

Significant Structure of Liquid Ammonia

by

Hai Bang Lee*, Mu Shik Jhon*, Seihun Chang

Department of Chemistry, Seoul National University, Seoul

(Received Nov. 21, 1964)

액체 암모니아의 구조와 성질

서울대학교 문리과 대학 화학과

이 해 방* · 전 무 식* · 장 세 훈

(1964. 11. 21. 접수)

要 約

Modified significant structure theory of liquid를 써서 액체 암모니아의 partition function을 정하여 액체 암모니아의 몰부피, 증기압, 한계점, 증발엔트로피, 표면장력을 계산한 결과 실험치와 잘 맞는 값을 얻었다.

Abstract

The partition function of liquid ammonia was developed by applying the modified significant structure theory of liquid.⁵

The molar volume, vapor pressure, vaporization entropy were calculated over a wide temperature range. The critical properties for the liquid were also calculated. And surface tensions of the liquid were calculated in a similar manner developed for water by Chang and Pak.¹⁰

The results show good agreement with experimental observations.

Introduction

H. Eyring and coworkers¹⁻³ have proposed significant structure theory of liquid and tried its application to a number of liquids. Lately Chang and coworkers^{5, 10} have proposed modified significant structure theory of liquid and calculated thermodynamic properties of several liquid. Applying the modified significant structure theory of liquid, the authors developed the partition function of liquid ammonia and calculated thermodynamic properties and surface tensions, which show good agreement with experimental values.

Partition function

The significant structure theory of liquid assumes that the molecules in liquid have solid-like degrees of freedom and gas-like degrees of freedom. The X-ray analysis of solid ammonia⁴ shows that the molecules cannot rotate freely in solid state.

And the value of entropy of fusion (6.914 e. u.)⁸ may indicate that the solid-like molecules in the liquid cannot rotate freely.

We assume that they do torsional oscillation with the frequency of which can be approximated to have the same value of the lattice vibration of the molecules.

* : Department of Chemistry, Dong Guk University, Seoul

Then, according to the significant structure theory of liquid, the partition function of liquid ammonia can be written as follows.

$$f_l = \left[\frac{e^{E_s/RT}}{(1 - e^{-\theta/T})^6} \left\{ 1 + n(x-1) \exp \frac{-aE_s}{n(x-1)RT} \right\} f_v \right]^{\frac{1}{x} \cdot N}$$

$$\left[\frac{(2\pi mkT)^{3/2}}{h^3} \frac{eV}{N} \frac{\sqrt{\pi} \{8\pi^2(I_A I_B I_C)^{1/3} kT\}^{3/2}}{3h^3} \right]$$

$$f_v \left]^{(1 - \frac{1}{x}) \cdot N}, \right.$$

where E_s , θ , V_s are parameters corresponding, respectively, to the heat of sublimation, Einstein characteristic temperature and molar volume of solid-like molecule in the liquid. And x is a proportionality constant, giving $a E_s V_s / n(V - V_s)$ the strain energy in the system as the molecule shifts to one of the neighboring vacancies.

And n is the number of nearest neighbors around a molecule, which is given by $n = 12V_s/V_l$, assuming a close-packed structure, where V_l is the molar volume of the liquid at triple point.

The moment of inertia I_A , I_B , I_C are 4.44×10^{-40} g-cm², 2.82×10^{-40} g-cm², 2.82×10^{-40} g-cm², respectively, symmetry number σ is 3 and others have the usual meanings.

The parameters are calculated in a similar manner as proposed by Chang and coworkers⁵.

Properties at the triple point and the parameters are given in Table 1.

Table 1. Triple point data and parameters

T_t : 195.45°K. ⁸	E_s : 6332.0 cal/mol
P_t : 0.0605 atm.	n : 11.543
V_t : 23.204 cc.	V_s : 22.319 cc.
H_v : 6047.1 cal./mol.	θ : 142.63°K.
	a : 0.009236.

Thermodynamic Properties

1. Molar volume and vapor pressure

The molar volume and vapor pressure at various temperature are calculated using the above partition function.

