

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

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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  $T^s$ ,

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

where

$$RT_C = 3P_C V_C, \quad (2)$$

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

$$b = \frac{c}{3} \frac{RT_C}{P_C} = 0.08664 \frac{RT_C}{P_C}, \quad (4)$$

and

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

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

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

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

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

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

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

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),

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

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:

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

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

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

If the temperature, pressure and volume of the gas are expressed in terms of  $T_C$ ,  $P_C$  and  $V_C$ , respectively, then  $T = \theta T_C$ ,  $P = \pi P_C$  and  $V = \phi V_C$ . The reduced equation of state obeying the principle of corresponding states is easily derived from the Redlich-Kwong equation:

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

Using the dimensionless thermodynamic variables  $\theta$ ,  $\pi$  and  $\phi$ , the Gibbs free energy in (11) can be rewritten as

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

with

$$C = \frac{3}{2} \ln \frac{2\pi mkT_C}{h^2} - \ln \frac{N}{e} + \ln V_C = -7.07228 + \frac{3}{2} \ln MT_C + \ln V_C. \quad (14)$$

Here  $M$  is the molecular weight,  $T_C$  is in units of K and  $V_C$  in units of  $\text{cm}^3$ . 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,  $\phi$ , is obtained from the cubic equation for  $\phi$  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

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

The derivative of  $\phi$  with respect to  $\theta$  in (19) is calculated in the Appendix.

We now try to solve the cubic equation (15) for  $\phi$ . 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  $\theta$  is given as  $\theta_1$  and  $\theta_2$  with  $\theta_1 < \theta_2$ .  $\theta$ , 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  $\theta$  has values in the region from  $\theta_1$  to  $\theta_2$  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

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

$\phi_G$  in (28) corresponds to the root for the gaseous state,  $\phi_L$  in (29) to that of the liquid state, and  $\phi_M$  in (30) is the root in the region from  $\phi_L$  to  $\phi_G$ . Especially,  $\phi_M$  equals to  $\phi_G$  at  $\theta = \theta_2$  and to  $\phi_L$  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 ( $\Delta H$ /kJ mol<sup>-1</sup>) at 1 atm derived from the Redlich-Kwong equation at  $s = 0.5$ .

Gas	Redlich-Kwong gas		Experimental results [7]	
	$T_B$	$\Delta H$	$T_B$	$\Delta H$
CO	82.5	6.56	81.7	6.04
Cl <sub>2</sub>	240.2	21.77	238.7	20.42
Br <sub>2</sub>	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 <sub>2</sub> O	341.4	35.87	373.2	40.66
NH <sub>3</sub>	266.0	21.67	239.7	23.35
N <sub>2</sub> O	179.3	16.10	184.7	16.55
H <sub>2</sub> S	212.1	19.67	212.8	18.66
CS <sub>2</sub>	317.2	28.87	319.4	26.74
CCl <sub>4</sub>	336.5	28.02	349.7	30.00
CH <sub>4</sub>	115.2	9.61	111.7	8.18
C <sub>2</sub> H <sub>6</sub>	183.5	15.46	184.5	14.71
C <sub>3</sub> H <sub>8</sub>	225.2	18.52	231.1	18.77
C <sub>4</sub> H <sub>10</sub>	261.7	21.12	272.7	22.39
C <sub>2</sub> H <sub>4</sub>	169.7	14.33	169.4	13.54
C <sub>3</sub> H <sub>6</sub>	220.4	18.40	225.4	18.41
1-C <sub>4</sub> H <sub>8</sub>	256.8	20.93	266.9	21.91
C <sub>2</sub> H <sub>2</sub>	181.3	15.86	189.2	16.95
c-C <sub>6</sub> H <sub>12</sub>	338.3	27.63	353.9	29.96
C <sub>6</sub> H <sub>6</sub>	337.6	28.45	353.9	30.76
CH <sub>3</sub> OCH <sub>3</sub>	238.1	20.38	248.3	21.51
CH <sub>3</sub> Cl	242.9	21.53	248.9	21.42
CH <sub>3</sub> Br	264.6	24.40	276.7	23.91
CH <sub>3</sub> I	308.5	27.29	315.6	27.20

