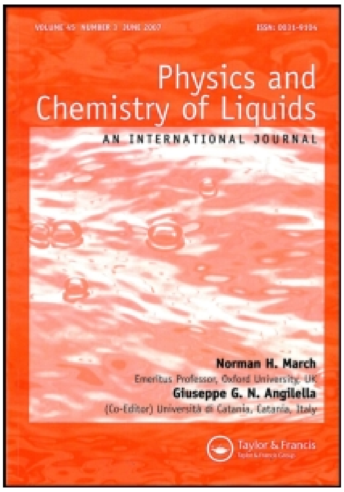

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INFLUENCE OF TRANSITIONS AMONG DEGENERATED STATES OF ATOMS AND MOLECULES ON SOME PHYSICO-CHEMICAL QUANTITIES OF LIQUIDS: VAPORIZATION ENTROPIES OF LIQUID 3d-METALS

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The equation, describing the vaporization entropies of liquid 3d-metals and taking into account the electronic distribution of 3d-metals' atoms, is received by the use of the assumption about the general character of the relationship, which characterizes the influence of transitions among degenerated states of atoms and molecules on physico-chemical quantities of liquids. It is shown that the vaporization entropies of these metals can be calculated adequately by means of this equation.

Keywords: Degenerated states; vaporization entropies; electronic distribution; liquid 3d-metals

1. INTRODUCTION

Many molecular and atomic systems possess degenerated (or quasi-degenerated) states in the liquid phase. These states may have different nature: conformational, electronic, vibronic *etc.* It is clear that the values of some physico-chemical quantities, which describe the liquid phase of the above mentioned systems and depend on the number of intermolecular (interatomic) interactions in this phase, will be defined by intra-molecular (intra-atomic) transitions among these states. Let the number of these states be equal to N. Then an increase in N will lead to an increase in the number of these transitions and, therefore, to an increase in the number of the above mentioned interactions. The latter increase will cause changes of these quantities. One of these quantities is (for instance) viscosity of liquids. As was shown in the works [1, 2] for different organic liquids their viscosity η is described adequately by taking into account the numbers of their molecular conformations, which possess much the same full energy. This calculation may be done on the basis of the function $G(N)$ given below, which describes the increase of viscosity due to the increase of the probability (and, therefore, the number) of intermolecular collisions by the realization of conformational transitions among different molecular conformations:

$$G(N) = (1 - \theta \ln N)^{-1}. \tag{1}$$

Here N is the number of energetically degenerated (or quasi-degenerated) conformational states of the one separate molecule; states, among which the conformational transitions are realized. The dimensionless constant θ in (1) is equal to 0.05681.

The aim of the present work is to show on the basis of the consideration of the vaporization entropies for 3d-metals at their normal boiling points that (1) has a general character and may be used for the calculation of physico-chemical quantities, which are different from η.

2. THEORY

First of all it is to note that from the physical point of view (if we consider the above mentioned physico-chemical quantities) there is no difference between various kinds of molecular (atomic) degenerations, provided all they lead only to the increase of the number of intermolecular (interatomic) interactions in the liquid phase. It means that the form of the influence of different kinds of degenerations on the values of these quantities will be also identical. Thus, if we find the equation, which describes the dependence of the values of one of these quantities on the number N for one particular case we shall be able to use it also for the adequate description of the other mentioned quantities for various new cases of degenerated molecular (atomic) systems in the liquid phase. In order to do it let us consider the first equation from our earlier work [1]. This equation was used for the calculation of the viscosity of organic liquids and has the following form:

$$\eta = (1 - \theta \ln N)^{-1} \left(\sum_{i,j}^{S} \mu_{ij} n_i n_j \right) (d/M)^{2/3}. \tag{2}$$

In Eq. (2) d and M are respectively density (kg/m^3) and molecular mass (kg/mol) of the liquid under consideration: n_i and n_j are the numbers of atoms entering in the molecular structure of the molecule of the liquid and belonging to the i-th and j-th sorts. In the process of flow these atoms take part in passing of the moment of motion quantity μ_{ij} ($N \times s$) due to the bimolecular collisions in the liquid phase along the axis, which is parallel to the liquid's flow direction. S (see Eq. (2)) is the total number of different atoms in the molecule which are capable of participation in the intermolecular impulse transfer (μ_{ij}) taking account of molecular stereochemistry.

