Thermodynamic Quantities of Square-Well Gases at Isobaric Process

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Z. Naturforsch. **65a,** 561 – 567 (2010); received September 30, 2008 / revised January 8, 2009

The thermodynamic functions for square-well gases evaluated till the third virial coefficient are investigated at an isobaric process. Some thermodynamic functions are analytically expressed as functions of intensive variables, temperature, and pressure. Some thermodynamic quantities for H_2O are calculated numerically and drawn graphically. In critical states, the heat capacity, thermal expansivity, and isothermal compressibility diverge to infinity at the critical point while the Gibbs free energy, volume, enthalpy, and entropy are continuous at the critical point. In the coexistence of two phases, the boiling temperatures and the enthalpy changes of vaporization are obtained by numerical calculations for 16 substances. The Gibbs free energy indicates a polygonal line; entropy, volume, and enthalpy jump from the liquid to the gaseous phase at the boiling point. The heat capacity does not diverge to infinity but shows a finite discrepancy at boiling point. This suggests that a first-order phase transition at the boiling point and a second-order phase transition at the critical point may occur.

Key words: Square-Well Potential; Gibbs Free Energy; Isobaric Process; Critical Constants; Enthalpy Changes of Vaporization; First- and Second-Order Phase Transition.

1. Introduction

Recently, the behaviours in the neighbourhood of the critical point and the coexistence of gaseous and liquid phases have been illustrated, introducing some thermodynamic functions at the isobaric process for van der Waals [1], Lennard-Jones [2], and Redlich-Kwong gases [3]. Especially, all thermodynamic functions at isobaric processes contain the two intensive variables T and P, practically derived from the Gibbs free energy $G(T,P,N)$ which may be defined as the relation to the partition function $Y(T,P,N)$ in T-P grand canonical ensemble by $G(T,P,N) = -kT \log Y(T,P,N)$, see textbooks as e. g. [4 – 6] or [2, 7]. From the viewpoint of an isobaric process, an attempt to investigate the thermodynamic functions of square-well gases at isobaric process is useful to evaluate the critical constants, the boiling temperatures, and the enthalpy changes of vaporization. It may be significant to provide the properties of thermodynamic quantities by discussing first- and second-order phase transitions.

2. Thermodynamic Functions of Square-Well Gases at Isobaric Process

Imperfect gases are represented by the third virial coefficient

$$\frac{PV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2}, \tag{1}$$

where $B(T)$ is the second virial coefficient and $C(T)$ is the third virial coefficient. The Helmholtz free energy $A(T,V)$ [5] is expressed with the temperature function $\varphi(T)$ as

$$A(T,V) = -\left[RT \log V - \frac{RTB(T)}{V} - \frac{RTC(T)}{2V^2}\right] + \varphi(T). \tag{2}$$

The first term in (2) is the configurational part and the second one, $\varphi(T)$, is the kinetic part [1, 7]. In classical statistic mechanics [6] the partition function of imperfect gases in canonical ensemble may be defined as

$$Z(T,V,N) = \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} \frac{1}{N!} \cdot \exp\left[N\left(\log V - \frac{B(T)}{V} - \frac{C(T)}{2V^2}\right)\right]. \tag{3}$$

The partition function in the T-P grand canonical ensemble is represented by the Laplace transform of $Z(T,V,N)$

$$Y(T,P,N) = \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} \frac{1}{N!} \cdot \int_0^\infty \exp\left[N\left(\log V - \frac{B(T)}{V} - \frac{C(T)}{2V^2} - \frac{PV}{RT}\right)\right] \mathrm{d}V. \tag{4}$$

If N now becomes very large, one can calculate $Y(T,P,N)$ in a saddle point method. From the condition that the derivative of the integrand of (4) equals zero, we obtain a cubic equation for V which is equivalent to the imperfect equation in (1):

$$V^3 - \frac{RT}{P}V^2 - \frac{RTB(T)}{P}V - \frac{RTC(T)}{P} = 0. \tag{5}$$

The Gibbs free energy per mol is expressed from (4) as

$$G(T,P) = -RT\left[C + \frac{3}{2}\log T + \log V - \frac{B(T)}{V} - \frac{C(T)}{2V^2} - \frac{PV}{RT}\right] \tag{6}$$

with

$$C = \frac{3}{2}\log\frac{2\pi mk}{h^2} - \log\frac{N}{e} = -7.07228 + \frac{3}{2}\log M, \tag{7}$$

where M is the molecular weight.