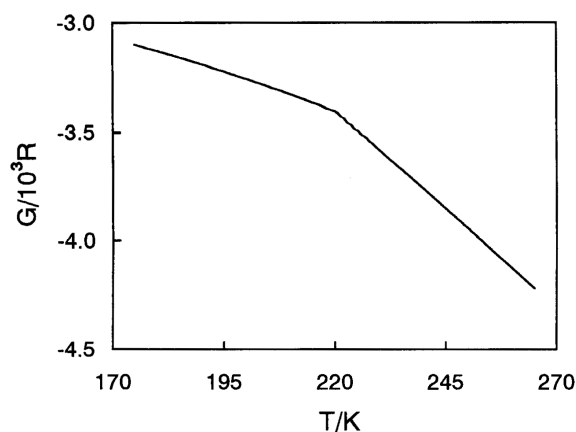


Fig. 1. The Gibbs free energy of C<sub>3</sub>H<sub>6</sub> plotted against the temperature at  $P = 1$  atm.  $T_B = 220.4$  K.

The enthalpy changes are written as

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

To satisfy Maxwell's rule between  $\phi_L$  and  $\phi_G$  this cubic equation determines  $\phi_M$ . In the phase equilib-

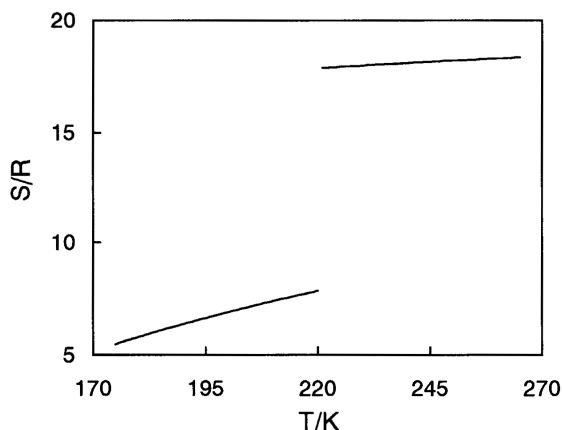


Fig. 2. The entropy of C<sub>3</sub>H<sub>6</sub> plotted against the temperature at  $P = 1$  atm.  $T_B = 220.4$  K.

rium 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  $\theta_B$  is located in the range between  $\theta_1$  to  $\theta_2$ .  $\Delta H(\theta_B = T_B/T_C, \pi = 1/P_C)$  in (33) equals the enthalpy change of vaporization at  $T_B$  and 1 atm. Assuming that the reduced volume in the liquid phase  $\phi_L$  is transformed into  $\phi_G$  in the gaseous phase at the reduced boiling point, some thermodynamic quantities as functions of the variable  $\theta$  may be derived from (13)–(19), and  $\phi$  in (25), (28), and (29) denoted as  $\phi_L$  in the region of  $\theta < \theta_B$  and  $\phi_G$  in  $\theta > \theta_B$ .

### 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,  $\Delta H$ , 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<sub>2</sub>O and NH<sub>3</sub>.  $\Delta H$  of Br<sub>2</sub>, N<sub>2</sub>O, C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub>, 1-C<sub>4</sub>H<sub>8</sub>, CH<sub>3</sub>Cl, CH<sub>3</sub>Br, and CH<sub>3</sub>I are all within a few percent. Numerical results obtained with these thermodynamic functions for C<sub>3</sub>H<sub>6</sub> 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

