БЕЙОРГАНИКАЛЫҚ ХИМИЯ
НЕОРГАНИЧЕСКАЯ ХИМИЯ
INORGANIC CHEMISTRY

DOI 10.31489/2020Ch1/90-96

UDC 669+54–142

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Relationship of associated clusters degree with metal ionization according to the cluster-associate model

This article deals with a cluster-associate model of kinematic viscosity of liquid metals. This model was derived from the concept of chaotized particles. According to the proposed model, the authors calculated average values clusters association degree contained in liquid metal. 28 metals of the second — sixth periods of D.I. Mendeleyev element table were studied for calculation. The authors compare the first potential of metal ionization with the obtained values of clusters association degree. This comparison showed a regular change in clusters association degree closely connected with the change in the first ionization potential. In combination with the Fraenkel equation, an approximate equation was obtained to calculate activation energy. The obtained equation for the cluster-associate pattern of viscosity temperature dependence is used in calculating the activation energy of viscous melt flow for twenty-eight metals. The obtained results on activation energy were compared to experimental data. This comparison showed that the activation energy data obtained from the proposed model is described better by the approximating dependence. Tables and figures are given in the work for visual confirmation of the obtained results. Thus, in the process of comparing the first potential of metal ionization for all periods of D.I. Mendeleyev element system with clusters association degree, their regular connection was revealed. This connection makes it possible to assert the functional aspect of the cluster-associate pattern.

Keywords: viscosity, chaotized particles, degree of cluster association, cluster-associate pattern, liquid metals, activation energy, crystal mobile particles, ionization potential, modified Fraenkel equation.

Introduction

In 2008 in the Chemical and Metallurgical Institute named after Zh. Abishev doctors of technical sciences V.P. Malyshev and A.M. Turdukozhayeva developed a concept of chaotized particles based on Boltzmann distribution. According to the concept, three aggregate states of the substance are considered from a single point of view by its structure less component. In all cases, particles which differ only in the energy magnitude of chaotic motion are considered. According to the concept of chaotized particles in each of the three aggregate states there are *crystal mobile*, *liquid mobile* and *vapor mobile* particles. However with the temperature rise and overcoming of various chaotization energy barriers, the proportion of these particles changes.

The proportion of these particles is calculated according to the equations

$$P_{crm} = 1 - \exp\left(-T_m / T\right)$$

$$P_{vm} = \exp\left(-T_b / T\right)$$

$$P_{lqm} = 1 - P_{crm} - P_{vm} - \exp\left(-T_m / T\right) - \exp\left(-T_b / T\right).$$

Here P_{crm} is the proportion of crystal mobile particles; P_{vm} is the proportion of vapor mobile particles; P_{lqm} is the proportion of liquid mobile particles; T — temperature; T_m — melting temperature, T_b — boiling temperature.

Earlier in the work [1] three models were proposed with the consideration of different content of crystal mobile, liquid mobile and vapor mobile particles. But the need to test each of the three viscosity models and to choose the most adequate brings some elements of uncertainty in the design method of such a dependence, in addition complicating the data processing procedure. This led us to develop a single cluster-associate model

$$\nu = \nu_r \left(T_r / T\right)^a . \quad (1)$$

According to the concept of chaotized particles, a cluster is a probabilistic form of the existence of various low-energy complexes from crystal mobile particles. Calculations of clusters proportion and quantity for a mole of substance at the melting and boiling point have shown that the concept of chaotized particles allows to quantify the formation of clusters with their distribution by the number of particles in the liquid at any temperature.

In the same work [1], the model validity (1) to the calculation of liquid metals viscosity was shown. It has been shown that the model (1) for many metals most adequately describes the temperature dependence of viscosity and can be used to calculate the viscosity at high temperatures without the performance of experiment. For many metals equations for viscosity were derived.

Experimental

In the work [2] three models (taking into account crystal mobile, liquid mobile and vapor mobile particles) of kinematic viscosity of metals were compared with their ionization potentials for all periods of D.I. Mendeleyev element system, analysis of which revealed regular connection of values of this potential with model numbers ranked by increase of temperature influence on viscosity. In this work we will compare cluster-associate pattern (1) by the degree of clusters association with the first ionization potential of the considered metals for all periods of D.I. Mendeleyev element system.

This comparison is shown in Table 1 and Figure 1.