At the critical state, (T_c, P_c, V_c), the cubic equation is obtained by

$$(V - V_\mathrm{c})^3 = 0, \tag{8}$$

and (5) is represented as

$$V^3 - \frac{RT_\mathrm{c}}{P_\mathrm{c}}V^2 - \frac{RT_\mathrm{c}B(T_\mathrm{c})}{P_\mathrm{c}}V - \frac{RT_\mathrm{c}C(T_\mathrm{c})}{P_\mathrm{c}} = 0. \tag{9}$$

Applying to (8) and (9), the critical constants can be estimated by

$$B(T_\mathrm{c})^2 - 3C(T_\mathrm{c}) = 0, \tag{10}$$

$$V_\mathrm{c} = -B(T_\mathrm{c}), \tag{11}$$

and

$$P_\mathrm{c} = \frac{RT_\mathrm{c}}{3V_\mathrm{c}}. \tag{12}$$

We now try to solve exactly the cubic equation (9) for V. Substituting $V = x + RT/3P$, the standard cubic equation without x^2-term is obtained:

$$x^3 + 3Px - 2Q = 0. \tag{13}$$

The coefficients P and Q in (13) are given, respectively, by

$$P = -\left[\frac{1}{9}\left(\frac{RT}{P}\right)^2 + \frac{RTB(T)}{3P}\right] \tag{14}$$

and

$$Q = \frac{1}{27}\left(\frac{RT}{P}\right)^3 + \frac{1}{6}\left(\frac{RT}{P}\right)^2 B(T) + \frac{1}{2}\left(\frac{RT}{P}\right)C(T). \tag{15}$$

The discriminant for the cubic equation is given as

$$D = -\frac{1}{128}\left(\frac{RT}{P}\right)^4 B(T)^2 + \frac{1}{27}\left(\frac{RT}{P}\right)^4 C(T) - \frac{1}{27}\left(\frac{RT}{P}\right)^3 B(T)^3 + \frac{1}{6}\left(\frac{RT}{P}\right)^3 B(T)C(T) + \frac{1}{4}\left(\frac{RT}{P}\right)^2 C(T)^2. \tag{16}$$

If $P > P_\mathrm{c}$ the discriminant is always positive and a real root and two complex conjugated roots are given. Also, if the discriminant is zero, a triple real root is found at the critical point in (8) and (9), or a double real root and a single root are found in the region of $P < P_\mathrm{c}$. In the latter case, the temperature T is given as T_1 and T_2 keeping an inequality, $T_1 < T_2$. T therefore is located in $T < T_1$ for the only liquid phase and is done in $T > T_2$ for only gaseous phase. If the phase is only gaseous or liquid, then the solutions in (9) consist of a real root and two conjugate complex roots since the discriminant is always positive. A real root is represented as

$$V = \frac{RT}{3P} + x = \frac{RT}{3P} + \sqrt[3]{R_1} + \sqrt[3]{R_2}, \tag{17}$$

where

$$R_1 = Q + \sqrt{D} \tag{18}$$

and

$$R_2 = Q - \sqrt{D}. \tag{19}$$

The temperature is situated in the region from T_1 to T_2 in the coexistence of gaseous and liquid phases. The discriminant is always negative and three real roots are expressed as, respectively,

$$V_{\mathrm{G}} = \frac{RT}{3P} + 2\sqrt{-P}\cos\frac{\varphi}{3}, \tag{20}$$

$$V_{\mathrm{L}} = \frac{RT}{3P} + 2\sqrt{-P}\cos\left(\frac{\varphi+2\pi}{3}\right), \tag{21}$$

and

$$V_{\mathrm{M}} = \frac{RT}{3P} + 2\sqrt{-P}\cos\left(\frac{\varphi+4\pi}{3}\right) \tag{22}$$

with

$$\varphi = \arccos\frac{Q}{\sqrt{-P^3}}. \tag{23}$$

V_{G} in (20) corresponds to the root for the gaseous state, V_{L} in (21) to that of the liquid state, and V_{M} in (22) is the root in the region from V_{L} to V_{G}. Especially, V_{M} equals to V_{G} at $T = T_1$ and to V_{L} at $T = T_2$ in the case that this cubic equation consists of a double root and a single root at $D = 0$.

