Thermodynamic Quantities of Redlich-Kwong Gases in Isobaric Processes of Coexistence of Two Phases

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Z. Naturforsch. **60a,** 783 – 788 (2005); received September 12, 2005

The coexistence of gaseous and liquid phases in an isobaric process are investigated by applying the thermodynamic functions of the Redlich-Kwong equation. The boiling temperatures and the enthalpy changes of vaporization of 45 substances are obtained by numerical calculations. The results agree with the experimental data within a few percent for the 45 considered substances. Some thermodynamic quantities for C_3H_6 at 1 atm are calculated numerically as a function of T and drawn graphically. 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 jump at the boiling point. This suggests that a first-order phase transition may occur at the boiling point.

Key words: Redlich-Kwong Gas; Gibbs Free Energy; Isobaric Process;
Enthalpy Changes of Vaporization; First-order Phase Transition.

1. Introduction

Recently the behaviour near the critical point has been illustrated, analysing some thermodynamic functions in isobaric processes for van der Waals [1] and Lennard-Jones gases [2]. Especially, all thermodynamic functions in isobaric processes containing the two intensive variables T and P have been derived from the Gibbs free energy $G(T,P,N)$ which may be defined in terms of the partition function $Y(T,P,N)$ in the T-P grand canonical ensemble by $G(T,P,N) = -kT\log Y(T,P,N)$, see textbooks as e. g. [3 – 5] or [2, 6]. An attempt to investigate the thermodynamic quantities of Redlich-Kwong gases in isobaric processes is useful in order to compare them with various experimental data at 1 atm [7] and to discuss the observed first-order phase transition at the boiling point [3]. The Redlich-Kwong equation [8] is often considered as satisfactory among all two-parameter equations which retain the correction term that van der Waals attributed to the volume occupied by the molecules of the gas [9].

In this work, the changes in the Gibbs free energy and enthalpy in the state of coexistence of gaseous and liquid phases are obtained. Using the vapor-pressure equations for Redlich-Kwong gases, the boiling temperatures and the enthalpy changes by vaporization are obtained by numerical calculations. These thermodynamic quantities at atmospheric pressure for C_3H_6 are determined through numerical calculations and are graphically displayed for an isobaric process. The first-order phase transition of Redlich-Kwong gases at the boiling point is discussed.

2. Thermodynamic Functions in Isobaric Processes of Redlich-Kwong Gases

A Redlich-Kwong gas may be defined by an equation of state in which the van der Waals a-term is compensated by T^s,

$$P = \frac{RT}{V-b} - \frac{a}{T^s V(V+b)}, \tag{1}$$

where

$$RT_C = 3P_C V_C, \tag{2}$$

$$a = \frac{1}{9c}\frac{R^2 T_C^{2+s}}{P_C} = 0.42748\frac{R^2 T_C^{2+s}}{P_C}, \tag{3}$$

$$b = \frac{c}{3}\frac{RT_C}{P_C} = 0.08664\frac{RT_C}{P_C}, \tag{4}$$

and

$$\frac{b}{V_C} = c = \sqrt[3]{2} - 1 = 0.259921. \tag{5}$$

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Here the critical temperature, pressure and volume of a gas are expressed in terms of T_C, P_C and V_C, respectively. Equation (1) for $s = 0.5$ becomes the ordinary Redlich-Kwong equation [8]. The Helmholtz free energy $A(T,V)$ [4] is expressed in terms of a function $\varphi(T)$ of the temperature as

$$A(T,V) = -\int \left(\frac{RT}{V-b} - \frac{a}{bT^s V} - \frac{a}{bT^s(V+b)} \right) \mathrm{d}V + \varphi(T). \tag{6}$$