Table 1

Comparison of the first ionization potentials of the metal with the degree of cluster association

Period	Me	Valence shell	I_1, eV	$\bar{a}$	Period	Me	Valence shell	I_1, eV	$\bar{a}$
2	Li	$2s^1$	5.390	1.01	5	Rb	$5s^1$	4.176	1.22
	Be	$2s^2$	9.320	9.51		Sr	$5s^2$	5.692	2.01
3	Na	$3s^1$	5.138	1.35		Ag	$4d^{10}5s^1$	7.574	1.82
	Mg	$3s^2$	7.644	2.57		Cd	$4d^{10}5s^2$	8.991	1.80
	Al	$3s^2p^1$	5.984	1.03		In	$4d^{10}5s^25p^1$	5.785	0.96
4	K	$4s^1$	4.339	1.22		Sn	$4d^{10}5s^25p^2$	7.342	0.97
	Ca	$4s^2$	6.111	1.68		Te	$4d^{10}5s^25p^4$	9.01	2.77
	Fe	$3d^64s^2$	7.87	3.54	6	Cs	$6s^1$	3.894	1.19
	Co	$3d^74s^2$	7.86	3.05		Ba	$6s^2$	5.211	1.56
	Ni	$3d^84s^2$	7.63	1.92		Au	$4f^{14}5d^{10}6s^1$	9.22	1.44
	Cu	$3d^{10}4s^1$	7.724	1.65		Hg	$4f^{14}5d^{10}6s^2$	10.43	0.90
	Zn	$3d^{10}4s^2$	9.391	1.90		Tl	$4f^{14}5d^{10}6s^26p^1$	6.106	1.32
	Ga	$3d^{10}4s^24p^1$	6.00	0.91		Pb	$4f^{14}5d^{10}6s^26p^2$	7.145	0.79
	Ge	$3d^{10}4s^24p^2$	7.88	2.81		Bi	$4f^{14}5d^{10}6s^26p^3$	7.287	1.36

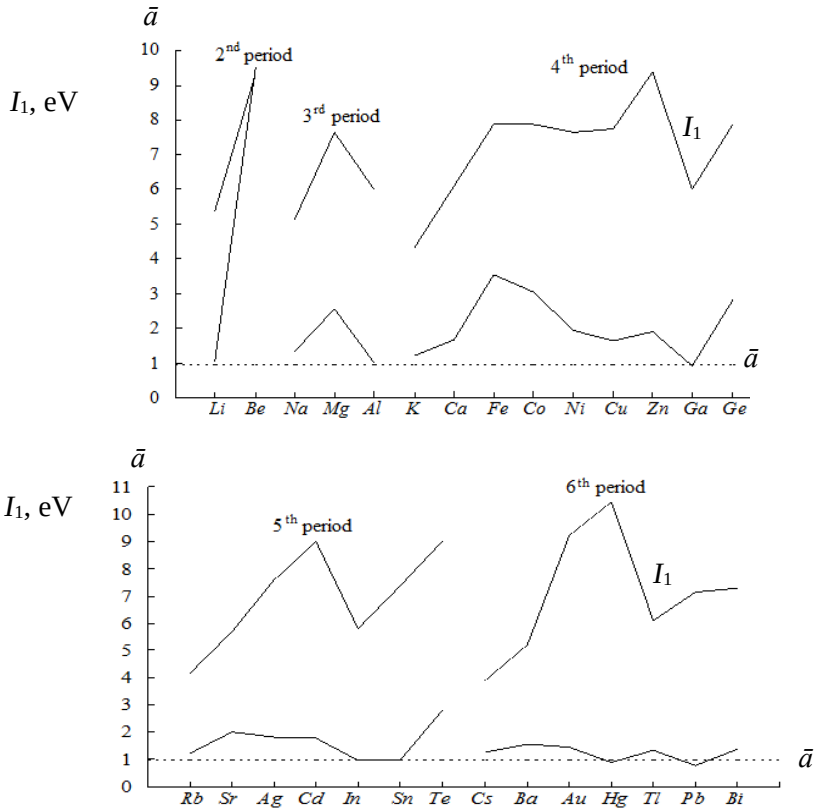
As can be seen from the table and the figure, in general there is a symbate (consistent) change in the degree of clusters association with the increase or decrease of the first potential value of metal ionization for all periods of Mendeleyev element system. Some departure of this model becomes apparent for silver in the fifth period and for gold, mercury, thallium and lead in the sixth period, that is connected with big tendency to clusters association from metal atoms for beryllium, with influence of 4*d*-subshellfor silver, with completion

of 4*f*- and 5*d*-subshells development for metals of the sixth period, and mercury and lead also have 6*s*-subshell accompanied by lanthanide contraction and sharp increase in ionization potential.

