Thermodynamic Functions at Isobaric Process of van der Waals Gases

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The thermodynamic functions for the van der Waals equation are investigated at isobaric process. The Gibbs free energy is expressed as the sum of the Helmholtz free energy and PV, and the volume in this case is described as the implicit function of the cubic equation for V in the van der Waals equation. Furthermore, the Gibbs free energy is given as a function of the reduced temperature, pressure and volume, introducing a reduced equation of state. Volume, enthalpy, entropy, heat capacity, thermal expansivity, and isothermal compressibility are given as functions of the reduced temperature, pressure and volume, respectively. Some thermodynamic quantities are calculated numerically and drawn graphically. The heat capacity, thermal expansivity, and isothermal compressibility diverge to infinity at the critical point. This suggests that a second-order phase transition may occur at the critical point.

Key words: Van der Waals Gases; Isobaric Process; Second-order Phase Transition.

1. Introduction

There is a continuing problem concerning the thermodynamic behaviours in a supercritical state. The van der Waals equation as one of many empirical state equations, can be given some qualitative illustrations of observed P-V isotherm, the critical state and the phase equilibrium between gas and liquid states. There seems to be a problem associated with the fact that thermodynamic quantities have been expressed quantitatively as functions of temperature and pressure as intensive variables, while the van der Waals equation has been applied to investigate deviations from the equation of the ideal state of a gas by virial expansion [1, 2].

The Gibbs free energy can be described as the sum of the Helmholtz free energy, $A(T, V)$, and PV. The Gibbs free energy, however, must essentially be represented by the variables temperature and pressure. The volume V in the Gibbs free energy equation always satisfies the cubic equation for V in the van der Waals equation and becomes an implicit function of temperature and pressure. The determinant of the cubic equation is naturally zero at the critical point. Some thermodynamic functions that contain the derivative of $V(T, P)$ with respect to T or P depend strongly on the properties of the determinant. In the case of these functions, a singularity will occur thermodynamically at a critical point, while the volume $V(T, P)$ becomes a complicated expression as a root of the cubic equation. Introducing a reduced equation of state obeying the principle of corresponding states, the Gibbs free energy can be replaced by a function of reduced temperature, pressure and volume. Some thermodynamic quantities are written in a form, applicable to all substances, which does not require the specific constants, a and b, for any gas. From the viewpoint of an isobaric process, this may be significant to provide the properties of thermodynamic quantities in the supercritical state and the second-order phase transition of van der Waals gases at the critical point.

In this work, the Gibbs free energy is obtained from the Helmholtz free energy in comparison with the imperfect gases in classical statistical mechanics [1], and also this free energy becomes a function of reduced temperature, pressure and volume. The volume, enthalpy, entropy, heat capacity, thermal expansivity and isothermal compressibility are included as variables. These thermodynamic quantities are determined through numerical calculations and are graphically displayed for an isobaric or isothermal process.

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The second-order phase transition of van der Waals gases at the critical point is discussed.

2. Thermodynamic Functions

A van der Waals gas is defined by the equation of state

$$P = \frac{RT}{V-b} - \frac{a}{V^2}. \tag{1}$$

The Helmholtz free energy $A(T,V)$ [3] is expressed with the temperature function $\varphi(T)$ as

$$A(T,V) = -\int \Big(\frac{RT}{V-b} - \frac{a}{V^2}\Big)\mathrm{d}V + \varphi(T). \tag{2}$$

In classical statistical mechanics [1], the partition function of an imperfect gas is represented by

$$Z(T,V,N) = \Big(\frac{2\pi mkT}{h^2}\Big)^{3N/2}\frac{Z_V}{N!} = Z_{\mathrm{id}}Z_V. \tag{3}$$

