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Transient State Theory of Significant Liquid Structure applied to Cyclohexane

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액체구조에 관한 천이상태이론의 싸이클로 헥산에 대한 적용

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요 약

싸이클로헥산의 분자는 액체상태에서 대부분이 chair form으로 되어 있음이 알려져 있다. 이 사실로부터 싸이클로헥산의 액체는 Chair form 만으로 되어있다는 가정하에 액체구조의 천이상태이론을 적용시켜 상태합을 구하고 이로부터 싸이클로헥산의 몰부피, 증기압, 한계점, 증발엔트로피 및 압축률 등의 열역학적 량을 계산한 결과 측정치와 잘 맞는 값을 얻었다.

Abstract

It is known that almost all cyclohexane molecules are chair form in liquid state. Therefore, only chair form is considered in formulating the partition function for liquid cyclohexane, according to the Transient State Theory of Significant Liquid Structure proposed by Pak, Ahn and Chang. The thermodynamic quantities such as molar volume, vapor pressure, entropy of vaporization and compressibility of the liquid are calculated. The results are in good agreement with experimental values.

Introduction

It is known that cyclohexane has two forms, the boat and the chair forms. Both forms maintain normal tetrahedral angle and consequently their rings are free from angular strain. An extensive study of cyclohexane by electron diffraction method(1) has shown that practicaly all the molecules are in the symmetrical chair form. From several theoretical and semiempirical results the magnitude of the energy difference between the two forms are estimated to be in the range between 1.31 to 10.6 K cal/mole.(2,4,5,6)

In 1952, Turner(4) has estimated that the value is 5.6 K cal/mole(in the gas phase at 25°C) in favor of the chair form. From this result, the calculated equilibrium ratio between the boat form and the chair form, N_b/N_C, is in the order of 10^{-4} at the temperature of liquid range.

"Therefore, we may conclude that the contribution of the boat form to the various thermodynamic properties of the liquid cyclohexane is negligibly small. In this paper, various thermodynamic properties of the liquid are calculated assuming that all the molecules in the stable state are in the chair form.

Partition Function

Recently, Pak, Ahn and Chang(10) have proposed the Transient State Theory of Significant Liquid Structure to compensate the theoretical defects of the Significant Liquid Structure Theory developed by

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H. Eyring and his coworkers(8,9), and they have applied the theory to various lquids with success. In the theory, it is assumed that liquid molecules are partitioned by solid-like, transient and gas-like degrees of freedom. The fractions of the respective molecules are taken as $\frac{V_s}{V}\alpha$, $\frac{V_s}{V}(1-\alpha)$ and $\frac{V-V_s}{V}$, respectively, where V_s and V are molar volume of the solid and of the liquid at the triple point, respectively; α is the fraction of bonded molecules, which possess solid-like degree of freedom. The solid-like molecules transform into transient state molecules when it aquire strain energy,

$$\epsilon=\frac{aE_s}{n(V/V_s-1)}.$$

Here "n" stands for the number of nearest neighboring sites to a molecules, which is given by 12 V_s/V_t, where V_t being the molar volume of the liquid at the triple point; E_s is the ground state energy of the liquid molecules and "a" is the proportionality constant. The gas-like molecules are assumed to be ideal. According to the above theory the partition function for cyclohexane can be written as

$$f=\frac{(N_s+N_t)}{N_s!N_t!}\cdot f_s^{N_s}\cdot f_t^{N_t}\cdot f_g^{N_g}\cdot\frac{1}{N_g!}$$

$$=\frac{\left[\frac{V_s}{V}\cdot N\right]!}{\left[\frac{V_s}{V}\alpha N\right]!\left[\frac{V_s}{V}(1-\alpha)N\right]!}\left[\frac{e^{Es/RT}}{(1-e^{-\theta s/T})^3}\right]^{\frac{Vs}{V}\alpha N}\cdot$$

$$\left[\frac{n\cdot\frac{V-V_s}{V_s}e^{(Es-E)/RT}}{(1-e^{-\theta t/T})^3}\right]^{\frac{Vs}{V}(1-\alpha)N}\cdot$$

$$\left[\frac{(2\pi mkT)^{3/2}}{h^3}\cdot\frac{eV}{N}\right]^{\frac{V-Vs}{V}N}\cdot$$

$$\left[\frac{\sqrt{\pi}(8\pi^2kT)^{3/2}(I_AI_BI_C)^{1/2}}{\sigma h^3}\prod_{i=1}^{48}\frac{1}{1-e^{-h\nu_i/kT}}\right]^N \quad (1)$$

where θ_s and θ_t are Einstein characteristic temperatures for the molecules of solid-like and transient, respectively. The subscript s, t, and g denote solid-like, transient state and gas-like molecules, respectively. The other notations have the usual physical meaning. α is evaluated by the method developed by Pak, Ahn and Chang, and given by $\alpha=\frac{f_s}{f_s+f_t}$ when the expression of α is introduced to equation (I), the following expression can be obtained.