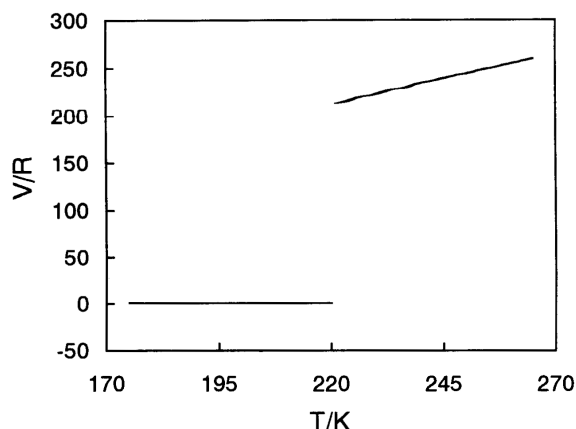


Fig. 3. The volume of  $C_3H_6$  plotted against the temperature at  $P = 1$  atm.  $T_B = 220.4$  K.

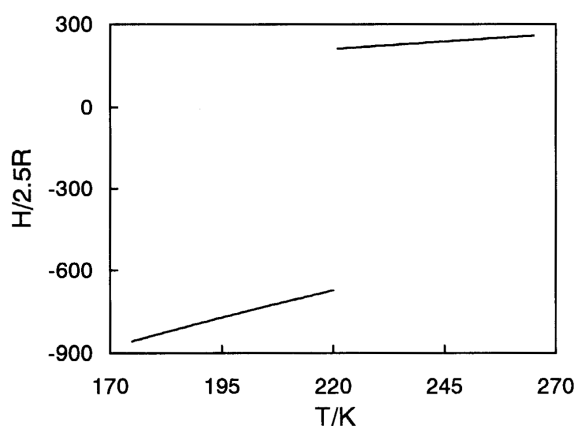


Fig. 4. The enthalpy of  $C_3H_6$  plotted against the temperature at  $P = 1$  atm.  $T_B = 220.4$  K.

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  $\Delta H$  can be improved by fitting the parameter  $s$  in (1). The  $T_B$  and  $\Delta H$  values of 41 substances in Table 2 agree well with the experimental data [7] within a few per cent.

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

Gas	$s$	Redlich-Kwong gas		Experimental result [7]	
		$T_B$	$\Delta H$	$T_B$	$\Delta H$
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 <sub>2</sub>	0.41	76.5	5.69	77.4	5.58
O <sub>2</sub>	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 <sub>2</sub>	0.40	83.3	6.63	85.0	6.53
Cl <sub>2</sub>	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 <sub>2</sub> O	0.66	361.5	42.06	373.2	40.66
NH <sub>3</sub>	0.60	233.7	23.91	239.7	23.35
N <sub>2</sub> O	0.54	181.6	16.74	184.7	16.55
H <sub>2</sub> S	0.46	209.2	18.88	212.8	18.66
CS <sub>2</sub>	0.45	311.8	27.43	319.4	26.74
CCl <sub>4</sub>	0.59	345.3	30.46	349.7	30.00
CH <sub>4</sub>	0.35	109.5	8.23	111.7	8.18
C <sub>2</sub> H <sub>6</sub>	0.45	180.6	14.71	184.5	14.71
C <sub>3</sub> H <sub>8</sub>	0.52	226.5	18.88	231.1	18.77
C <sub>4</sub> H <sub>10</sub>	0.58	267.6	22.73	272.7	22.39
C <sub>5</sub> H <sub>12</sub>	0.64	303.4	26.17	309.2	25.77
C <sub>6</sub> H <sub>14</sub>	0.70	336.4	29.35	341.9	28.85
C <sub>7</sub> H <sub>16</sub>	0.75	364.6	32.22	371.6	31.70
C <sub>10</sub> H <sub>22</sub>	0.90	438.4	39.87	447.3	39.28
C <sub>2</sub> H <sub>4</sub>	0.46	167.0	13.77	169.4	13.54
C <sub>3</sub> H <sub>6</sub>	0.52	221.8	18.76	225.4	18.41
1-C <sub>4</sub> H <sub>8</sub>	0.57	262.0	22.33	266.9	21.91
C <sub>2</sub> H <sub>2</sub>	0.59	186.3	17.27	189.2	16.95
c-C <sub>6</sub> H <sub>12</sub>	0.61	348.8	30.56	353.9	29.96
C <sub>6</sub> H <sub>6</sub>	0.60	347.6	31.23	353.3	30.76
CH <sub>3</sub> OH	0.86	324.8	36.77	337.8	35.25
C <sub>2</sub> H <sub>5</sub> OH	0.99	341.8	39.87	351.5	38.74
CH <sub>3</sub> COCH <sub>3</sub>	0.67	321.1	29.90	329.4	29.12
CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>	0.77	344.4	32.78	350.3	32.22
CH <sub>3</sub> CHO	0.63	284.1	26.57	293.6	29.12
CH <sub>3</sub> OCH <sub>3</sub>	0.58	243.9	21.98	248.2	21.51
C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub>	0.72	287.4	28.40	289.7	28.03
CHCl <sub>3</sub>	0.59	327.5	29.79	334.3	29.71
CH <sub>3</sub> F	0.60	193.3	17.90	194.8	17.70