Z_{id} is the partition function of an ideal gas with the variable of T, and Z_V is the configurational partition function with the variable V. The first and second term in (3) correspond to the free energy Z_V and Z_{id}, respectively. The free energy in (2) is rewritten as [1, 2]

$$A(T,V) = -RT\Big[\frac{3}{2}\ln\frac{2\pi mkT}{h^2} - \ln\frac{N_{\mathrm{A}}}{e} + \ln(V-b) + \frac{a}{RTV}\Big], \tag{4}$$

where N_{A} is Avogadro's number and e the base of the natural logarithm. We can arrive at the Gibbs free energy by adding to PV:

$$\begin{aligned} G(T,P) &= A(T,V) + PV \\ &= -RT\Big[\frac{3}{2}\ln\frac{2\pi mkT}{h^2} - \ln\frac{N_{\mathrm{A}}}{e} + \ln(V-b) \\ &\quad + \frac{a}{RTV} - \frac{PV}{RT}\Big]. \end{aligned} \tag{5}$$

The volume in (5) always satisfies the roots of the cubic equation for V in (1):

$$V^3 - \Big(b + \frac{RT}{P}\Big)V^2 + \frac{a}{P}V - \frac{ab}{P} = 0. \tag{6}$$

If the temperature, pressure and volume of a gas are expressed in terms of T_{C}, P_{C} and V_{C}, respectively, then $T = \theta T_{\mathrm{C}}$, $P = \pi P_{\mathrm{C}}$, and $V = \phi V_{\mathrm{C}}$. The reduced equation of state obeying the principle of corresponding states is easily derived from the van der Waals equation:

$$\Big(\pi + \frac{3}{\phi^2}\Big)\Big(\phi - \frac{1}{3}\Big) = \frac{8}{3}\theta. \tag{7}$$

By applying θ, π, and ϕ, the Gibbs free energy can be written as

$$\begin{aligned} G(\theta,\pi) = -RT_{\mathrm{C}}\theta\Big[C + \frac{3}{2}\ln\theta + \ln\Big(\phi - \frac{1}{3}\Big) \\ + \frac{9}{8\theta\phi} - \frac{3\pi\phi}{8\theta}\Big]. \end{aligned} \tag{8}$$

The constant C in (8) can be rewritten as

$$\begin{aligned} C &= \frac{3}{2}\ln\frac{2\pi mkT_{\mathrm{C}}}{h^2} - \ln\frac{N_{\mathrm{A}}}{e} + \ln V_{\mathrm{C}} \\ &= -7.07228 + \frac{3}{2}\ln MT_{\mathrm{C}} + \ln V_{\mathrm{C}}, \end{aligned} \tag{9}$$

where M is the molecular weight, T_{C} is in units of K and V_{C} in units of cm^3. The Gibbs free energy, as a function of the molecular weight and the critical constants of a particular gas, is not applicable to all substances.

The reduced volume in this free energy, ϕ, is obtained by the cubic equation for ϕ in (7) as

$$\phi^3 - \Big(\frac{1}{3} + \frac{8\theta}{3\pi}\Big)\phi^2 + \frac{3}{\pi}\phi - \frac{1}{\pi} = 0. \tag{10}$$

Similarly, as mentioned in the case of V for (6), the root of ϕ in (10) is written as an implicit function of θ and π. The Gibbs free energy in (8), therefore, can be described as a function of θ and π. All thermodynamic functions can be derived from the Gibbs free energy in the known way.

We can exactly solve the cubic equation for ϕ. Substituting $\phi = x + a$, the standard cubic equation without x^2 can be replaced by

$$x^3 + px + q = 0. \tag{11}$$

The coefficients p and q in (11) result from

$$a = \frac{1}{9}\Big(1 + \frac{8\theta}{\pi}\Big), \tag{12}$$

$$P = \frac{p}{3} = -(a^2 - \frac{1}{\pi}) \tag{13}$$

and

$$Q = -\frac{q}{2} = a^3 - \frac{3a}{2\pi} + \frac{1}{2\pi}. \tag{14}$$

The determinant of the cubic Eq. (11) is defined as

$$\begin{aligned} D &= P^3 + Q^2 \qquad (15) \\ &= \frac{a^3}{\pi} - \frac{3a^2}{4\pi^2} - \frac{3a}{2\pi^2} + \frac{1}{\pi^3} + \frac{1}{4\pi^2}. \end{aligned}$$