The first term in (6) is the configurational part, and the second one is the kinetic part [1, 6], namely

$$\varphi(T) = -kT \ln \left(\frac{2\pi mkT}{h^2} \right)^{3N/2}. \tag{7}$$

In classical statistical mechanics [5] the partition function of the Redlich-Kwong equation in the canonical ensemble may be defined as

$$Z(T,V,N) = \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} \frac{1}{N!} \exp \left[N \ln(V-b) + \frac{a}{bkT^{s+1}} \ln \frac{V+b}{V} \right]. \tag{8}$$

The partition function in the T-P grand canonical ensemble then can be obtained by the Laplace transform of $Z(T,V,N)$ from (8),

$$Y(T,P,N) = \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} \frac{1}{N!} \int_0^\infty \exp \left[N \left\{ \ln(V-b) + \frac{a}{bRT^{s+1}} \ln \frac{V+b}{V} - \frac{PV}{RT} \right\} \right] \mathrm{d}V. \tag{9}$$

If N now becomes very large, one can calculate $Y(T,P,N)$ in a saddle point approximation. From the condition that the derivative of the integrand of (9) equals zero, we obtain a cubic equation for V which is equivalent to the Redlich-Kwong equation:

$$V^3 - \frac{RT}{P} V^2 + \left(\frac{a}{T^s P} - \frac{RTb}{T^s P} - b^2 \right) V - \frac{ab}{T^s P} = 0. \tag{10}$$

We arrive at the Gibbs free energy per mol from (9):

$$G(T,P) = -RT \left[\frac{3}{2} \ln \frac{2\pi mkT}{h^2} - \ln \frac{N}{e} + \ln(V-b) + \frac{a}{bRT^{s+1}} \ln \frac{V+b}{V} - \frac{PV}{RT} \right]. \tag{11}$$

If the temperature, pressure and volume of the 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 Redlich-Kwong equation:

$$\left(\pi + \frac{1}{c\theta^s \phi(\phi + c)} \right) (\phi - c) = 3\theta. \tag{12}$$

Using the dimensionless thermodynamic variables θ, π and ϕ, the Gibbs free energy in (11) can be rewritten as

$$G(\theta,\pi) = -RT_\mathrm{C}\theta \left[C + \frac{3}{2} \ln \theta + \ln(\phi - c) + \frac{1}{3c^2\theta^{s+1}} \ln \frac{\phi + c}{\phi} - \frac{\pi\phi}{3\theta} \right] \tag{13}$$

with

$$C = \frac{3}{2} \ln \frac{2\pi mkT_\mathrm{C}}{h^2} - \ln \frac{N}{e} + \ln V_\mathrm{C} = -7.07228 + \frac{3}{2} \ln MT_\mathrm{C} + \ln V_\mathrm{C}. \tag{14}$$

Here M is the molecular weight, T_C is in units of K and V_C in units of cm^3. The Gibbs free energy is a function of the molecular weight and the critical constants of a particular gas. The reduced volume in this free energy, ϕ, is obtained from the cubic equation for ϕ found from (12) as

$$\phi^3 - \frac{3\theta}{\pi}\phi^2 + \left(\frac{1}{c\pi\theta^s} - \frac{3c\theta}{\pi} - c^2\right)\phi - \frac{1}{\pi\theta^s} = 0. \quad (15)$$

We finally arrive at the entropy, volume, enthalpy and heat capacity, calculated from the Gibbs free energy:

$$S = R\left[C + \frac{3}{2}(1+\ln\theta) + \ln(\phi - c) - \frac{s}{3c^2\theta^{s+1}}\ln\frac{\phi+c}{\phi}\right], \quad (16)$$

$$V = V_C\phi = \frac{RT_C}{3P_C}\phi, \quad (17)$$

$$H = RT_C\left[\frac{3}{2}\theta - \frac{(s+1)}{3c^2\theta^s}\ln\frac{\phi+c}{\phi} + \frac{\pi\phi}{3}\right], \quad (18)$$

and

$$C_p = R\left[\frac{3}{2} + \frac{s(s+1)}{3c^2\theta^{s+1}}\ln\frac{\phi+c}{\phi} + \left\{\frac{(s+1)\theta}{\phi - c} - \frac{s\pi}{3}\right\}\left(\frac{\mathrm{d}\phi}{\mathrm{d}\theta}\right)_\pi\right]. \quad (19)$$

The derivative of ϕ with respect to θ in (19) is calculated in the Appendix.

