_{\mathrm{c}}} \cdot \frac{T_{\mathrm{c}}}{T} \cdot \frac{Z_{\mathrm{c}}}{Z}$$

ρ is defined as supercritical density when $D > 1$ and defined as non-supercritical density when $D < 1$ [5]. The results in Table 2 reveal that gases involved in the reaction are in the state of compression and *n*-heptane is in supercritical state. The excellence in mass and heat transfer can be exhibited only when a medium reaches a state of supercritical density. On the other hand, the microenvironment of the reaction is impacted by wrapping gas components and activated complex with the clusters produced through the conglomeration of supercritical medium. Besides, the solubility difference of gas components in medium certainly also influences the shift of reaction equilibrium. The corresponding temperature range is close to that of industrial ammonia synthesis with a small p_{t} value. Thus, it is useful to study the supercritical ammonia synthesis within this temperature range.

Table 2 Calculation values of D and ρ of components at 540 K and 15 MPa

substance	D	$\rho/\mathrm{g \cdot cm^{-3}}$
hydrogen	0.1010	0.0032
nitrogen	0.0495	0.0155
ammonia	0.0132	0.0031
n-heptane	1.5305	0.3505

As the temperature rises, the total pressure to reach supercritical state has to rise as well, which is displayed as the increase of $p_{\mathrm{t,\ min}}$ in V_i-p_{t} chart.

In the temperature range of 598 K–698 K that is for the ammonia synthesis at present, the p_{t} value should be increased to 24–185 MPa to ensure the negativity of the V_i value of the medium. The V_i-p_{t} changing trends are displayed in Fig. 2(c) and Fig. 2(d). Since pressure rises, higher device strength is demanded. Accordingly, the costs in equipment and the expenses of medium and gas circulation performance will increase dramatically. When $p_{\mathrm{t}} < 24$ MPa, each V_i in the system is positive which means the system is the mixture of compressed gases that is similar to the normal industrial ammonia synthesis system. *n*-Heptane has turned into inert components, whose V_i-p_{t} relationship is shown in Fig. 2(e), causing a decrease in the effective partial pressures of synthesis gas and ultimately leading to the decrease of synthesis efficiency [1].

3.2.2 Changes of ammonia concentration & medium proportion

At the supercritical temperature of the medium, *n*-heptane, V_i is calculated with various ammonia concentrations and medium proportions. The result shows that $p_{\mathrm{t,\ min}}$ is relevant to the composition. Figure 3 shows the V_i-p_{t} relationships of the medium, where, $\mathrm{H_2/N_2} = 3$; $C_{\mathrm{A}} = 2\%, 8\%, 15\%$ (per pass conversion yield: 4%, 15%, 24% respectively); $C_{\mathrm{M}} = 30\%$. From Fig. 3, raising the ammonia concentration and decreasing $p_{\mathrm{t,\ min}}$ are favorable to reach the supercritical state. But it is unfavorable for ammonia synthesis reaction as the reverse reaction of chemical equilibrium becomes stronger along with the increase of ammonia concentration. Figure 4 shows the V_i-p_{t} relationships of medium, where, $\mathrm{H_2/N_2} = 3$; $C_{\mathrm{A}} = 8\%$; $C_{\mathrm{M}} = 20\%, 30\%, 40\%$. The result indicates it is advantageous to reach the supercritical state when the medium concentration increases and $p_{\mathrm{t,\ min}}$ decreases. Yet, it is disadvantageous

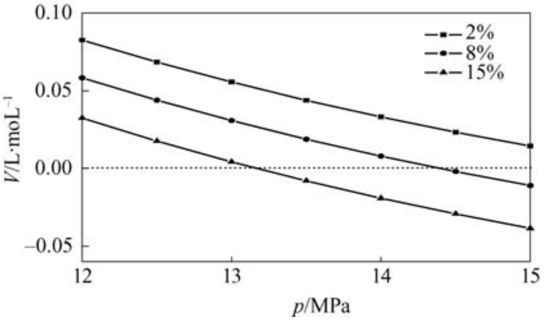


Fig. 3 Effect of ammonia concentration on the partial molar volume of medium
$\mathrm{H_2/N_2} = 3$; $C_{\mathrm{M}} = 30\%$; $T = 540$ K, *n*-heptane as medium; ■ $C_{\mathrm{A}} = 2\%$; ● $C_{\mathrm{A}} = 8\%$; ▲ $C_{\mathrm{A}} = 15\%$

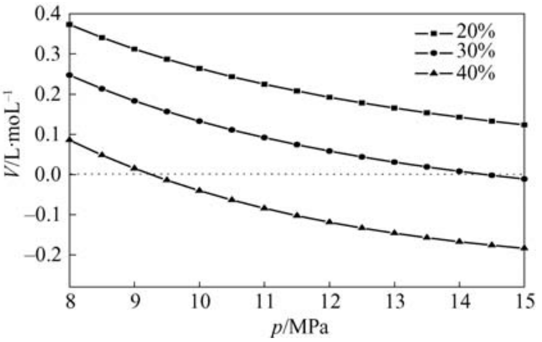


Fig. 4 Effect of medium concentration on the partial molar volume of medium
$\mathrm{H_2/N_2} = 3$; $C_{\mathrm{A}} = 8\%$; $T = 540$ K; *n*-heptane as medium; ■ $C_{\mathrm{M}} = 20\%$; ● $C_{\mathrm{M}} = 30\%$; ▲ $C_{\mathrm{M}} = 40\%$

to the ammonia synthesis reaction when the effective partial pressure of synthesis gas decreases as the medium concentration increases.

