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# Rotational Partition Function for Diatomic Molecules in the Liquid State

by

HAI BANG LEE*, HYUNGSUK PAK* and SEIHUN CHANG

*Dept. of Chemistry, College of Liberal Arts and Sciences,*
*Seoul National University, Seoul Korea*

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# 이원자 분자 액체에 대한 회전 상태합

서울 대학교 문리과대학 화학과

이 해 방* · 박 형 석* · 장 세 헌

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## 요 약

액체의 천이상태 이론을 이원자분자에 적용시키는데 있어서 위치 에너지를 도입시켜 회전상태합을 다시 고려했다. 이 상태합을 액체 할로겐에 적용시켜, 몰부피, 증기압, 증발엔트로피 같은 열역학적 성질을 계산한 결과 측정치와 잘 맞았다.

## Introduction

According to the *transient state theory* the rotational motion of the solid-like molecules in the liquid state is assumed as a rigid rotator or as a harmonic oscillator. (1)-(6) In order to determine whether the solid-like molecules rotate in the liquid state, the reference was made to the crystal structure, the heat of fusion, and the heat capacity at the solid state. In the liquid state the molecules do not rotate freely, but they only oscillate to a limited extend; since the molecular interaction is considerably strong.

The rotational energy is expressed as

$$E_{rot}=\frac{1}{2I}\left(P_{\theta}^{2}+\frac{P\varphi^{2}}{\sin\theta}\right)+U \tag{1}$$

Where $I$ is the moment of inertia, and $P_{\theta}$ and $P\varphi$ are the angular momentum. This form has been proved to have a wide variety of applicabilities. (7)

For the rigid diatomic molecule, the potential energy is given as

$$U=-B\cos\theta$$

where $B$ is the potential energy barrier and $\theta$ is the angle between the molecular axis and the direction of the field.

The rotational partition function can be given by integrating the Boltzman factor over the angle and momenta as

$$\begin{aligned} f_{rot}&=\frac{1}{\sigma h^{2}}\iint_{-\infty}^{+\infty}\int_{0}^{2\pi}\int_{0}^{\pi} e^{-E rot/kT}\,d\theta\, d\varphi\, dP_{\theta}\, dP\varphi \\ &=\frac{8\pi^{2}IkT}{\sigma h^{2}}\ \frac{kT}{B}\sinh\frac{B}{kT} \end{aligned} \tag{2}$$

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* Premedical Course, Catholic Medical College, Seoul, Korea

where $\sigma$ is the symmetry number.

In the present work, it is assumed that the potential energy barrier, $B$, is proportional to the neighboring molecules. According to the transient state theory, the neighboring probability of the molecule is proportional to $V_s/V$, and accordingly the potential energy barrier can be expressed as

$$B=\xi(V_s/V)$$

where $\xi$ is a proportionality constant.

## The Complete Partition Function for the Diatomic Liquid

According to the transient state theory the liquid molecules are partitioned by the three kinds of degrees of freedom, i.e., the solid-like, the transient and the gas-like, assuming the molecular sized vacancies move at random. The partition function of liquid halogens can be given as follows:

$$F=\left[\frac{e^{Es/RT}}{(1-e^{-\theta s/T})^3}\left\{1+n\left(\frac{1-e^{-\theta s/T}}{1-e^{-\theta t/T}}\right)^3\frac{V-V_s}{V_s}\right.\right.$$
$$\left.\left.\exp\left(-n\frac{aEs}{\frac{V-V_s}{V_s}R\,T}\right)\right\}\right]^{\frac{V_s}{V}N}\left[\frac{(2\pi mkT)^{3/2}}{h^3}\cdot\right.$$
$$\left.\frac{eV}{N}\right]^{\frac{V-V_s}{V}N}\cdot\left[\frac{8\pi^2IkT}{2h^2}\ \frac{kT}{B}\ \sinh\frac{B}{kT}\cdot\right.$$
$$\left.\frac{1}{1-e^{-h\nu i/kT}}\right]^N \tag{3}$$

Where $Es$ is the ground state energy; $\theta_s$, $\theta_t$, the Einstein characteristic temperatures for the solidl-like, and the transient, respectively; $a$ is the proportionality constant; $V_s$ and $V$ are the molar volumes of the solid at the triple point and the liquid at a given temperature, respectively.