We now try to solve the cubic equation (15) for ϕ. Substituting $\phi = x + a$, the standard cubic equation without x^2-term is obtained:

$$x^3 + 3Px - 2Q = 0. \quad (20)$$

The value of a and the coefficients, P and Q in (20) are given, respectively, by

$$a = \frac{\theta}{\pi}, \quad (21)$$

$$P = -\left(\frac{\theta^2}{\pi^2} - \frac{1}{3c\pi\theta^s} + \frac{c\theta}{\pi} + \frac{c^2}{3}\right), \quad (22)$$

and

$$Q = \left(\frac{\theta^3}{\pi^3} - \frac{\theta^{1-s}}{2c\pi^2} + \frac{3c\theta^2}{2\pi^2} + \frac{c^2\theta}{2\pi} + \frac{1}{2\pi\theta^s}\right). \quad (23)$$

The determinant of the cubic equation is given as

$$D = P^3 + Q^2. \quad (24)$$

If the determinant is zero, a triple real root is found at the critical point ($\pi = 1$, $\theta = 1$ and $\phi = 1$) [1], or a double real root and a single root are found in the region of $\pi < 1$. In the latter case, the reduced temperature θ is given as θ_1 and θ_2 with $\theta_1 < \theta_2$. θ, therefore, satisfies $\theta < \theta_1$ in case of the pure liquid phase and $\theta > \theta_2$ in case of the gaseous phase. If the phase is purely gaseous or liquid, then the solutions of (15) consist of a single real root and of two conjugate complex roots, since the determinant is always positive. The real root is represented as

$$\phi = a + x = a + \sqrt[3]{R_1} + \sqrt[3]{R_2}, \quad (25)$$

where

$$R_1 = Q + \sqrt{D} \quad (26)$$

and

$$R_2 = Q - \sqrt{D}. \quad (27)$$

The reduced temperature θ has values in the region from θ_1 to θ_2 if there is coexistence of gaseous and liquid phases. The determinant is always negative, and the three real roots are expressed as, respectively,

$$\phi_G = a + 2\sqrt{-P}\cos\frac{\varphi}{3}, \quad (28)$$

$$\phi_L = a + 2\sqrt{-P}\cos\left(\frac{\varphi + 2\pi}{3}\right), \quad (29)$$

and

$$\phi_M = a + 2\sqrt{-P}\cos\left(\frac{\varphi + 4\pi}{3}\right), \quad (30)$$

with

$$\varphi = \arccos\frac{Q}{\sqrt{-P^3}}. \quad (31)$$

ϕ_G in (28) corresponds to the root for the gaseous state, ϕ_L in (29) to that of the liquid state, and ϕ_M in (30) is the root in the region from ϕ_L to ϕ_G. Especially, ϕ_M equals to ϕ_G at $\theta = \theta_2$ and to ϕ_L at $\theta = \theta_1$ in the case that this cubic equation consists of a double root and a single root at $D = 0$. If the gaseous and liquid phases coexist, the change of the Gibbs free energy between the gaseous and liquid phases at arbitrary reduced temperature and pressure is obtained as

$$\Delta G = -RT_C\theta\left[\ln\frac{\phi_G - c}{\phi_L - c} + \frac{1}{3c^2\theta^{s+1}} \cdot \ln\frac{(\phi_G + c)\phi_L}{(\phi_L + c)\phi_G} - \frac{\pi}{3\theta}(\phi_G - \phi_L)\right]. \quad (32)$$

Table 1. Boiling temperatures (T_B/K) and enthalpy changes of vaporization (ΔH/kJ mol^{-1}) at 1 atm derived from the Redlich-Kwong equation at $s = 0.5$.

