Statistical Thermodynamical Calculation of the Surface Entropy of Liquids

by

Sunghye Park, Hyungsuk Pak and Seihun Chang

Department of Chemistry, Seoul National University, Seoul

(Received Nov. 21, 1964)

액체 포면 엔트로피의 통계 열역학적 계산

서울대학교 문리과대학 화학과

박 성 혜 · 박 형 석 · 장 세 헌

(1964. 11. 21 접수)

요 약

액체에 관한 hole theory 를 사용하여 여러가지 액체들의 표면장력과 표면 각층의 excess molar surface entropy 들을 계산하였다. 표면 첫째층의 것은 이상적인 분자가 표면을 형성할 때의 값 Rln2보다 다소 큰 값을 보여주며 액체 내부에 들어감에 따라 점점 줄어들어 저온에서는 셋째층부터 거의 없어진다.

그리고 알곤, 질소, 메탄, 벤젠 및 할로겐들의 표면장력을 계산하여 측정치와 비교하였다.

Abstract

The excess molar surface entropies of each surface layers are calculated applying the modified significant structure theory of liquid. The calculated excess molar surface entropy for the first top surface layer is slightly greater than the entropy of surface formation of ideal molecules,[5] the latter is equal to Rln2. The excess entropy for the second surface layer is small and that for the third layer is negligible at low temperatures.

The surface tensions of argon, nitrogen, methane, benzene and halogens are calculated applying the modified significant structure theory of liquid.

Introduction

Many workers [1-5] show that surface of liquid is not a mathematical plane but it consists of several molecular layers. Through these several molecular layers, the density of the liquid undergoes gradual changes before it changes abruptly to the vapor phase. This is shown theoretically by Hill[6] and Chang et al.[7]

This leads to the thought that the randomness of molecules changes accordingly in the surface region of a liquid.

Chang and co-workers[7] have calculated surface tension of various liquids applying the significant structure theory of liquid which was proposed by H. Eyring et al. Recently, the surface tensions of carbon tetrachloride,[8] water,[9] ethylene chloride,[10] fluorine[11] and ammonia[12] have been calculated using the modified significant structure theory of liquid proposed by Chang et al. In this paper, the authors calculate the excess molar surface entropy for various liquids and surface tensions of argon, nitrogen, benzene and halogens applying the latter theory.

Partition function

According to the theory of modified signicant liquid structure,[13] liquid may possess both solid-like and gas-like degrees of freedom, but the former is not necessarily equal to that of solid itself. The fractions of the two degrees of freedom are represented as V_s/V and $(V-V_s)/V$, respectively, where V_s is the molar volume of solid-like molecules in liquid and V is the molar volume of liquid itself. Thus, the partition function can be written as follows;

$$F=\left[\frac{b_s\,e^{Es/RT}}{(1-e^{-\theta/T})^3}\left\{1+n_h e^{-\epsilon/kT}\right\}\right]^{\frac{V}{V_s}N}.$$

$$\left[\frac{b_g}{\lambda^3}-\frac{eV}{N}\right]^{\frac{V-V_s}{V}N}$$

where b_s and b_g are respectively the interatomic vibrational and molecular rotational partition functions for the solid-like and gas-like molecules. E_s ang θ are respectively the ground state energy and Einstein characteristic temperature of the solid-like molecules. And n_h and ϵ are respectively the number of vacancies available to one of the solid-like molecules and the energy required for a hole-molecule pair to exchange positions, which can be written as,

$$n_h=n'\left(\frac{V-V_s}{V_s}\right)\quad\text{and}\quad\epsilon=\frac{aE_sV_s}{n(V-V_s)RT}$$

n and a being the proportionality constant and λ is equal to $h/(2\pi mkT)^{1/2}$.

