

THE SPECIFIC HEAT OF THE SURFACE FORMATION OF LIQUIDS

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The semi-phenomenological method, allowing one to establish the temperature dependence of the specific heat of the surface formation (SHS) of liquids on the base of density value at two arbitrary temperatures is considered.

The given method is applied to the liquid alkaline metals and the correlation between thermal direction coefficient, SHS, bond energy and liquid molecular mass is established

The processes, carrying out on the two phases interface are special and differ from volume phenomena significantly. The osculating phases are divided by the narrow transitive layer, the atomic (molecular) structure of which strongly differs from structures of divided phases. In a particular, the interatomic distances in the subsurface layers of crystal (liquid) are in average on ~10% more, than in the volume. That's why the physical parameters, with the help of which the volume phenomena are described, aren't enough for surface phenomena and it is need to introduce the new characteristics, connected with the surface immediately. One of such values is the specific heat of the surface formation (SHS), which means energy physically, needed for isothermal formation of free unit surface. As all values characterizing the thermodynamic properties of the surface are expressed by the surface tension and it connects immediately with the specific heat of the surface formation, so the urgency of investigation of the last one becomes more significant.

In spite of the many theoretical and experimental investigations [see 1-4], because of the complexity of the structure of subsurface layer and unknowing of the potential of intermolecular interaction, nowadays the uniform approach to the surface phenomena in liquids doesn't exist.

In the given article some practically suitable semi-phenomenological method of the establishment of temperature dependence of the specific heat of the surface formation of liquids is suggested.

With the help of the potential method [5] and also thermodynamical cycles one [6] it can be shown that the temperature dependence of the surface tension coefficient of liquids (σ) in the general case is defined as follows

$$\frac{d\sigma}{dT} = -\frac{q}{T} \quad (1)$$

where q is the heat quantity, absorbing at the reversible isothermal change of unit surface area and is equal to the difference of the specific surface energy and the work at the isothermal expansion of the interface on the unit. (This value is often called by the specific heat of the surface formation). From another hand, the thermal direction coefficient of the surface tension of many liquids is well expressed by the following expression [7]:

$$\frac{d\sigma}{dT} = -B\left(\frac{\rho}{\mu}\right)^{2/3} \quad (2)$$

where ρ is the liquid density; μ is the liquid molecular mass. $B=2,1g\cdot cm^2/sec^2\cdot grad.$ is the numerical coefficient. From the formulae (1) and (2), we have:

$$q = 2,1\left(\frac{\rho}{\mu}\right)^{2/3} \cdot T = A \cdot \rho^{2/3} \cdot T \quad (3)$$

where $A=2,1\mu^{2/3}$ is the constant value for the given liquid (table 2).

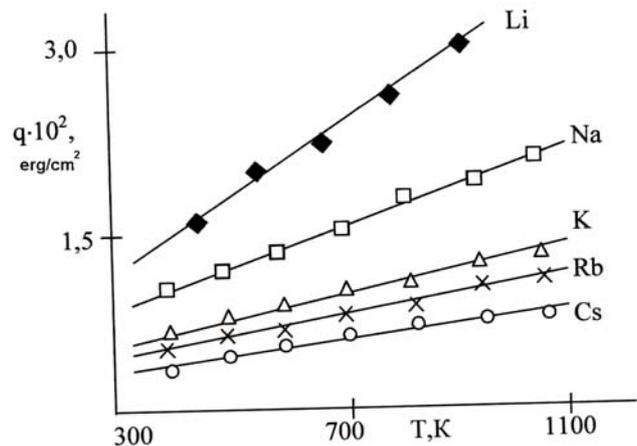


Fig.1. The temperature dependence of the specific heat of the surface formation of liquid alkaline metals.

As it is followed from the formula (3), the heat of the surface formation depends on the temperature. Knowing the temperature dependence of the liquid density with the help of formula (3), we can establish the analytical form of dependence $q=q(T)$. With the help of experimental values of liquid alkaline metals density, taken from the formula [8] at the different temperatures, we have calculated q values. The corresponding results are given in the fig.1. As it is seen, in the temperature interval $400K \leq T \leq 1100K$ for all chosen

liquids, the dependence $q=q(T)$ has linear character, i.e. the specific heat of the surface formation of liquid alkaline metals with the temperature increase increases according to the linear law. As the given linearity doesn't mean the temperature independence of the thermal angular coefficient

of the heat of the surface formation, i.e. $\alpha_T = \frac{dq}{dT} = const$, so it is obviously, that

$$q(T) = \alpha_T \cdot T + C \quad (4)$$

For the finding of integration constant C , we assume, that at the arbitrary temperature $T=T_r$, the heat of the surface formation, calculated by means of the known density $\rho=\rho_r$, is equal q_r . Then from the formula (4), we have:

$$q(T) = q_r + \alpha_T \cdot (T - T_r) \quad (5)$$

The formula (5) is the analytical expression of above mentioned linear dependence $q=q(T)$ and allows to establish the temperature dependence of the specific heat of the surface formation of liquids by means of the density values at two arbitrary temperatures. Indeed, let's suppose that at the temperatures T_1 and T_2 , the density is equal to ρ_1 and ρ_2 correspondingly. Then with the help of the formulae (5) and (3), after simple transformations, we obtain:

$$q(T) = 2 \cdot l \cdot \mu^{-2/3} \left[\rho_1^{2/3} T_1 + \frac{T - T_1}{T_2 - T_1} (\rho_2^{2/3} T_2 - \rho_1^{2/3} T_1) \right] \quad (6)$$

(In the formula (6), it is supposed, that $T_2 > T_1$, i.e. $\rho_2 < \rho_1$).