	Redlich-Kwong gas		Experimental results [7]	
Gas	T_B	ΔH	T_B	ΔH
CO	82.5	6.56	81.7	6.04
Cl_2	240.2	21.77	238.7	20.42
Br_2	327.8	31.05	331.9	30.17
HCl	185.7	17.03	188.1	16.2
HBr	207.3	19.09	206.1	17.66
H_2O	341.4	35.87	373.2	40.66
NH_3	266.0	21.67	239.7	23.35
N_2O	179.3	16.10	184.7	16.55
H_2S	212.1	19.67	212.8	18.66
CS_2	317.2	28.87	319.4	26.74
CCl_4	336.5	28.02	349.7	30.00
CH_4	115.2	9.61	111.7	8.18
C_2H_6	183.5	15.46	184.5	14.71
C_3H_8	225.2	18.52	231.1	18.77
C_4H_{10}	261.7	21.12	272.7	22.39
C_2H_4	169.7	14.33	169.4	13.54
C_3H_6	220.4	18.40	225.4	18.41
1-C_4H_8	256.8	20.93	266.9	21.91
C_2H_2	181.3	15.86	189.2	16.95
c-C_6H_{12}	338.3	27.63	353.9	29.96
C_6H_6	337.6	28.45	353.9	30.76
CH_3OCH_3	238.1	20.38	248.3	21.51
CH_3Cl	242.9	21.53	248.9	21.42
CH_3Br	264.6	24.40	276.7	23.91
CH_3I	308.5	27.29	315.6	27.20

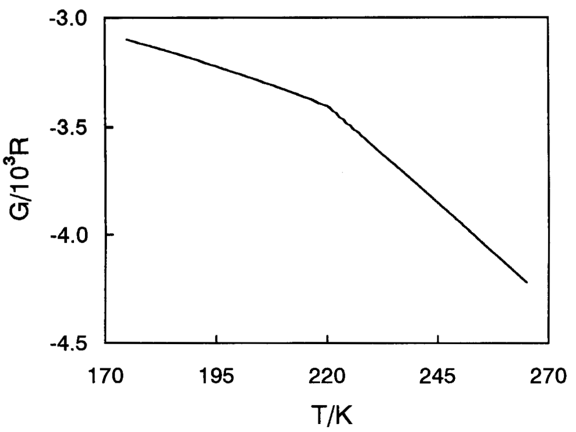

Fig. 1. The Gibbs free energy of C_3H_6 plotted against the temperature at $P = 1$ atm. $T_B = 220.4$ K.

The enthalpy changes are written as

$$\Delta H = RT_C\left[-\frac{s+1}{3c^2\theta^s}\ln\frac{(\phi_G+c)\phi_L}{(\phi_L+c)\phi_G}+\frac{\pi}{3}(\phi_G-\phi_L)\right]. \tag{33}$$

To satisfy Maxwell's rule between ϕ_L and ϕ_G this cubic equation determines ϕ_M. In the phase equilibrium between gaseous and liquid states, the vapour pressure equation for Redlich-Kwong gases is equivalent to terms within the brackets of (32) at $\Delta G = 0$; in this equation the internal configuration of vibrations and rotations in the gaseous and liquid states of a gas [10] are neglected. Also, the reduced boiling temperature θ_B is located in the range between θ_1 to θ_2. $\Delta H(\theta_B = T_B/T_C, \pi = 1/P_C)$ in (33) equals the enthalpy change of vaporization at T_B and 1 atm. Assuming that the reduced volume in the liquid phase ϕ_L is transformed into ϕ_G in the gaseous phase at the reduced boiling point, some thermodynamic quantities as functions of the variable θ may be derived from (13)–(19), and ϕ in (25), (28), and (29) denoted as ϕ_L in the region of $\theta < \theta_B$ and ϕ_G in $\theta > \theta_B$.