## Appendix

The derivative of  $\phi$  in (25) with respect to  $\theta$  can be represented as

$$\left(\frac{d\phi}{d\theta}\right)_\pi = \frac{da}{d\theta} + \frac{1}{3} \left[ \frac{1}{\sqrt[3]{R_1^2}} \left( \frac{dQ}{d\theta} + \frac{1}{2\sqrt{D}} \frac{dD}{d\theta} \right) + \frac{1}{\sqrt[3]{R_2^2}} \left( \frac{dQ}{d\theta} - \frac{1}{2\sqrt{D}} \frac{dD}{d\theta} \right) \right]. \quad (A.1)$$

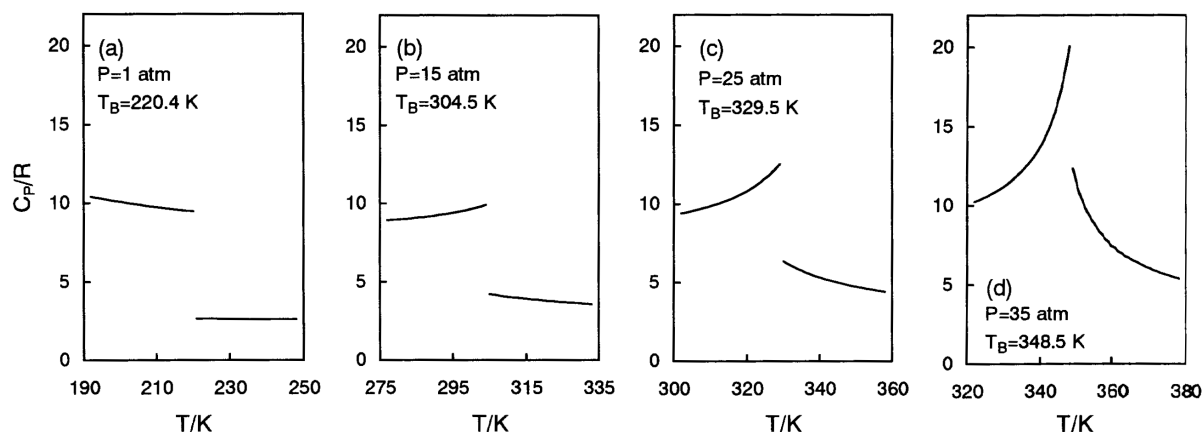


Fig. 5. The heat capacities at various pressures of  $C_3H_6$  plotted against the temperature. (a)  $T_B = 220.4$  K at  $P = 1$  atm; (b)  $T_B = 304.5$  K at  $P = 15$  atm; (c)  $T_B = 329.5$  K at  $P = 25$  atm; and (d)  $T_B = 348.5$  K at  $P = 35$  atm.

The derivatives of  $\phi_G$  from (28) and  $\phi_L$  from (29) with respect to  $\theta$  are obtained as

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

and

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

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

where

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

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