The entropy, volume, enthalpy, and heat capacity are expressed deriving from the Gibbs free energy:

$$V = \left(\frac{\partial G}{\partial P}\right)_T, \tag{24}$$

$$\begin{aligned} S = R\Bigg[&C + \frac{5}{2} + \frac{3}{2}\log T + \log V - \frac{B(T)}{V} - \frac{C(T)}{2V^2} \\ &- T\left(\frac{1}{V}\frac{\mathrm{d}B(T)}{\mathrm{d}T} + \frac{1}{2V^2}\frac{\mathrm{d}C(T)}{\mathrm{d}T}\right)\Bigg], \end{aligned} \tag{25}$$

$$H = RT\left[\frac{3}{2} - T\left(\frac{1}{V}\frac{\mathrm{d}B(T)}{\mathrm{d}T} + \frac{1}{2V^2}\frac{\mathrm{d}C(T)}{\mathrm{d}T}\right)\right] + PV, \tag{26}$$

and

$$\begin{aligned} C_{\mathrm{P}} = R\Bigg[&\frac{3}{2} - 2T\left(\frac{1}{V}\frac{\mathrm{d}B(T)}{\mathrm{d}T} + \frac{1}{2V^2}\frac{\mathrm{d}C(T)}{\mathrm{d}T}\right) \\ &+ T^2\left(\frac{1}{V^2}\frac{\mathrm{d}B(T)}{\mathrm{d}T} + \frac{1}{V^3}\frac{\mathrm{d}C(T)}{\mathrm{d}T}\right)\frac{\mathrm{d}V}{\mathrm{d}T} \\ &- T^2\left(\frac{1}{V}\frac{\mathrm{d}^2B(T)}{\mathrm{d}T^2} + \frac{1}{2V^2}\frac{\mathrm{d}^2C(T)}{\mathrm{d}T^2}\right)\Bigg]. \end{aligned} \tag{27}$$

Thermal expansivity α at constant pressure and isothermal compressibility β are defined by

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{28}$$

and

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T. \tag{29}$$

If the gaseous and liquid phases coexist, the change of the Gibbs free energy between the gaseous and liquid phases at arbitrary temperature and pressure is obtained as

$$\begin{aligned} \Delta G = -RT\Bigg[&\log\frac{V_{\mathrm{G}}}{V_{\mathrm{L}}} - \left(\frac{1}{V_{\mathrm{G}}} - \frac{1}{V_{\mathrm{L}}}\right)B(T) \\ &- \frac{1}{2}\left(\frac{1}{V_{\mathrm{G}}^2} - \frac{1}{V_{\mathrm{L}}^2}\right)C(T) - \frac{P}{RT}(V_{\mathrm{G}} - V_{\mathrm{L}})\Bigg]. \end{aligned} \tag{30}$$

The enthalpy changes of vaporization are written as

$$\begin{aligned} \Delta H = -RT^2\Bigg[&\left(\frac{1}{V_{\mathrm{G}}} - \frac{1}{V_{\mathrm{L}}}\right)\frac{\mathrm{d}B(T)}{\mathrm{d}T} \\ &+ \frac{1}{2}\left(\frac{1}{V_{\mathrm{G}}^2} - \frac{1}{V_{\mathrm{L}}^2}\right)\frac{\mathrm{d}C(T)}{\mathrm{d}T}\Bigg] + P(V_{\mathrm{G}} - V_{\mathrm{L}}). \end{aligned} \tag{31}$$

To satisfy Maxwell's rule between V_{L} and V_{G}, this cubic equation determines V_{M}. Also, the boiling temperature T_{B} is located in the range between T_1 to T_2. $\Delta H(T_{\mathrm{B}}, P)$ in (31) equals the enthalpy change of vaporization at T_{B} K and 1 atm. Assuming that the volume in the liquid phase V_{L} is transformed into V_{G} in the gaseous phase at boiling point, some thermodynamic quantities as functions of variable T may be derived from (6) and (24)–(27), and V in (17), (20), and (21) are denoted V_{L} in the region of $T < T_{\mathrm{B}}$ and V_{G} in $T > T_{\mathrm{B}}$.