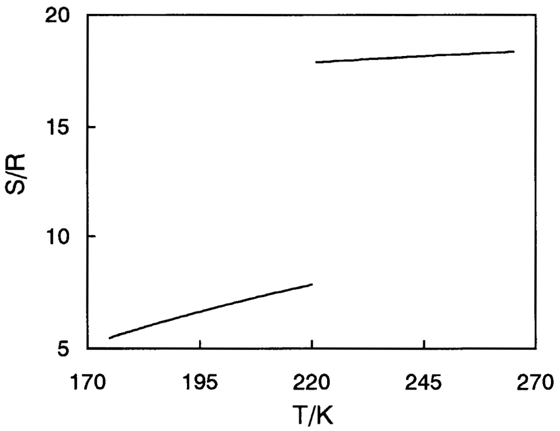

Fig. 2. The entropy of C_3H_6 plotted against the temperature at $P = 1$ atm. $T_B = 220.4$ K.

3. Numerical Results

Some thermodynamic functions are written as functions of the variables T and P and are generally applicable to all substances by using the two critical constants T_C and P_C [7]. Boiling temperatures at 1 atm, T_B, are easily found from (32), and the enthalpies of vaporization, ΔH, in (33) are obtained using these boiling temperatures. The boiling temperatures and the enthalpy changes by vaporization are shown in Table 1. These results of T_B agree well with the experimental data [7] within a few percent, except for H_2O and NH_3. ΔH of Br_2, N_2O, C_3H_8, C_3H_6, 1-C_4H_8, CH_3Cl, CH_3Br, and CH_3I are all within a few percent. Numerical results obtained with these thermodynamic functions for C_3H_6 are displayed in Figs. 1–5. The Gibbs free energy in Fig. 1 indicates a polygonal line with a break at the boiling temperature. In the curves for

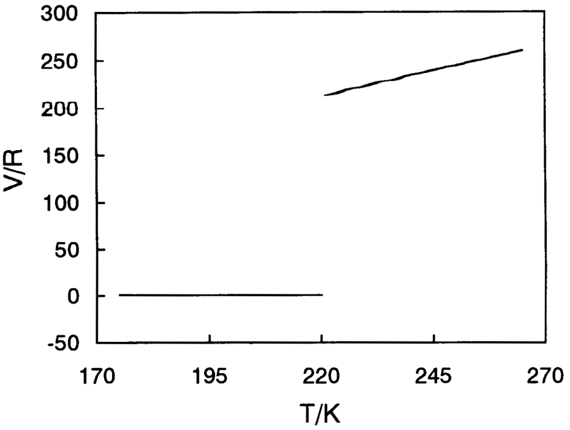

Fig. 3. The volume of C_3H_6 plotted against the temperature at $P = 1$ atm. $T_B = 220.4$ K.

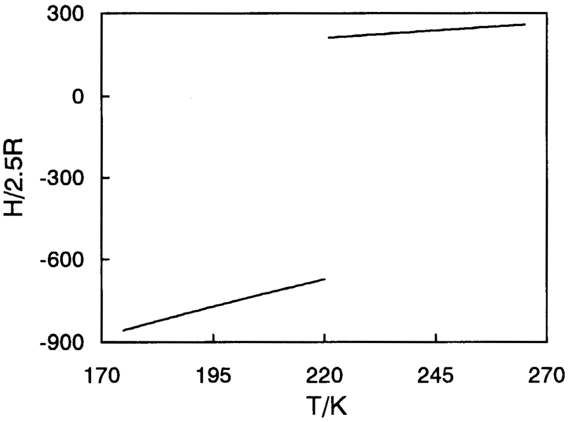

Fig. 4. The enthalpy of C_3H_6 plotted against the temperature at $P = 1$ atm. $T_B = 220.4$ K.

the 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 Fig. 5, the heat capacities do not diverge to infinity but show a discontinuity at the boiling point. The heat capacity at 35 atm shows a singularity at the boiling point. This singularity suggests a phase transition. The generalized diagrams of some thermodynamic quantities accompanying the first-order phase transition are typically described in textbooks of physical chemistry [3]. Comparing Figs. 1 – 5 with these diagrams [3], the behaviour in the neighbourhood of the boiling point corresponds to a first-order phase transition.