If $\pi > 1$ or $\theta > 1$, then the determinant is always positive, and a real root and two complex conjugated roots are given. Especially, the triple real roots are found at $D = 0$. A real root is given by

$$\phi = a + x = a + \sqrt[3]{R_1} + \sqrt[3]{R_2}, \tag{16}$$

where

$$R_1 = Q + \sqrt{D} \tag{17}$$

and

$$R_2 = Q - \sqrt{D}. \tag{18}$$

Since the coefficient in the term $(\mathrm{d}\phi/\mathrm{d}\theta)_\pi$ satisfies the reduced equation of state in (10), the volume is given as the form missing $(\mathrm{d}\phi/\mathrm{d}\theta)_\pi$,

$$V = (\frac{\partial G}{\partial P})_T = \frac{1}{P_C}(\frac{\partial G}{\partial \pi})_\theta = V_C\phi. \tag{19}$$

ϕ becomes the real root in (16). The entropy is obtained as

$$\begin{aligned} S &= -(\frac{\partial G}{\partial T})_P = -\frac{1}{T_C}(\frac{\partial G}{\partial \theta})_\pi \qquad (20) \\ &= R[C + \frac{3}{2} + \frac{3}{2}\ln\theta + \ln(\phi - \frac{1}{3})]. \end{aligned}$$

The entropy in (20) involves the constant C. However this entropy, which is dependent on C, becomes generally applicable to all substances. The enthalpy is obtained as

$$\begin{aligned} H &= -T^2[\frac{\partial}{\partial T}(\frac{G}{T})]_P = -\theta^2[\frac{\partial}{\partial \theta}(\frac{G}{\theta})]_\pi \qquad (21) \\ &= RT_C(\frac{3}{2}\theta - \frac{9}{8\phi} + \frac{3\pi\phi}{8}). \end{aligned}$$

The heat capacity at constant reduced pressure is easily derived from the enthalpy,

$$\begin{aligned} C_P &= (\frac{\partial H}{\partial T})_P = \frac{1}{T_C}(\frac{\partial H}{\partial \theta})_\pi \qquad (22) \\ &= R[\frac{3}{2} + \frac{\theta}{\phi - 1/3}(\frac{\partial \phi}{\partial \theta})_\pi], \end{aligned}$$

where the derivative of ϕ with respect to θ can be given as

$$(\frac{\mathrm{d}\phi}{\mathrm{d}\theta})_\pi = \frac{8}{9\pi}[1 + (\frac{\mathrm{d}x}{\mathrm{d}a})_\pi] \tag{23}$$

with

$$\begin{aligned} (\frac{\mathrm{d}x}{\mathrm{d}a})_\pi = \frac{1}{3}\Big[& \frac{1}{\sqrt[3]{R_1^2}}(\frac{\mathrm{d}Q}{\mathrm{d}a} + \frac{1}{2\sqrt{D}}\frac{\mathrm{d}D}{\mathrm{d}a}) \qquad (24) \\ & + \frac{1}{\sqrt[3]{R_2^2}}(\frac{\mathrm{d}Q}{\mathrm{d}a} - \frac{1}{2\sqrt{D}}\frac{\mathrm{d}D}{\mathrm{d}a})\Big]. \end{aligned}$$

$\mathrm{d}Q/\mathrm{d}a$ and $\mathrm{d}D/\mathrm{d}a$ can easily be obtained. The thermal expansivity at constant reduced pressure is defined by

$$\alpha = \frac{1}{V}(\frac{\partial V}{\partial T})_P = \frac{1}{T_C}\frac{1}{\phi}(\frac{\mathrm{d}\phi}{\mathrm{d}\theta}). \tag{25}$$