The square-well potential (Fig. 1)

$$U(r) = \begin{cases} \infty, & \text{for} \quad r < \sigma, \\ -\varepsilon, & \text{for} \quad \sigma < r < g\sigma, \\ 0, & \text{for} \quad r > g\sigma, \end{cases} \tag{32}$$

has been used for the second and third virial coefficients [8]:

$$B(T) = b\left[1 - (g^3 - 1)\right]f \tag{33}$$

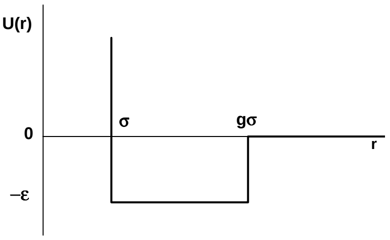

Fig. 1. Square-well potential.

Table 1. Parameters for the square-well potential determined from experimental data of the second virial coefficients [9].

Gas	ε / kT	σ / Å	g
Ne	1.2678	2.914	4.40
Ar	7.9812	3.534	3.60
Kr	9.5585	3.833	3.80
Xe	11.0846	4.189	4.00
N_2	4.8152	3.789	4.00
O_2	5.0784	3.584	4.20
F_2	7.5924	3.382	3.60
CO	12.3595	3.688	3.00
HCl	25.6016	3.809	3.20
H_2O	10.2086	3.446	5.20
CO_2	9.6210	3.889	4.20
CF_4	7.1576	4.425	4.20
SF_6	7.5655	4.969	4.60
CH_4	10.1382	3.912	3.60
C_2H_4	9.0970	4.376	4.20
C_2H_6	11.47134	4.486	4.00

Table 2. Critical constants for the critical temperatures (T_c / K), critical pressures (P_c / MPa), and critical volumes (V_c / cm^3 mol^{-1}). Boiling temperatures (T_B / K) and enthalpy changes of vaporization (ΔH / kJ mol^{-1}) at 0.1013 MPa. Present works (upper entries) and experimental results (lower entries) [10].

Gas	T_c	P_c	V_c	T_B	ΔH
Ne	44.1	2.70	45.4	30.2	3.13
	44.4	2.76	41.7	27.0	1.84
Ar	148.8	4.88	84.4	97.7	12.4
	150.8	4.87	74.9	87.3	6.53
Kr	211.0	5.50	106.4	137.4	17.5
	209	5.50	91.2	119.8	9.6
Xe	287.1	5.80	137.2	196.2	23.6
	289.7	5.84	118	165.0	13.0
N_2	124.7	3.40	101.5	83.9	9.36
	126.2	3.39	89.5	77.4	5.58
O_2	153.0	4.99	85.1	100.3	12.1
	154.6	5.05	73.4	90.2	6.8
F_2	141.5	5.30	74.0	92.4	12.0
	144.3	5.22	66.2	85.0	6.53
CO	129.4	3.53	101.6	87.4	11.3
	132.9	3.50	93.1	81.7	6.0
HCl	329.2	8.34	109.4	210.6	33.2
	324.6	8.31	81.0	188.1	16.2
H_2O	593.2	22.38	73.5	355.8	55.2
	647.3	22.05	56.0	373.2	40.7
CO_2[a]	289.9	7.39	108.8	209.0	18.4
	304.2	7.38	94.0	217.0	
CF_4	215.7	3.73	160.3	144.2	16.3
	227.6	3.74	140.0	145.2	12.0
SF_6[a]	302.5	3.74	223.6	215.3	19.7
	318.7	3.76	198.0	222.5	17.1
CH_4	189.0	4.58	114.5	124.6	15.5
	190.6	4.60	99.0	111.7	8.2
C_2H_4	274.1	4.89	155.0	179.8	21.4
	282.4	5.04	129.0	169.4	13.5
C_2H_6	297.1	4.88	168.5	194.9	23.8
	305.4	4.88	148.0	184.5	14.7