In addition to Table 1, the precisions of T_B and ΔH can be improved by fitting the parameter s in (1). The T_B and ΔH values of 41 substances in Table 2 agree well with the experimental data [7] within a few percent.

Table 2. Boiling temperatures (T_B/K) and enthalpy changes of vaporization (ΔH/kJ mol^{-1}) at 1 atm derived from the Redlich-Kwong equation involving the parameter s.

		Redlich-Kwong gas		Experimental result [7]	
Gas	s	T_B	ΔH	T_B	ΔH
Ne	0.35	27.0	1.85	27.0	1.84
Ar	0.36	86.5	6.61	87.3	6.53
Kr	0.39	119.9	9.55	119.8	9.66
Xe	0.39	164.8	13.30	165.0	13.00
N_2	0.41	76.5	5.69	77.4	5.58
O_2	0.38	89.0	6.94	90.2	6.82
CO	0.43	80.8	6.13	81.7	6.04
NO	1.00	119.3	14.02	121.4	13.81
F_2	0.40	83.3	6.63	85.0	6.53
Cl_2	0.45	236.1	20.69	238.7	20.42
HCl	0.47	183.8	16.52	188.1	16.15
HBr	0.44	202.9	17.94	206.1	17.66
H_2O	0.66	361.5	42.06	373.2	40.66
NH_3	0.60	233.7	23.91	239.7	23.35
N_2O	0.54	181.6	16.74	184.7	16.55
H_2S	0.46	209.2	18.88	212.8	18.66
CS_2	0.45	311.8	27.43	319.4	26.74
CCl_4	0.59	345.3	30.46	349.7	30.00
CH_4	0.35	109.5	8.23	111.7	8.18
C_2H_6	0.45	180.6	14.71	184.5	14.71
C_3H_8	0.52	226.5	18.88	231.1	18.77
C_4H_{10}	0.58	267.6	22.73	272.7	22.39
C_5H_{12}	0.64	303.4	26.17	309.2	25.77
C_6H_{14}	0.70	336.4	29.35	341.9	28.85
C_7H_{16}	0.75	364.6	32.22	371.6	31.70
$C_{10}H_{22}$	0.90	438.4	39.87	447.3	39.28
C_2H_4	0.46	167.0	13.77	169.4	13.54
C_3H_6	0.52	221.8	18.76	225.4	18.41
1-C_4H_8	0.57	262.0	22.33	266.9	21.91
C_2H_2	0.59	186.3	17.27	189.2	16.95
c-C_6H_{12}	0.61	348.8	30.56	353.9	29.96
C_6H_6	0.60	347.6	31.23	353.3	30.76
CH_3OH	0.86	324.8	36.77	337.8	35.25
C_2H_5OH	0.99	341.8	39.87	351.5	38.74
CH_3COCH_3	0.67	321.1	29.90	329.4	29.12
$CH_3COOC_2H_5$	0.77	344.4	32.78	350.3	32.22
CH_3CHO	0.63	284.1	26.57	293.6	29.12
CH_3OCH_3	0.58	243.9	21.98	248.2	21.51
$C_2H_5NH_2$	0.72	287.4	28.40	289.7	28.03
$CHCl_3$	0.59	327.5	29.79	334.3	29.71
CH_3F	0.60	193.3	17.90	194.8	17.70