Only the first multiplier in Eq. (2) describes the dependence of η on the number N of energetically degenerated (or quasi-degenerated) conformational states of one separate molecule. Using (1) and joining the second and the third multipliers of Eq. (2) in one quantity η_r, we may write it in the following form:

$$\eta = G(N) \times \eta_r. \tag{3}$$

It follows from (3) that the physico-chemical quantity η for real molecules may be defined by means of Eq. (1) and some quantity η_r. The last quantity describes the viscosity of the same molecules in the hypothetical case as if they were rigid in the liquid phase. It means that for all these "rigid" molecules there are no intra-molecular conformational transitions. Taking into account all the above mentioned reasons, it is clear that, in general case, Eq. (1) is the desired equation. It describes an increase in some investigated physico-chemical quantity (for instance, viscosity) due to an increase in the number of intermolecular interactions (collisions in the case of viscosity). When we pass from such "rigid" molecules (atoms) to their real analogs with allowed intra-molecular (intra-atomic) transitions between their intra-molecular (intra-atomic) states in the liquid phase then it will lead to the appearance of the number N of these states and to the corresponding increase in the number of intermolecular or interatomic interactions by $G(N)$ times.

So, one can write for the above mentioned physico-chemical quantities Q_s, whose increase (as compared to corresponding quantities Q_x, r of the investigated molecular or atomic systems considered as "rigid") is caused by the increase in the number of intermolecular (interatomic) interactions due to the transitions among all degenerated or quasi-degenerated states of these systems, the following general equality:

$$Q_s = G(N) \times Q_r. \tag{4}$$

It is interesting to verify the validity of this equality using a new example.

Bearing in mind this purpose, let us consider the vaporization entropies of 3d-metals at their normal boiling points. At first we will consider 3d-metals' atoms as ideal particles (points), which don't interact with each other and haven't any electronic structure. Taking into account that the experimental values of 3d-metals' vaporization entropies don't change in wide limits and using the principle of corresponding states, we may consider that the value of entropies' changes ΔS_r connected with the vaporization of such ideal 3d-metals' atoms is constant. Then, passing to the real 3d-metals' atoms, we have to take into consideration that for the one separate atom of any 3d-metal the intra-atomic transitions among different electronic populations of its valent atomic orbitals AO lead to the increase in the number of its interatomic interactions with neighbouring atoms in the liquid phase. These different electronic populations of its AO are its different degenerated electronic states. Their number is equal to N and is different for various 3d-metals' atoms. Further, bearing in mind (4), we may write for the entropy's change ΔS, which accompanies the vaporization process of 3d-metals, the following equation:

$$\Delta S = G(N) \times \Delta S_r = (1 - \theta \ln N)^{-1} \times \Delta S_r, \qquad (5)$$

where ΔS_r is constant.

3. RESULTS AND DISCUSSION

In order to verify (5) the experimental values of 3d-metals' vaporization enthalpies ΔH and their normal boiling points T were used. These values taken from Refs. [3, 4] are presented in Table I together with the experimental values of 3d-metals' vaporization entropies ΔS. The electronic distribution on the 3d-metals' valent AO of 3d-, 4s- and 4p-types (needed for the calculation of the number N of their atomic electronic states in the liquid phase) was taken from Refs. [5, 6] and is given in Table II side by side with their values of the number N.