[a] Boiling temperatures and the enthalpy changes for CO_2 and SF_6 are obtained at boiling pressures of 0.518 and 0.227 MPa, respectively.

and

$$C(T) = \frac{b^2}{8}\Big[5 - 17f + (32g^3 - 18g^2 - 48)f^2 - (5g^6 - 32g^3 + 18g^2 + 26)f^3\Big],\ g \ge 2, \tag{34}$$

where

$$b = \frac{2}{3}\pi N\sigma^3 \tag{35}$$

and

$$f = \exp\left(\frac{\varepsilon}{KT}\right) - 1. \tag{36}$$

3. Numerical Results

The parameters of the square-well potential for 16 substances, ε, σ, and g, are determined from the experimental data of second virial coefficients [9] by the least squares method as shown in Table 1. Although the virial equation of state is approximated till the third virial coefficient, critical temperatures and pressures in Table 2 may be qualitatively evaluated while critical volumes for all gases except Ne, Ar, CO, and F_2 are deviated from experimental results [10]. Numerical results obtained with these thermodynamic functions for H_2O at $P_c = 22.38$ MPa are displayed in Figures 2–6. The Gibbs free energy consists of two slightly different tangents in both sides at $T_c = 593.2$ K while it is formed as continuous curve. Volume, entropy, and enthalpy are continuous at $T_c = 593.2$ K, whereas these quantities show a sudden change in the neighbourhood of the critical point. As shown in Figure 6, the

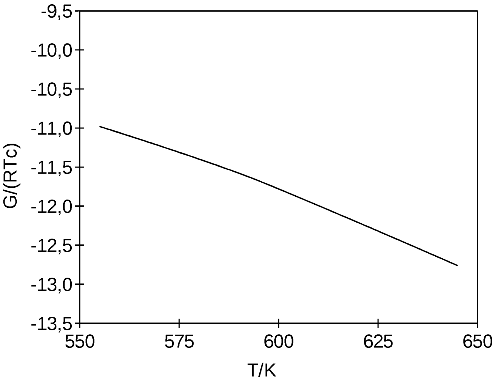

Fig. 2. Gibbs free energy for H_2O, plotted against temperature at $P_C = 22.38$ MPa; $T_C = 593.2$ K.

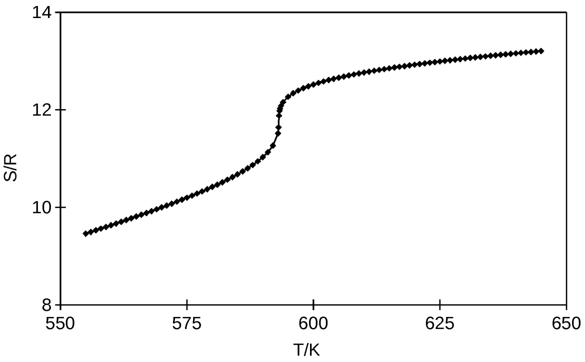

Fig. 3. Entropy for H_2O, plotted against temperature at $P_C = 22.38$ MPa; $T_C = 593.2$ K.

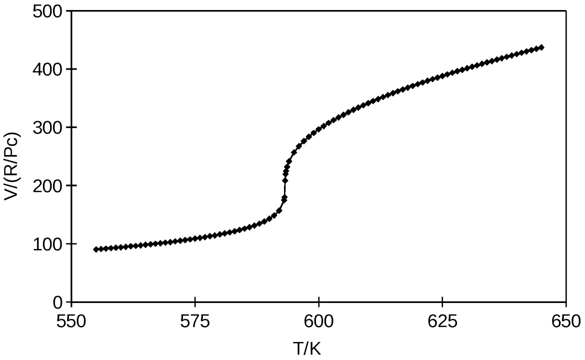

Fig. 4. Volume for H_2O, plotted against temperature at $P_C = 22.38$ MPa; $T_C = 593.2$ K.