It is assumed that the partition function for the surface layers of a non-polar liquid can be approximated as to have the same form as for the bulk liquid, except the correction for the ground state energy of the solid-like molecules as proposed by Chang et al.[7] It is

assumed further that for a polar liquid or for a liquid asymmetric molecule, molecules on the top surface layer will orientate and changes in rotational degrees of freedom will take place. For example, solid-like molecules of benzene cannot rotate in bulk liquid, but molecules on the top surface layer can rotate about the axis as shown theoretically by Mortensen and Eyring.[14]

Thus, the authors assume that the solid-like molecules such as benzene and ammonia,[12] which cannot rotate in bulk liquid, can rotate freely about the figure axis only in the first top surface layer, and if the molecules, such as water[9] and ammonia,[12] have appreciable electric moments, they can have the molecular orientation. However, the molecules in the other surface layers are practically in a symmetrical field that they shall have the same degrees of freedom as for the bulk liquid.

Calculation and results

The excess molar surface entropy of i-th surface layer is given by $\Delta S_i=S_i-S_l$, where S_i is molar entropy of i-th surface layer and S_l is molar entropy of bulk liquid which can be obtained from the partition functions of i-th surface layer and of bulk liquid, respectively, that is,

$$S_i=-\left(\frac{\partial A_i}{\partial T}\right)_{Vi}=klnF_i+kT\left(\frac{\partial lnF_i}{\partial T}\right)_{Vi},$$

$$S_l=-\left(\frac{\partial A_l}{\partial T}\right)_{Vl}=klnF_l+kT\left(\frac{\partial lnF_l}{\partial T}\right)_{Vl}$$

and the molar entropy of surface formation is given by

$$\Delta S=\sum_{i=1}^{l}(S_i-S_l)\frac{Q_1}{Q_i},$$ where Q_1 is the molar area of the first top surface layer and Q_i is for the i-th surface layer. Since the layer thicknesses are the same for all the surface layers, $\frac{Q_1}{Q_i}$ is equal to V_1/V_i, where V_i is the molar volume of the i-th layer.

Therefore

$$\angle S=\sum_{i=1}^{l}(S_i-S_l)\frac{V_1}{V_i}$$

The calculated excess molar surface entropies for various substances are listed in the following tables.

Excess molar surface entropy

Argon

T°K	ΔS_1 e. u.	ΔS_2 e. u.	ΔS_3 e. u.	ΔS e. u.
83.96 (T$_t$)	1.855	0.288	0.027	2.208
87.49 (T$_b$)	1.699	0.219	0.034	1.983
97.76	1.586	0.227	0.035	1.886

Methane

T_oK	ΔS_1 e. u.	ΔS_2 e. u.	ΔS_3 e. u.	ΔS e. u.
90.65 (T_t)	1.527	0.142	0.000	1.680
99.67	1.401	0.123	0.000	1.535
111.67 (T_b)	1.350	0.126	0.013	1.502
123.15	1.302	0.136	0.012	1.466

Nitrogen

T°K	ΔS_1 e. u.	ΔS_2 e. u.	ΔS_3 e. u.	ΔS e. u.
63.30 (T_t)	1.709	0.183	0.000	1.910
68.41	1.578	0.158	0.000	1.751
77.34 (T_b)	1.495	0.154	0.017	1.685
99.52	0.901	0.237	0.042	1.216

Carbon tetrachloride

T°K	ΔS_1 e. u.	ΔS_2 e. u.	ΔS_3 e. u.	ΔS e. u.
273.15	2.107	0.156	0.017	2.296
293.15	2.189	0.183	0.016	2.408
323.15	2.314	0.209	0.015	2.567
349.90 (T_b)	2.386	0.284	0.028	2.742

Benzene

T°K	ΔS_1 e. u.	ΔS_2 e. u.	ΔS_3 e. u.	ΔS e. u.
278.68 (T_t)	2.408	0.179	0.011	2.613
298.15	2.283	0.170	0.014	2.483
328.15	2.204	0.206	0.018	2.451
353.25 (T_b)	2.147	0.238	0.032	2.448

Chlorine

T°K	ΔS_1 e. u.	ΔS_2 e. u.	ΔS_3 e. u.	ΔS e. u.
172.12 (T_t)	1.908	0.140	0.000	2.058
193.15	1.900	0.125	0.000	2.036
239.05 (T_b)	2.010	0.213	0.019	2.272

Bromine

T°K	ΔS_1 e. u.	ΔS_2 e. u.	ΔS_3 e. u	ΔS e. u.
265.85 (T_t)	2.028	0.171	0.000	2.217
293.15	2.024	0.171	0.000	2.214
323.15	2.088	0.203	0.000	2.317