$$f_t=\left[\frac{e^{Es/RT}}{(1-e^{-\theta s/T})^3}\left\{1+\lambda(x-1)e^{-\frac{aEs}{n(x-1)RT}}\right\}\right]^{N\frac{Vs}{V}}\cdot$$

$$\left[\frac{(2\pi mkT)^{3/2}}{h^3}\cdot\frac{eV}{N}\right]^{N\frac{V-Vs}{V}}\cdot$$

$$\left[\frac{\sqrt{\pi}(8\pi^2kT)^{3/2}(I_AI_BI_C)^{1/2}}{6h^3}\prod_{i=1}^{48}\frac{1}{1-e^{-h\nu_i/kT}}\right]^N \quad (2)$$

where $\lambda=n\left(\frac{1-e^{-\theta s/T}}{1-e^{-\theta t/T}}\right)^3\frac{b_t}{b_s}$, $x=\frac{V}{V_s}$

where b_t and b_s represent the partition functions for degrees of freedom of molecular rotation and intra-molecular vibration of transient state molecules and those of solid-like molecules, respectively. Cyclohexane has a normal entropy of fusion (2.24 e.u.)(7). From this fact and the X-ray data of solid at the triple point, it can be assumed that the molecules rotate freely in the liquid state. The moment of inertia(3) are 193.86×10⁻⁴⁰ g·cm² for I_A and I_B, and 333.95×10⁻⁴⁰g·cm² for I_C, and symmetry number is 6.

The parameters are determined according to the method proposed by Pak, Ahn and Chang. The melting point data and parameters determined are listed in the table I.

Table I. Melting point data and parameters

P	0.0526 atm	θ_s	76.271°K
V	109.6 cc/mole	θ_t	75.146°K
T	279.82°K	E_s	8823.2 Cal/mole
H_v	8184.5 Cal/mole	a	0.03187
V_s	100.2 cc/mole		

The Calculation of Thermodynamic Properties

The various thermodynamic properties can be easily calculated from respective thermodynamic expressions obtained from the equation

$$A=-kT\ln f$$

1. Molar vloume and vapor pressure; Molar volume and vapor pressure are obtained by plotting Helmholtz free energy against molar volume for the given temperature. The negative slope of the common tangential line of the plotted curve at the liquid and the gaseous regions gives the vapor pressure and the corresponding tangential points at the liquid region gives the molar volume of the liquid. The calculated and observed values of liquid molar volumes and vapor pressures at various temperatures are given in table II and III

Table II Molar volume

$T°K$	$V_{calc.}$ (cc)	$V_{obs.}$(cc)(13, 14)	$\varDelta\%$
279. 82(m. p.)	106. 4	106. 4	0. 00
298. 15	109. 6	108. 7	0. 83
303. 15	110. 3	109. 4	0. 82
313. 15	111. 5	110. 6	0. 79
323. 142	112. 9	112. 2	0. 62
343. 15	115. 8	115. 1	0. 59
353. 90(b. p.)	117. 4	116. 9	0. 39

Table III. Vapor pressure

$T°K$	$P_{calc.}$ (atm)	$P_{obs.}$ (atm) (13,14)	$\varDelta\%$
279. 82(m. p.)	0. 0526	0. 0526	0. 00
298. 15	0. 1288	0. 1284	0. 31
303. 15	0. 1605	0. 1605	0. 26
313. 15	0. 2441	0. 2430	0. 45
323. 142	0. 3602	0. 3575	0. 75
343. 15	0. 7270	0. 7156	1. 59
353. 90(b. p.)	1. 022	1. 000	2. 22

2. **Entropy of Vaporization**; Entropy is calculated from the following equations:

$$S_{vap}=S_g-S_l \text{ and } S_g=-\left(\frac{\partial A_g}{\partial T}\right)_V,\ S_l=-\frac{(\partial A_l)}{\partial T}\Big)_V$$

The calculated and experimental values are tabulated in table IV.

Table IV. Entropy of vaporization

$T°K$	$S_{calc.}$ e. u.	$S_{obs.}$ e. u. (13)	$\varDelta\%$
298. 15	26. 64	—	—
353. 90(b. p.)	20. 88	20. 3	2. 5

3. **Critical values**; Critical values are calculated using the condition of $\left(\frac{\partial p}{\partial V}\right)_T=0$ and $\left(\frac{\partial^2 p}{\partial V^2}\right)_T=0$, and given in table V

Table V. Critical values

	$T°K$	P_c. atm	V_c. c. c.
Calc.	564	50. 2	340. 6
Obs. (14)	554	40. 4	311. 7
$\varDelta\%$	1. 8	24	8. 5

4. **Compressibility**; Compressibility is calculated using the following expression,

$$\beta=-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T,\quad \left(\frac{\partial V}{\partial p}\right)_T=\frac{1}{\left(\frac{\partial p}{\partial V}\right)_T}$$

$$=1/-\frac{\partial^2 A}{\partial V^2}$$

The calculated value at 304. 15 °K agrees reasonably with experimental data as shown in table VI

TableVI. Compressibility

$T°K$	Calc. (atm)	Obs. (atm)(13)
298. 15	138×10^{-6}	
304. 15	140×10^{-6}	124×10^{-6}
313. 15	144×10^{-6}	
323. 142	154×10^{-6}	
343. 15	178×10^{-6}	

Discussion

The deviation of the calculated molar volume from the observed values steadily decreases, giving the maximum value of 0. 83% near the melting point. However the deviation of the calculated vapor pressure steadily increases giving 2. 2% at the boiling point. Entropy of vaporization at the boiling point deviates as much as 2. 5%. The small deviations may be attributed to various assumption made in formulating the partition function, such as ideal behavior of the gas-like molecules and the negligence of the boat type molecules, etc. The large deviations of the critical values are indipensable consequence of these assumptions. The calculated values of compressibility also agree very well with the experimental data. The increasing tendency of compressibility with temperature is fairly reasonable. Neverthless, it is ascertained that the Transient State Theory of Significant Liquid Structure is applicable to the liquid cyclohexane very well.

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