The necessary equations for calculating the properties are given below;

$$-\frac{A}{RT} = \frac{1}{x}(\sigma + y) + \left(1 - \frac{1}{x}\right)(\gamma + \ln x) + \ln f_v, \text{ and}$$

$$p = -\left(\frac{\partial A}{\partial V}\right)_T = \frac{RT}{V_s} \left\{ -(\sigma - \gamma + 1 + y - x - \ln x) \frac{1}{x} + \frac{n e^{-w}(1 + \omega)}{1 + n(x-1)e^{-w}} \right\} \frac{1}{x}.$$

Where $\sigma = \frac{E_s}{RT} - 6 \ln(1 - e^{\theta/T})$,

$$\gamma = \ln \left[\frac{(2\pi mkT)^{3/2}}{h^3} \frac{eV_s}{N} \frac{\{8\pi^2(I_A I_B I_C)^{1/3} kT\}^{3/2} \sqrt{\pi}}{3h^3} \right]$$

$$y = \ln \{1 + n(x-1)e^{-w}\} \text{ and } \omega = aE_s/n(x-1)RT.$$

If the values of Helmholtz free energy, A , thus obtained are plotted against the values of V for a given temperature, the slope of a common tangent line of liquid and gaseous portion give the vapor pressure and the corresponding tangential points give the molar volumes of liquid and gas, respectively.

The results obtained are shown in Table 2 and 3 and compared with experimental values.

Table 2. Vapor pressure

T°K	Calc. (atm.)	Obs. (atm.) ⁹	Δ%
195.45(T. P.)	0.0605	0.0605	0.00
213.15	0.2165	0.2161	0.19
229.15	0.5654	0.5693	-0.69
239.75(B. P.)	0.9827	0.9879	-0.53
253.15	1.8308	1.8774	-2.48
273.15	4.0583	4.2380	-4.24
293.15	8.0109	8.4585	-5.29

Table 3. Molar volume

T°K	Calc. (cc)	Obs. (cc) ⁹	Δ%
195.45(T. P.)	23.20	23.20	0.00
213.15	23.74	23.86	-0.51
229.15	24.24	24.51	-1.12
239.75(B. P.)	24.58	24.98	-1.62
253.15	25.02	25.61	-2.30
273.15	25.83	26.67	-3.15
293.15	26.76	27.91	-4.10

2. Critical values

Critical values are calculated using the conditions of $\left(\frac{\partial p}{\partial V}\right)_T = 0$ and of $\left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0$. These values are shown in Table 4 and compared with observed values.

Table 4. Critical values

	Calc.	Obs. ^a	$\Delta\%$
T_c °K	469.2	405.45	15.71
V_c cc	72.98	72.95	0.004
P_c atm	188.6	111.3	69.45

3. Vaporization entropy

Vaporization entropy at various temperatures can be calculated using the following equation;

$$\begin{aligned} \frac{\Delta S_{vap}}{R} = & \frac{1}{x_g} \left[-6 \ln(1 - e^{-\theta/T}) + \frac{6 \frac{\theta}{T} \cdot e^{-\theta/T}}{1 - e^{-\theta/T}} \right. \\ & + \ln \{ 1 + n(x_g - 1)e^{-w_g} \} + \frac{n(x_g - 1)e^{-w_g} \cdot w_g}{1 + n(x_g - 1)e^{-w_g}} \\ & + \left(1 - \frac{1}{x_l} \right) (\gamma + 3 + \ln x_l) - \frac{1}{x_l} \left[-6 \ln(1 - e^{-\theta/T}) \right. \\ & + \frac{6 \frac{\theta}{T} \cdot e^{-\theta/T}}{1 - e^{-\theta/T}} + \ln \{ 1 + n(x_l - 1)e^{-w_l} \} \\ & \left. \left. + \frac{n(x_l - 1)e^{-w_l} \cdot w_l}{1 + n(x_l - 1)e^{-w_l}} \right] \right] - \left(1 - \frac{1}{x_l} \right) (\gamma + 3 + \ln x_l), \end{aligned}$$

where x_g : x for gaseous portion,

w_g : w for gaseous portion,

x_l : x for liquid portion and

w_l : w for liquid portion.

The calculated values have shown good agreements with experimental observations in Table 5.