It is clear, that formula (6) has universal character, i.e. it is suitable for all normal liquids.

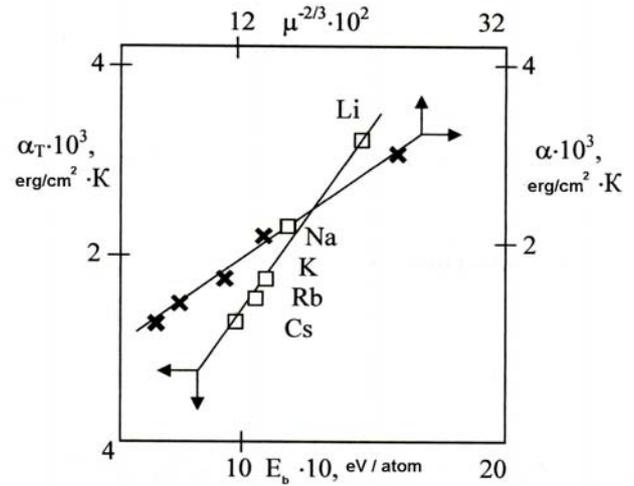


Fig.2. The dependence of thermal angular coefficient (α_T) on the bond energy (E_b) and molecular masses (μ) of liquid alkaline metals.

As it follows from the above mentioned, at the presence of the density data in the wide temperature interval it is necessary the specific heat of surface formation to calculate on the formula (3); and on the two density values, the dependence $q=q(T)$ can be established on the formula (6). For the liquid alkaline metals q values, calculated by the both methods, well coincide (table 1).

Table 1.

SHS of liquid direction metals, calculated on the formulae (3) (q_3) and (6) (q_6).

T, K	Na		K		Rb		q_6 / q_3		
	q_3	q_6	q_3	q_6	q_3	q_6	Na	K	Rb
400	98.29	98.28	63.48	63.49	54.51	54.52	0.9999	1.0001	1.0001
500	120.72	120.71	77.83	77.84	67.13	67.13	0.9999	1.0001	1.0000
600	142.27	143.14	91.53	92.19	78.76	79.75	1.0061	1.0072	1.0126
700	162.92	165.57	104.58	106.54	89.77	92.37	1.0162	1.0187	1.0283
800	182.82	188.00	116.97	120.89	101.83	104.99	1.0283	1.0335	1.0310
900	201.66	210.43	128.66	135.24	113.60	117.61	1.0435	1.0511	1.0353
1000	219.58	232.86	139.63	149.59	125.32	130.23	1.0605	1.0713	1.0392

The specificity is the decrease of the thermal angular coefficient α_T with the increase molecular mass of alkaline metals. Formally, such dependence follows from the formula (6), according to $\alpha_T \sim \mu^{-2/3}$ (fig.2). One of the probable physical causes of α_T decrease at the increase of molecular mass, is

the decrease of bond energy at the transition from lithium to cesium, i.e. it is obviously, that the more strong the bond between atoms, the more big the energy is needed for the formation of unit surface. The values of bond energy E_b , taken from the formula (9), are given in the table 2.

Table 2.

The values of some parameters for alkaline elements.

	Li	Na	K	Rb	Cs
μ	6.94	23	39.10	85.50	132.9
$A \cdot 10$	5.73	2.59	18.20	1.80	0.81
$\alpha_T \cdot 10^2, \text{ erg/cm}^2 \cdot \text{K}$	32.03	20.61	13.17	11.82	9.66
$E_b \cdot 10, \text{ eV [9]}$	15.80	11.30	9.50	8.90	8.10
$T_{\text{m}}, \text{ K [7]}$	453	371	350	313	302

The dependence α_T on bond energy is shown on the fig.2. As it is seen, our exposition about correlation between α_T and E_b takes place really.

It is note, that described in the present work the semi-phenomenological approach allows us to establish also the temperature dependence of liquid surface tension on two density values.

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- Thus, in the given paper, the semi-phenomenological method of the definition of the specific heat of the surface formation (SHS) of liquids on the base of density values at two arbitrary temperatures is suggested. By this method, the temperature dependence of the

specific heat of the surface formation of liquid alkaline metals has been calculated and correlation between the thermal direction coefficient, SHS, bond energy and liquid molecular mass is established.

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MAYELƏRİN XÜSUSİ SƏTHƏMƏLƏGƏLMƏ İSTİLİYİ

İşdə iki ixtiyari müxtəlif temperaturda mayenin sıxlığını bilməklə xüsusi səthəmələgəlmə istiliyinin (XSİ) temperatur asılılığını hesablamağa imkan verən yarım fenomenoloji metod verilir. Bu metodla qələvi metalların mayələrinin XSİ-nin termik bucaq əmsalı ilə mayenin rabitə enerjisi arasında korrelyasiya olduğu aşkarlanmışdır.

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УДЕЛЬНАЯ ТЕПЛОТА ПОВЕРХНОСТООБРАЗОВАНИЯ ЖИДКОСТЕЙ

Рассматривается полуфеноменологический метод, позволяющий на основании значений плотности при двух произвольных температурах установить температурную зависимость удельной теплоты поверхностообразования (УТП) жидкостей.

Предложенный метод применен к жидким щелочным металлам и установлена корреляция между термическим угловым коэффициентом, УТП, энергией связи и молекулярной массой жидкости.

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