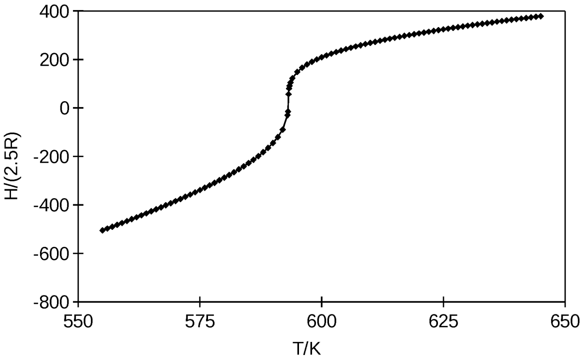

Fig. 5. Enthalpy for H_2O, plotted against temperature at $P_C = 22.38$ MPa; $T_C = 593.2$ K.

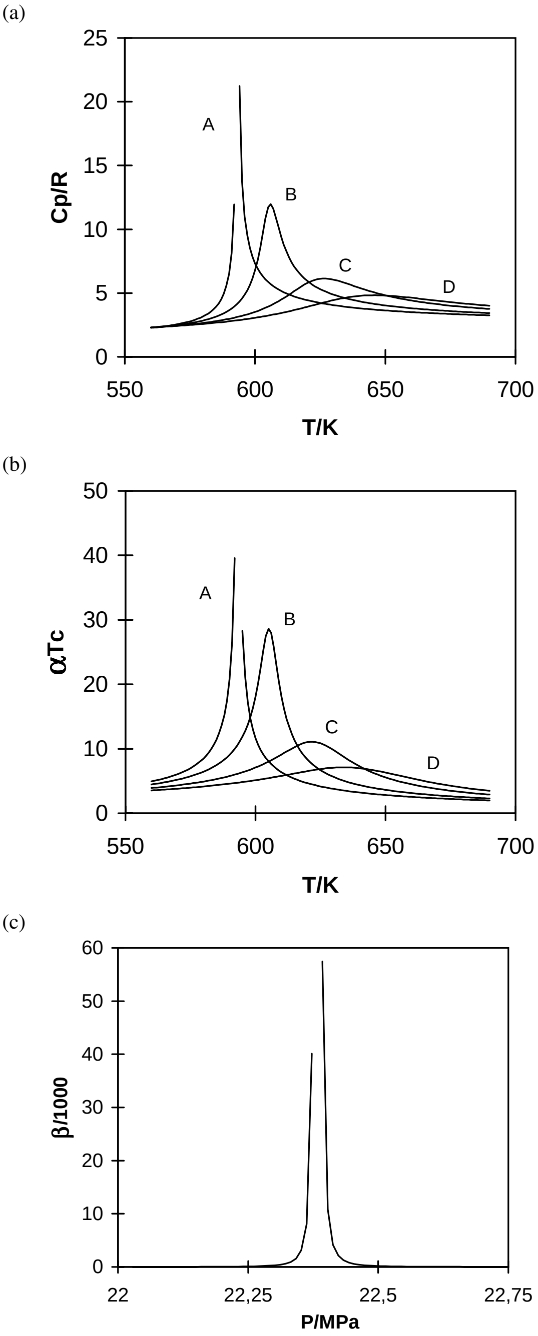

Fig. 6. (a) heat capacities C_p and (b) thermal expansivity α for H_2O, plotted against temperature at various pressures. A: $P = 22.38$ MPa; B: $P = 25.33$ MPa; C: $P = 30.40$ MPa; D: $P = 35.46$ MPa. (c) isothermal compressibility β for H_2O, plotted against pressure at $T = 593.2$ K.

heat capacity at $P_c = 22.38$ MPa diverges to infinity at $T = 593.2$ K and the other heat capacities at various pressures have a maximum value when P is larger than P_c. The values become smaller than the maximum when P is increased. A singularity of the heat capacity, however, is found at the critical point. The results in Figure 6 agree qualitatively with the cubic graphs for heat capacities of pure water [11]. The thermal expansivity at $P = P_c$, also, diverges to infin-

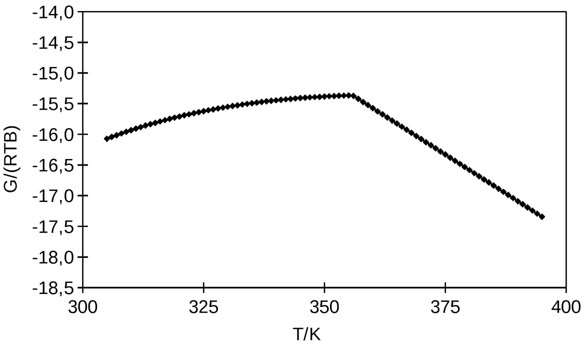

Fig. 7. Gibbs free energy for H_2O, plotted against temperature at $P = 0.101$ MPa; $T_B = 355.8$ K.