Here, it is assumed that the rotational partition functions as well as the interatomic vibrational partition function are the same for three states. The parameters included in equation (3) can be determined at the triple point for each liquid using the triple point data and the fundamental constants listed in Table 1.

The calculated parameters for liquid halogens are listed in Table 2.

## Result

From equation (3) and the statistical thermodynamical relations

$$A=-kT\ln F,\quad P=-\left(\frac{\partial A}{\partial V}\right)_T,\quad S=-\left(\frac{\partial A}{\partial S}\right)_T$$

the molar volume, the vapor pressure and the entropy of liquid can easily be found. The calculated and the observed molar volume and vapor pressure at various temperatures for halogens are compared in Table 3.

**Table 1. Triple point data and fundamental constants for halogen**

| | $F_2$(8)(9)(10) | $Cl_2$(3)(4) | $Br_2$(3) | $I_2$(3) |
|---|---|---|---|---|
| $T$°K | 53.54 | 172.12 | 265.85 | 387.30 |
| $P$ atm | 0.002182 | 0.01374 | 0.006105 | 0.1111 |
| $V$ cc/mole | 22.22 | 41.57 | 49.77 | 63.82 |
| $Vs$ cc/mole | 21.44 | 34.34 | 47.02 | 52.67 |
| $\Delta H_{vap}$ cal/mole | 1773 | 5626 | 7519 | 11510 |
| $I$ g.cm$^2$ | $25.3\times10^{-40}$ | $113.7\times10^{-40}$ | $340\times10^{-40}$ | $742\times10^{-40}$ |
| $n$ | 11.581 | 9.913 | 11.338 | 9.907 |
| $B$ erg | $3.8290\times10^{-15}$ | $4.3144\times10^{-14}$ | $5.8263\times10^{-14}$ | $9.7142\times10^{-14}$ |

**Table 2. Parameters for liquid halogens**

| | $F_2$ | $Cl_2$ | $Br_2$ | $I_2$ |
|---|---|---|---|---|
| $E_s$ cal/mole | 1750.4 | 6678.7 | 7780.4 | 14019 |
| $\theta_s$ °K | 58.123 | 255.10 | 43.488 | 132.89 |
| $\theta_t$ °K | 49.748 | 91.759 | 41.308 | 80.194 |
| $a$ | $9.408\times10^{-3}$ | $2.081\times10^{-1}$ | $2.134\times10^{-1}$ | $1.831\times10^{-1}$ |

The entropy of vaporization can be found from the difference between the entropies of the vapor and the liquid. The calculated values for halogens are compared with the observed values in Table. 4

## Discussion

For the diatomic molecules that have relatively low rotational potential energy barrier in liquid state such as nitrogen and oxygen, the free rigid rotator model proved to be valid by other wokers(4)(11). If the rotational potential energy barrier is very high, the harmonic oscillator approximation for the rotational degrees of freedom may be justified. As in the case of liquid halogens if the barrier is not so high but cannot be neglected, neither of the above approximation is satisfactory. Thomson et al(3) have tried to explain the deviation of the thermodynamic properties for liquid chlorine assuming the large expansion of the sliod molar volume which is not justified. In addition