Iodine

T_oK	ΔS_1 e. u.	ΔS_2 e. u.	ΔS_3 e. u.	ΔS e. u.
387.30 (T_t)	2.461	0.173	0.000	2.656
413.15	2.645	0.264	0.000	2.944
457.50	2.832	0.314	0.043	3.250

Ammonia

T_oK	ΔS_1 e. u.	ΔS_2 e. u.	ΔS_3 e. u.	ΔS e. u.
195.45 (T_t)	1.350	0.142	0.016	1.519
239.75 (T_b)	1.448	0.168	0.020	1.655
273.15	1.629	0.242	0.023	1.931
293.15	1.681	0.325	0.060	2.128

Ethylene chloride

T°K	ΔS_1 e. u.	ΔS_2 e. u.	ΔS_3 e. u.	ΔS e. u.
237.85 (T_t)	1.946	0.115	0.000	2.069
270.75	2.062	0.118	0.000	2.190
302.55	2.164	0.194	0.000	2.379
337.15	2.230	0.245	0.018	2.529

Water

T°K	ΔS_1 e. u.	ΔS_2 e. u.	ΔS_3 e. u.	ΔS e. u.
273.15 (T_t)	2.346	0.040	0.000	2.384
293.15	2.373	0.044	0.000	2.415
333.15	2.303	0.060	0.001	2.363
373.15 (T_b)	2.118	0.083	0.012	2.212

The surface tensions and their contributions to each surface layers of argon, nitrogen, methane, benzene and halogens calculated by the iteration method, proposed by Chang et al.[7] applying the modified significant structure theory of liquid[13] are tabulated in the following tables. And also the surface tensions of carbon tetrachloride,[8] fluorine,[11] ethylenechloride,[10] water,[9] and ammonia[12] can be found in the previous papers which were calculated by the similar method.

Surface tension

Argon

T°K	% Contribution of each layer			γcalc. (dyne/cm)	γobs. (dyne/cm)	Δ %
	1st	2nd	3rd			
83.96 (T_t)	85.52	12.72	1.76	13.37	13.5	−0.96
87.49 (T_b)	84.76	13.36	1.87	12.48	12.5	−0.96
97.76	81.64	16.13	2.22	9.95	9.9	0.56

Nitrogen

T°K	% Contribution of each layer			γcalc. (dyne/cm)	γobs. (dyne/cm)	Δ %
	1st	2nd	3rd			
63.30 (T$_f$)	90.24	9.76	0.00	11.78	12.05	−2.24
68.41	89.18	10.82	0.00	10.63	10.89	−2.39
77.34 (T$_b$)	85.22	13.52	1.26	8.73	8.91	−2.02

Methane

T°K	% Contribution of each layer			γcalc. (dyne/cm)	γobs. (dyne/cm)	Δ %
	1st	2nd	3rd			
90.65 (T$_f$)	91.25	8.75	0.00	17.14	18.20	−5.82
99.67	90.20	9.80	0.00	15.30	16.24	−5.79
111.67 (Tb)	87.09	11.91	1.00	13.01	13.70	−5.04
123.15	84.34	14.26	1.40	10.73	11.34	−5.38

Benzene

T°K	% Contribution of each layer			γcalc. (dyne/cm)	γobs. (dyne/cm)	Δ %
	1st	2nd	3rd			
278.68 (T$_f$)	89.60	9.61	0.79	37.04	30.96	19.6
298.15	88.38	10.77	0.85	34.31	28.36	21.0
328.15	85.84	12.88	1.28	29.98	24.44	22.7
353.25 (T$_b$)	83.39	15.02	1.59	26.15	21.24	23.1

Chlorine

T°K	% Contribution of each layer			γcalc. (dyne/cm)	γobs. (dyne/cm)	Δ %
	1st	2nd	3rd			
172.12 (T$_f$)	96.40	3.60	0.00	47.24	39.2	20.5
193.15	95.97	4.03	0.00	43.24	35.1	23.2
239.05 (T$_b$)	94.85	4.70	0.45	33.60	25.8	30.2