3.2.3 Changes of inert medium

Similar results are obtained by the calculation with other inert medium instead of *n*-heptane. At the supercritical temperature of medium of *n*-tridecane, the V_i-p_t relationship is shown in Fig. 5(a), where, $H_2/N_2/NH_3$/medium = 3/1/0.35/1.86 ($H_2/N_2 = 3$, $C_A = 8\%$, $C_M = 30\%$). At the supercritical temperature of the medium of aniline, V_i-p_t relationship is shown in Fig. 5(b), where, $H_2/N_2/NH_3$/medium = 3/1/0.35/4.35 ($H_2/N_2 = 3$, $C_A = 8\%$, $C_M = 50\%$).

From Fig. 2(b), Fig. 5(a) and (b), it can be learned that inert mediums of different critical parameters reach supercritical state under different conditions. Generally, the mediums of lower critical temperature and lower critical pressure are adopted to achieve the smaller $p_{t,\ min}$.

Under other conditions, the correlation of components' partial molar volume along with total pressure is similar to that of *n*-heptane and unnecessary to go into details.

To summarize, under the conditions of normal temperature or approximate critical temperature of medium or within the temperature range of industrial ammonia synthesis and under the respective corresponding total pressure and composition conditions, the partial molar volume of medium may be negative, corresponding to the higher supercritical density, which indicates a favorable environment is available for supercritical ammonia synthesis when the medium has a tendency of partial accumulation and is in the supercritical state. All in all, to study supercritical ammonia synthesis under the conditions of the current industrial ammonia synthesis, many factors should be fully taken into account, such as the category and activity temperature of catalyst, the critical characteristic, stability and solubility of medium, etc.

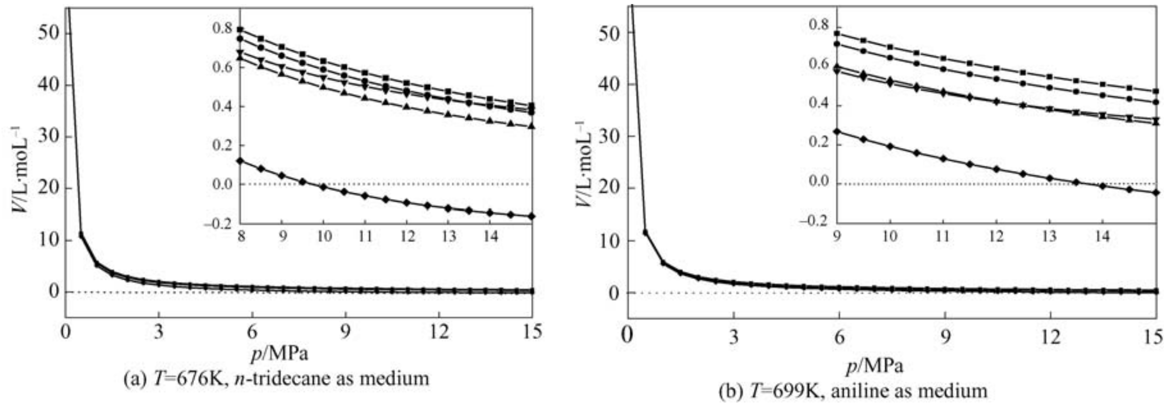
4 Conclusions

(1) In most cases, under the condition of the same temperature and pressure, the partial molar volumes of hydrogen, nitrogen, ammonia and medium finish in turns. The partial molar volumes of the hydrogen, nitrogen and ammonia are close to each other, while that of medium is comparatively smaller. The partial molar volume and molar volume rise along with temperature increasing and come down with pressure increasing.

(2) Under other conditions fixed, the lowest total pressure, at which the value of medium's partial molar volume is negative, rises with temperature rising and decreases with concentrations of ammonia and medium increasing.

(3) Applying the proper supercritical medium in ammonia synthesis gas and controlling the reaction conditions, theoretically, the system can reach the supercritical state in which the reaction of ammonia synthesis becomes possible. The condition is related to temperature, pressure, medium's critical characteristics and composition. The inert medium with different critical parameters demands different conditions to reach supercritical state. In general, the medium of low critical temperature and pressure reach the supercritical state at smaller total pressure.

(4) The partial molar volume value can be negative under the conditions of normal temperature or approximate critical temperature of medium or within the temperature range of industrial ammonia synthesis and corresponding total pressure and composition. At the approximate zero point of medium's partial molar volume value, the medium has higher supercritical density, which is favorable for the investigation of ammonia synthesis in supercritical state.



(a) T=676K, *n*-tridecane as medium

(b) T=699K, aniline as medium

Fig. 5 Effect of different mediums on the partial molar volume of medium
(a) $H_2/N_2 = 3$; $C_A = 8\%$; $C_M = 30\%$; $T = 676$ K; *n*-tridecane as medium; (b) $H_2/N_2 = 3$; $C_A = 8\%$; $C_M = 50\%$; $T = 699$ K; aniline as medium; ■ H_2; ● N_2; ▲ NH_3; ▼ molar volume; ♦ medium

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Notation

C_A	molar fraction of ammonia
C_M	molar fraction of medium
D	relative critical density
p_t	total pressure, MPa
$p_{t,\ \min}$	lowest total pressure when partial molar volume of supercritical medium is negative
V_i	partial molar volume of component i (*i* refers to H_2, N_2, NH_3 and medium)
ρ	density
subcript: c	supercritical value

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