The values of the number N for 3d-metals were calculated on the basis of the following rules:

(1) Only the unpaired electrons belonging to the valent AO of 3d- and 4p-types (possessing the most considerable spacial extent as compared to the AO of 4s-type) take part in the interatomic interaction in the liquid metallic phase;

(2) The unpaired electrons on the 3d-AO may populate the 4p-AO if they are empty. In this case the above mentioned atomic electronic

TABLE I The values of 3d-metals' vaporization entropies calculated on the basis of Eq. (5)

Ns.	*Metal:*	ΔH ($kJ \times mol^{-1}$)	$T(K)$	ΔS($J\times mol^{-1} \times K^{-1}$)	
				cacluc.	*exper.*
1	Sc	315	3123	108.57	100.86
2	Ti	410	3603	113.87	113.79
3	V	444.8	3673	121.10	121.10
4	Cr	338	2953	119.11	114.45
5	Mn	227	2353	97.99	96.47
6	Fe	354.3	3023	119.11	117.20
7	Co	375	3373	113.87	111.17
8	Ni	369.9	3173	113.87	116.57
9	Cu	302	2816	108.57	107.24
10	Zn	115.3	1179.4	97.99	97.77

TABLE II The electronic distribution on valent orbitals and the corresponding values of *N* for 3d-metals' atoms

Ns.	*Metal*:	*Atomic orbitals*:							*N*
		3*d*					4*s*	4*p*	
1	Sc	↑					↑	↑	$C_5^1 \times C_3^1 = 15$
2	Ti	↑	↑				↑	↑	$C_5^2 \times C_3^1 = 30$
3	V	↑	↑	↑	↑		↑		$C_8^4 = 70$
4	Cr	↑	↑	↑	↑	↑	↑		$C_8^5 = 56$
5	Mn	↑	↑	↑	↑	↑	↑	↑	$C_5^5 \times C_3^1 = 3$
6	Fe	↑↓	↑↓	↑	↑	↑	↑		$C_8^3 = 56$
7	Co	↑↓	↑↓	↑	↑	↑	↑	↑	$C_5^3 \times C_3^1 = 30$
8	Ni	↑↓	↑↓	↑↓	↑	↑	↑	↑	$C_5^2 \times C_3^1 = 30$
9	Cu	↑↓	↑↓	↑↓	↑↓	↑	↑	↑	$C_5^1 \times C_3^1 = 15$
10	Zn	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	$C_3^1 = 3$

states are caused by all the possible distributions of these unpaired 3d-electrons on all the metallic 3d- and 4p-AO. Let the number of these electrons be equal to *k* (*k* is less or equal to 5). As the total number of all these AO of 3d- and 4p-types is equal to eight then the number *N* of all the possible distributions (states) will be defined as C_8^k; where the symbol *C* means the number of all the possible combinations of these *k* electrons among these eight AO;

(3) If there is an electronic density on the 4p-AO then all the possible atomic electronic states of the metal under consideration arise due to two different distributions: on the 3d-AO and on the 4p-AO, which must be considered separately. If we have *k* unpaired electrons on the 3d-AO and one unpaired electron on the 4p-AO, then the numbers of the possible electronic distributions of these electrons on these AO will be C_5^k and C_3^1 respectively. In this case the total number of all the possible atomic electronic states *N* will be defined by means of the product of these two numbers. It is due to the fact that every possible electronic distribution of these *k* unpaired electrons on the 3d-AO combines with every possible electronic distribution of the unpaired electron on the 4p-AO. So, we may write for the calculation of *N* the following equality:

$$N = C_5^k \times C_3^1. \tag{6}$$

The numbers *N* calculated on the basis of these rules are presented in Table II. The use of these numbers in (5) shows that, if the value of the constant ΔS_r is equal to 91.87 ($\mathrm{J} \times \mathrm{mol}^{-1} \times \mathrm{K}^{-1}$), this equation describes the vaporization entropies of all 3d-metals adequately.

4. CONCLUSION

Thus, the following conclusion may be drawn. Equation (4) may be used for the calculation of different physico-chemical properties of liquids due to its general character. As will be shown in a later study, (1) holds for the calculation of surface tension of different liquids as well.

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