**Table 3. The molar volume and the vapor pressure of liquid halogens**

| | Molar volume (cc) | | | Vapor pressure (atm) | | |
|---|---|---|---|---|---|---|
| T°K | Calc. | Obs. | Δ% | Calc. | Obs. | Δ% |
| Fluorine | | | | | | |
| 53.54 | 22.22 | 22.22(8) | 0.00 | 0.002182 | 0.002182(8)(9) | 0.00 |
| 66.03 | 23.22 | 23.27(8) | −0.21 | 0.05763 | 0.0581(8)(9) | −4.33 |
| 77.22 | 24.23 | 24.33(8) | −0.41 | 0.3649 | 0.3689(8)(9) | −1.08 |
| 85.02 | 24.91 | 25.16(8) | −0.99 | 0.9638 | 1.000(8)(9) | −3.62 |
| Chlorine | | | | | | |
| 172.12 | 41.57 | 41.57(4) | 0.00 | 0.06105 | 0.06105(4) | 0.00 |
| 193.15 | 42.99 | 42.58(4) | 0.96 | 0.0777 | 0.07606(4) | 2.2 |
| 213.15 | 44.37 | 43.71(4) | 1.5 | 0.0793 | 0.2730(4) | 2.3 |
| 239.05 | 46.29 | 45.45(4) | 1.8 | 1.030 | 1.000(4) | 3.0 |
| Bromine | | | | | | |
| 265.85 | 49.77 | 49.77(3) | 0.00 | 0.06105 | 0.06105(3) | 0.00 |
| 273.15 | 50.16 | 50.16(3) | 0.00 | 0.08930 | 0.08671(3) | 2.98 |
| 293.15 | 51.04 | 51.25(3) | −0.41 | 0.2260 | 0.2276(3) | −0.70 |
| 303.15 | 51.58 | 51.83(3) | −0.48 | 0.3415 | 0.3474(3) | −1.69 |
| 323.15 | 52.52 | 53.01(3) | −0.92 | 0.7139 | 0.7421(3) | −3.80 |
| 331.93 | 53.09 | 53.55(3) | −0.86 | 0.9562 | 1.000(3) | −4.38 |
| Iodine | | | | | | |
| 387.30 | 63.82 | 63.82(3) | 0.00 | 0.1110 | 0.1110(3) | 0.00 |
| 393.15 | 64.26 | 64.12(3) | 0.22 | 0.1390 | 0.1386(3) | 0.29 |
| 413.15 | 65.68 | 65.13(3) | 0.84 | 0.2817 | 0.2790(3) | 0.75 |
| 433.15 | 67.05 | 66.36(3) | 1.04 | 0.5215 | 0.5221(3) | −0.11 |
| 457.50 | 68.90 | 68.51(3) | 0.57 | 1.023 | 1.024(3) | 1.9 |
| 463.15 | 69.06 | 69.24(3) | −0.26 | 1.182 | 1.183(3) | −0.06 |

**Table 4. Entropy of vaporization at the normal boiling point**

| | $F_2$ | $Cl_2$ | $B_2$ | $I_2$ |
|---|---|---|---|---|
| Calc. | 18.53 | 20.81 | 20.97 | 23.16 |
| Obs. | 18.38(10) | 20.41(4) | 20.78(3) | 22.73(3) |
| Δ% | 0.8 | 1.9 | 0.9 | 1.9 |

to this, it has been known that the application of the significant structure theory to liquid halogens is difficult.

Using the proposed rotational partition function, however, the various thermodynamic properties of liquid halogens are found that are in good agreement with the observed values.

The rotational partition function can be considered as free rigid rotator if the potential energy barrier is low, but it can be assumed to be the classical oscillator if the barrier is high as shown below;

$$\text{if } B \ll kT, \quad f_{rot}=\frac{8\pi^2 IkT}{\sigma h^2}$$

$$\text{if } B \gg kT, \quad f_{rot}=\frac{kT}{h\nu}\, e^{B/kT}$$

$$\text{where} \qquad \nu=\frac{1}{2\pi}\sqrt{\frac{B}{I}}$$

The proposed rotational partition function can also be linear polyatomic liquid. For the nonlinear polyatomic molecules more complex parititon function for the molecular rotation in the liquid state may be expected.

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