Bromine

T°K	% Contribution of each layer			γcalc. (dyne/cm)	γobs. (dyne/cm)	Δ %
	1st	2nd	3rd			
265.85 (T$_f$)	94.71	5.29	0.00	57.51	46.4	23.9
293.15	94.23	5.77	0.00	52.70	41.5	27.0
323.15	93.73	6.27	0.00	46.99	36.2	28.8

Iodine

T°K	% Contribution of each layer			γcalc. (dyne/cm)	γobs. (dyne/cm)	Δ %
	1st	2nd	3rd			
387.30 (T$_f$)	91.92	8.08	0.00	72.79	...	...
413.15	91.42	8.58	0.00	66.76	...	...
457.50	87.89	11.13	0.98	60.13	...	...

Discussion

Davies[5] shows that when a surface is formed, the molecules in the surface layer have a dfferent environment on the side of the vapor phase against that of the bulk liquid in which the molecules have other liquid molecules as the nearest neighbors. When compared with bulk liquid there is a new possibility of randomness in that a molecule may occupy a position either in the immediately subjacent bulk phase or in the surface. These two possibilities will give rise to an entropy increase of approximately Rln2, i.e., 1.4 e.u., this being a standard molar entropy change associated with surface forming.

The excess molar surface entropies of the top surface layer, ΔS_1, of argon, nitrogen and methane are nearly equal to the value, Rln 2.

However, for halogens and for complex molecules like benzene, ethylenechloride and carbon tetrachloride the values, ΔS_1 are generally greater than Rln2. It is considered that the molecules acquire, as they come to the top surface layer, different molecular degrees of freedom, i.e. rotational degrees of freedom, from, their original state in the bulk liquid.

For ammonia and water, the calculated values of ΔS_1 are comparatively small. It is the result from the assumption that molecules on the top surface layer orientate to some degrees.

Generally speaking, ΔS_1 decreases with increasing temperature. But for liquids of halogens and of complex molecules, ΔS_1 increases with increasing temperatures for a low liquid temperature range with a diminishing rate, ΔS_1 eventually decreassing to zero at the critical point. This is understood as the result that due to the change of molecular degrees 'fo freedom, the molar entropy for the top surface layer increases faster than for the bulk liquid for the low liquid temperature range.

ΔS_2, ΔS_3, increase, in general, with increasing temperature but they must also become zero at the critical point since the interface between liquid and vapor disappears.

The calculations indicate that most of the entropy of surface formation is derived from the top surface layer.

This is illustrated from the percent contribution by each surface tension.

References

(1) Rayleigh, Lord, *Phil. Mag.*, **33**, 1(1892).

(2) C. V. Raman and L. A. Rambdas, *ibid* **3**, 220 (1927).

(3) N. K. Adam, "The Physics and Chemistry of Surfaces", 2nd Ed., Oxford press (1938).

(4) W. D. Harkins, "The Phsical Chemistry of Surface Films", 3rd Ed., Reinhold pub. Co. (1957).

(5) J. T. Davies and E. K. Rideal, "Interfacial Phenomena", Academic press (1961).

(6) T. L. Hill, *J. Chem. Phys.*, **20**, 141 (1952).

(7) S. Chang, T. Ree, H. Eyring and J. Matzner, "Prog. Int. Res. Therm. Transp. Prop. A. S. M. E. " Academic press (1962).

(8) W. Paik and S. Chang, *This Journal* **8**, 29 (1964).

(9) H. Pak and S. Chang, *ibid.*, **8**, 121 (1964).

(10) W. S. Ahn and S. Chang, *ibid.*, **8**, 125 (1964).

(11) M. S. Jhon and S. Chang, *ibid.*, **8**, 65(1964).

(12) H. Lee, M. S. Jhon and S. Chang, *ibid.*, **8**, 179(1964).

(13) S. Chang, H. Pak, W. Paik, S. Park, M. S. Jhon and W. S. Ahn, *ibid.*, **8**, 33(1964).

(14) Mortensen and H. Eyring, *J. Phys. Chem.*, **64**, 846(1960).

(15) Intenational Critical Tables of Numerical Data, Physics, Chemistry and Technology.