The isothermal compressibility is defined by

$$\kappa_T = -\frac{1}{V}(\frac{\partial V}{\partial P})_T = \frac{1}{P_C}\frac{1}{\phi}(\frac{\mathrm{d}\phi}{\mathrm{d}\pi}), \tag{26}$$

where the derivative of ϕ with respect to π can be given as

$$\frac{\mathrm{d}\phi}{\mathrm{d}\pi} = -\frac{8\theta}{9\pi^2} + \frac{\mathrm{d}x}{\mathrm{d}\pi} \tag{27}$$

with

$$\begin{aligned} (\frac{\mathrm{d}x}{\mathrm{d}\pi})_\theta = \frac{1}{3}\Big[& \frac{1}{\sqrt[3]{R_1^2}}(\frac{\mathrm{d}Q}{\mathrm{d}\pi} + \frac{1}{2\sqrt{D}}\frac{\mathrm{d}D}{\mathrm{d}\pi}) \qquad (28) \\ & + \frac{1}{\sqrt[3]{R_2^2}}(\frac{\mathrm{d}Q}{\mathrm{d}\pi} - \frac{1}{2\sqrt{D}}\frac{\mathrm{d}D}{\mathrm{d}\pi})\Big], \end{aligned}$$

where

$$\frac{\mathrm{d}Q}{\mathrm{d}\pi} = -\frac{8\theta}{9\pi^2}(3a^2 - \frac{3}{2\pi}) + \frac{3a}{2\pi^2} - \frac{1}{2\pi^2} \tag{29}$$

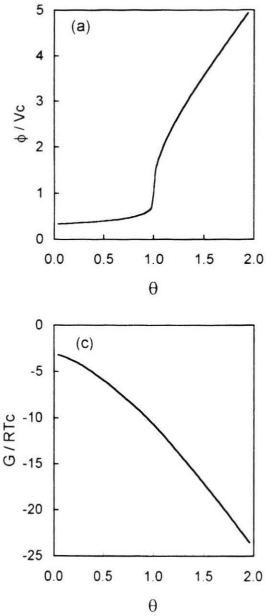

Fig. 1. Volume (a), enthalpy (b), Gibbs free energy (c) and entropy (d), plotted against the reduced temperature at $\pi = 1$. $C = 10.30$ in (9) for Ar.

and

$$\frac{\mathrm{d}D}{\mathrm{d}\pi} = -\frac{8\theta}{9\pi^2}\left(\frac{3a^2}{\pi} - \frac{3a}{2\pi^2} - \frac{3}{2\pi^2}\right) - \frac{a^3}{\pi^2} + \frac{3a^2}{2\pi^3} + \frac{3a}{\pi^3} - \frac{1}{\pi^4} - \frac{1}{\pi^3}. \qquad (30)$$

According to (23) or (27), the heat capacity, thermal expansivity and isothermal compressibility diverge to infinity at the critical point, whereas the Gibbs free energy, entropy, volume, and enthalpy, which are expressed as the form missing $(\mathrm{d}\phi/\mathrm{d}\theta)_\pi$, are continuous at this point.

3. Numerical Results

In the above-mentioned cases, most thermodynamic functions are written as functions of the variables θ, π, and ϕ and are generally applicable to all substances. In contrast, the Gibbs free energy and the entropy are not generally applicable as these are dependent on C in (9). C is required as the practical value of a particular gas to calculate numerically the Gibbs free energy and the entropy. Now, for example, when the critical data for Ar [4] are substituted for C, we obtain 10.30 as the value for Ar. Numerical results obtained with these thermodynamic functions are displayed in Figs. 1 - 4. The Gibbs free energy depends mainly on the function $C\theta$ and decreases linearly, except for small θ. The volume, entropy and enthalpy are continuous at $\theta = 1$, whereas these quantities show a sudden change in the neighborhood of the critical point. As shown in Fig. 2, the heat capacity at $\pi = 1$ diverges to infinity at $\theta = 1$, and the other heat capacities at various reduced pressures have a maximum value when π is larger than 1. The values become smaller than the maximum when π is increased. The heat capacities are converging to 5/2 R when θ is increased. The thermal expansivity at $\pi = 1$, also, diverges to infinity at $\theta = 1$, and these quantities at various reduced pressures show a