Appendix

The derivative of ϕ in (25) with respect to θ can be represented as

$$\left(\frac{\mathrm{d}\phi}{\mathrm{d}\theta}\right)_{\pi} = \frac{\mathrm{d}a}{\mathrm{d}\theta} + \frac{1}{3}\left[\frac{1}{\sqrt[3]{R_1{}^2}}\left(\frac{\mathrm{d}Q}{\mathrm{d}\theta} + \frac{1}{2\sqrt{D}}\frac{\mathrm{d}D}{\mathrm{d}\theta}\right) + \frac{1}{\sqrt[3]{R_2{}^2}}\left(\frac{\mathrm{d}Q}{\mathrm{d}\theta} - \frac{1}{2\sqrt{D}}\frac{\mathrm{d}D}{\mathrm{d}\theta}\right)\right]. \tag{A.1}$$

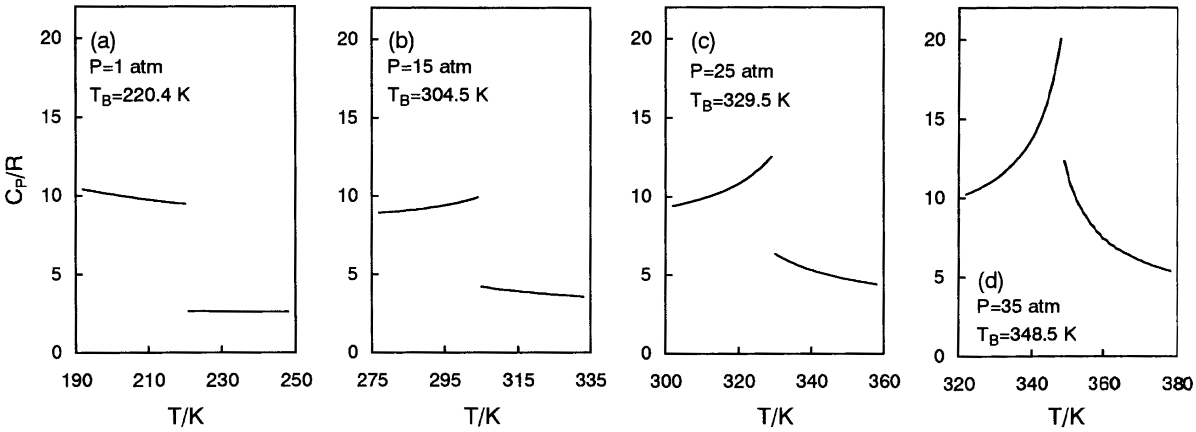

Fig. 5. The heat capacities at various pressures of C_3H_6 plotted against the temperature. (a) $T_B = 220.4$ K at $P = 1$ atm; (b) $T_B = 304.5$ K at $P = 15$ atm; (c) $T_B = 329.5$ K at $P = 25$ atm; and (d) $T_B = 348.5$ K at $P = 35$ atm.

The derivatives of ϕ_G from (28) and ϕ_L from (29) with respect to θ are obtained as

$$\left(\frac{d\phi_G}{d\theta}\right)_\pi = \frac{da}{d\theta} - \frac{1}{\sqrt{-P}}\frac{dP}{d\theta}\cos\frac{\varphi}{3} + \frac{2\sqrt{-P}}{3\sqrt{1-z^2}}\sin\frac{\varphi}{3}\frac{dz}{d\theta}, \tag{A.2}$$

and

$$\left(\frac{d\phi_L}{d\theta}\right)_\pi = \frac{da}{d\theta} - \frac{1}{\sqrt{-P}}\frac{dP}{d\theta}\cos\left(\frac{\varphi+2\pi}{3}\right) + \frac{2\sqrt{-P}}{3\sqrt{1-z^2}}\sin\left(\frac{\varphi+2\pi}{3}\right)\frac{dz}{d\theta}, \tag{A.3}$$

with

$$\frac{dz}{d\theta} = \frac{1}{\sqrt{-P^3}}\frac{dQ}{d\theta} + \frac{3Q}{2(\sqrt{-P})^5}\frac{dP}{d\theta}, \tag{A.4}$$

where

$$z = \frac{Q}{\sqrt{-P^3}}.$$

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