Table 5. Vaporization entropy

T°K	Calc. (e. u.)	Obs. (e. u.) ^a	$\Delta\%$
239.75	22.470	23.237	-3.98
253.15	21.440	21.368	0.34
273.15	19.463	18.805	3.50

4. Surface tension

Surface tension of liquid ammonia at various temperatures are calculated in a similar manner by Chang and Pak¹⁰ for liquid water, which assumes that the molecules in the first surface layer are asymmetrical field due to their dipole moments which will tend to orient to the direction of the field. The authors have assumed that the molecules in the first surface molecular layer are oriented, to some degree, to the direction of the dipole field formed by the second molecular layer, and that the molecules in the first molecular layer can rotate freely about the figure axis of the molecule.

Molecules other than in the first surface layer can be approximated to be in a symmetrical field. Therefore, there is no molecular orientation in the second layer and beneath. Then, the partition function for the top surface layer is given by the following equation;

$$\begin{aligned} \ln f_s = & \frac{1}{x_1} \left[\frac{E_{s1}}{RT} - 5 \ln(1 - e^{-\theta/T}) + \ln \frac{\sqrt{\pi} (8\pi^2 I_A k T)^{1/2}}{3h} \right. \\ & + \ln \frac{kT}{\mu X} \sinh \frac{\mu X}{kT} + \ln \{ 1 + n(x_1 - 1)e^{-w_1} \} \left. \right] \\ & + \left(1 - \frac{1}{x_1} \right) \left(\gamma + \ln \frac{kT}{\mu X} \sinh \frac{\mu X}{kT} + \ln x_1 \right), \end{aligned}$$

where $x_1 = V_1/V_s$, V_1 being the molar volume of the first surface layer, μ is the dipole moment and X is the field strength.

The ground state energy for each surface-layer can be calculated with the same method developed by Chang et al.¹¹

Calculated values are shown in Table 6 and compared with observed values.

Table 6. Surface tension

T°K	% Contribution			$\gamma_{calc.}$ (dyn/cm)	$\gamma_{obs.}$ ¹² (dyn/cm)	$\Delta\%$
	1st layer	2nd layer	3rd layer			
195.45 (T. P.)	90.40	9.00	0.60	58.26	(44.3)	31.5
239.75 (B. P.)	85.42	13.46	1.12	47.16	34.25	37.7
273.15	79.38	18.16	2.46	39.80	26.55	50.5
293.15	75.66	21.13	3.21	34.01	22.0	54.6

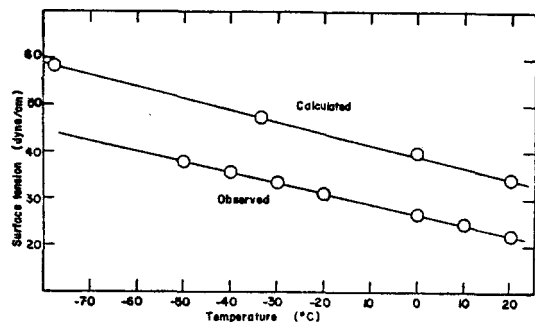


Fig. 1. Surface tension vs. temperature

Acknowledgement

The authors thank Mr. Hyungsuk Pak for his assistance in the calculation.

References

- (1) H. Eyring, Taikyue Ree and N. Hirai, *Proc. Nat. Acad. Sci.*, **44**, 683(1958).
- (2) E. Jack Fuller, Taikyue Ree and H. Eyring, *ibid.* **45**, 1594(1959).
- (3) H. Eyring and Taikyue Ree, *ibid.*, **47**, 526 (1961).
- (4) *Acta crystal.*, **12**, 823(1956).
- (5) Seihun Chang et al, *This Journal*, **8**, 33(1964).
- (6) Gerhard Herzberg, "Molecular Spectra and Molecular Structure," (D. Van Nostrand Co. Inc. 1962).
- (7) H. Remi, "Treatise on Inorganic Chemistry," Vol. 1 (Elsevier publish Co. 1963) 606.
- (8) "American Institute of Physics Handbook" (McGraw-hill, 1957).
- (9) Lange's "Handbook of Chemistry" 9th ed. (McGraw-hill, 1956).
- (10) Hyungsuk Pak and Seihun Chang, *This Journal* **8**, 121(1964).
- (11) Seihun Chang, T. Ree, H. Eyring and Ingrid Matzner, "Progress in International Research on Thermodynamic and Transport Properties," (A. S. M. E. Acad. Prees, New York, 1962).
- (12) Landolt-Börnstein, "Zahlen Werte und Function Aus Physik, Chemie, Astromie, Geophysik, Technik," 3 Teil Band, (Spring-Verlag, 1956).