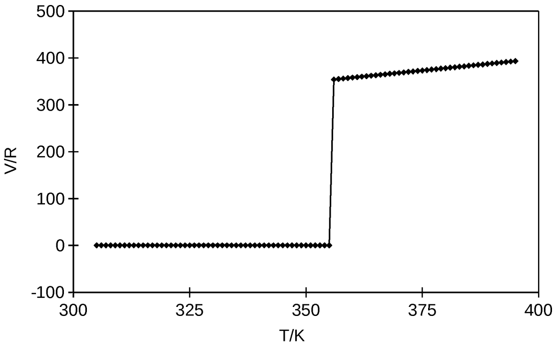

Fig. 9. Volume for H_2O, plotted against temperature at $P = 0.101$ MPa; $T_B = 355.8$ K.

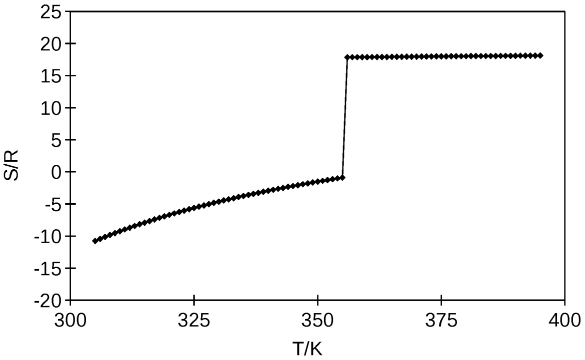

Fig. 8. Entropy for H_2O, plotted against temperature at $P = 0.101$ MPa; $T_B = 355.8$ K.

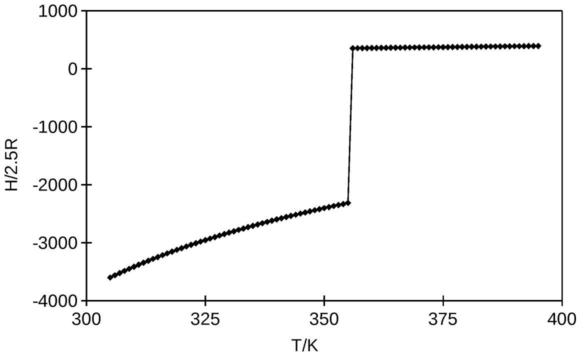

Fig. 10. Enthalpy for H_2O, plotted against temperature at $P = 0.101$ MPa; $T_B = 355.8$ K.

ity at $T = T_c$, and these quantities at various pressures show a tendency similar to that of the heat capacities (Fig. 6). The isothermal compressibility at $T = T_c$ diverges to infinity at $P = P_c$ (Fig. 6). 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]. Comparing Figures 2 – 6 with these diagrams [4], the behaviour in the neighbourhood of the critical point corresponds to a second-order phase transition.

Boiling temperatures T_B at 0.1013 MPa are easily found from (30), and the enthalpies of vaporization ΔH in (31) are obtained using these boiling temperatures. For CO_2 and SF_6 the boiling temperature are evaluated at boiling pressures of 0.518 and 0.227 MPa, respectively. Boiling temperatures and enthalpy changes of vaporization are shown in Tables 2. These results of T_B for CO, CO_2 (at 0.518 MPa), H_2O, CF_4, SF_6 (at 0.227 MPa), and C_2H_6 are in agreement with the experimental data within a few percent while ΔH is not qualitative approached [10]. Numerical results obtained with these thermodynamic functions for H_2O are displayed in Figures 7 – 11. The Gibbs free energy in Figure 7 indicates a polygonal line with a break at the boiling temperature. In the curves for entropy, volume, and enthalpy a jump is observed from the liquid to the gaseous phase at the boundary of the boiling point. As shown in Figure 11, the heat capacities do not diverge to infinity but show a discontinuity at the boiling point. The heat capacity at 16.2 MPa shows a singularity at this point. This singularity suggests a phase transition. The behaviour in the neighbourhood of the boiling point corresponds to a first-order phase transition [4].