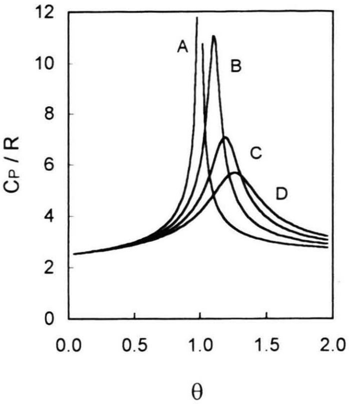

Fig. 2. Heat capacities, plotted against the reduced temperature at various reduced pressures. A: $\pi = 1.0$; B: $\pi = 1.5$; C: $\pi = 2.0$; D: $\pi = 2.5$.

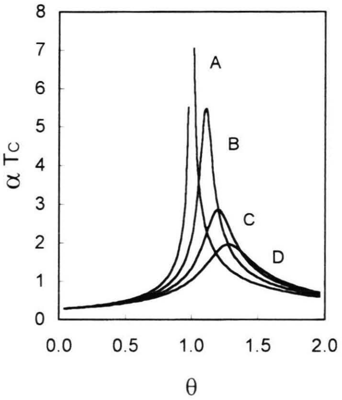

Fig. 3. Thermal expansivities, plotted against the reduced temperature at various reduced pressures. A: $\pi = 1.0$; B: $\pi = 1.5$; C: $\pi = 2.0$; D: $\pi = 2.5$.

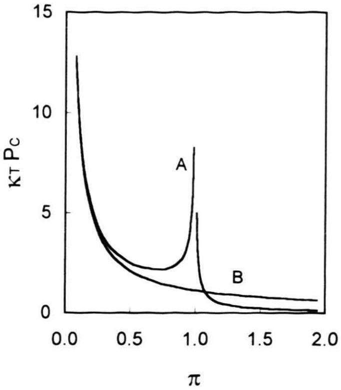

Fig. 4. Isothermal compressibilities, plotted against the reduced pressure at two reduced temperatures. A: $\theta = 1.0$; B: $\theta = 1.5$.

tendency similar to that of the heat capacities, as shown in Figure 3. The isothermal compressibility at $\pi = 1$ diverges to infinity at $\theta = 1$, as shown in Figure 4. If θ is larger than 1, then the isothermal compressibility is monotonically decreasing, as shown in Figure 4. Over all, the heat capacity, thermal expansivity and isothermal compressibility show a singularity at the critical point. This singularity suggests a phase transition. The generalized diagrams of some thermodynamic quantities accompanying a second-order phase transition are typically described in textbooks of physical chemistry [4]. Compared with these diagrams [4], those in Figs. 1 and 2 (A) correspond to a second-order phase transition. Furthermore, the results in Fig. 2 agree qualitatively with the cubic graphs for heat capacities of pure water [5].

[1] J. E. Mayer and M. G. Mayer, Statistical Mechanics. John Wiley & Sons, Inc., New York 1940, pp. 262 and 263.
[2] L. D. Landau and E. M. Lifshitz, Statistical Physics. Part 1. 3rd Ed., revised and enlarged by E. M. Lifshitz and P. Pitaevskii. Translated from the Russian by J. B. Sykes and M. J. Kearsley, Pergamon Press, Oxford 1950, pp. 232 - 235.
[3] J. C. Slater, Introduction to Chemical Physics. McGraw-Hill, New York 1939, p. 187.
[4] P. W. Atkins, Physical Chemistry 6th Ed., Oxford University, Oxford 1998, pp. 33 and 153.
[5] R. W. Shaw, T. B. Brill, A. A. Clifford, C. A. Eckert, and E. U. Franck, C&EN, Dec. **23**, 26 (1991).