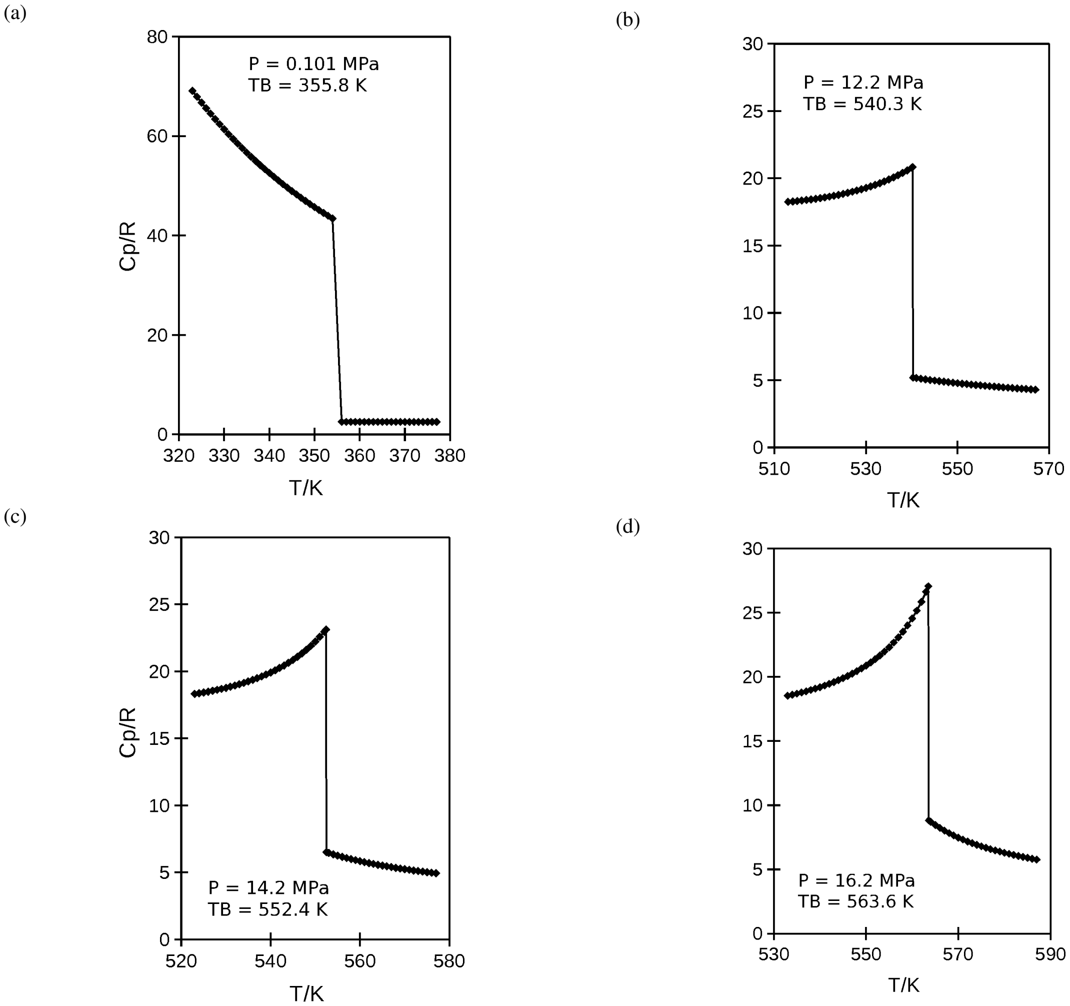

Fig. 11. Heat capacities at various pressures for H_2O, plotted against temperature. (a): $T_B = 355.8$ K at $P = 0.101$ MPa; (b): $T_B = 540.3$ K at $P = 12.2$ MPa; (c): $T_B = 552.4$ K at $P = 14.2$ MPa; (d): $T_B = 563.6$ K at $P = 16.2$ MPa.

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