The average value of cluster association for 28 metals is $\bar{a}$ = 1.94. The obtained values of clusters association degree of the tested metals were checked for range uniformity according to equations [3]:

$$r_{\substack{\max\\\min}} = \frac{\left|\overline{x} - x_{\substack{\max\\\min}}\right|}{S(x)\sqrt{\frac{n-1}{n}}} \le r_{cr}, \quad S(x) = \sqrt{\frac{\sum(x_i - \overline{x})^2}{n-1}},$$

where $x_{\substack{\max\\\min}}$ is the minimax value of the range; $\overline{x}$ is the average value; $S(x)$ is the mean-root-square error and n is the volume of the range, $r_{cr} = 1.483 f^{0.187}$ [3; 15] where $f = n - 2$.



I_1 is the first ionization potential; $\bar{a}$ — average degree of cluster association

Figure 1. Dependence of ionization potential and average value of clusters association degree for 28 metals in order of increasing of their atomic number

This test showed that for 28 metals, the range is not uniform: mean-root-square error $S(x)$ = 1.645; in equation $r_{\substack{\min\\\max}} \le r_{cr}$ is not observed $r_{\substack{\min\\\max}} = 4.68 > r_{cr} = 2.73$; $x_{\substack{\min\\\max}} = 9.51$(for Be).

Therefore, it is necessary to eliminate the «jumping out» value, i.e. the beryllium data. The high value of association degree of beryllium clusters is connected with its high position in the periodic table, partial possession of covalent links, high tendency to associate clusters of metal atoms, and high ionization potential. Beryllium generally refers to semi-metals, which causes its exclusion from a variety of metals.

The elimination of beryllium and reduction of range up to 27 metals leads to validity of range uniformity: $S(x)$ = 0.780; $r_{\substack{\min\\\max}} = 2.46 < r_{cr} = 2.71$; $x_{\substack{\min\\\max}} = 3.54$ (for Fe).

In this case for 27 metals $\bar{a}$ = 1.66± 0.32.

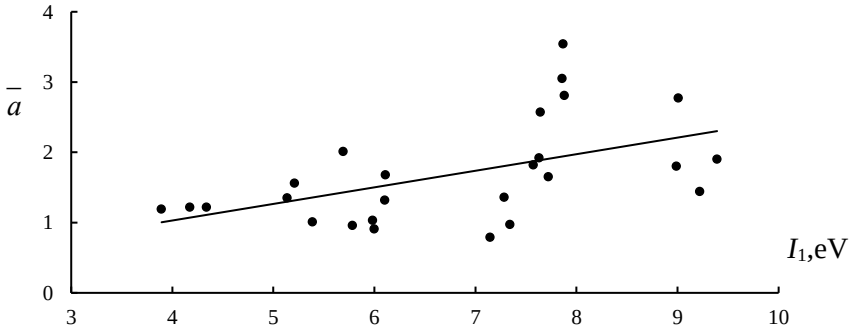
Results and Discussion

Research for calculation of clusters association degree are conducted on the most uniform simple substances — metals, therefore this indicator has low values and changes within ~1–4 (excepting beryllium) (Table 1). Without this semimetal, and in addition lower than normal associated mercury ($\bar{a}$ = 0.9) at its anomalously high ionization potential (10.43 eV), generally regular and probably significant, although weakly expressed as cendant dependence of cluster association with metal ionization potentials is observed

$$\bar{a} = 0.09 + 0.24I_1,\ R = 0.70,\ t_R = 6.7 > 2. \quad (2)$$

The weakness of this connection is explained by the secondary nature of associates formation in comparison with the primary processes of elementary *n*-particle clusters formation from crystal mobile particles, as it was demonstrated earlier on the example of more evident interconnection of the standard three models with metal ionization potentials. The conformity consists in a great tendency to association of ionic complexes — clusters, which have stronger attraction of universal mobile electrons.

The relationship between cluster association and ionization potential for 26 metals, without mercury and beryllium, is shown in Figure 2.



I_1 is the first ionization potential; $\bar{a}$ — average degree of cluster association.
Points are data from Table1, line — according to the equation (2) without data on Be and Hg

Figure 2. Relationship between cluster association and metal ionization potential

Ya.I. Fraenkel, on the basis of activation motion mechanism, obtained in 1927 the equation of dependence of dynamic viscosity on temperature

$$\eta = A\exp\left(\frac{E_a}{RT}\right), \quad (3)$$

where E_a is the activation energy; R is the gas constant; T is the temperature; A is some constant proposed by Arrenius.

As the kinematic viscosity is connected with dynamic viscosity on a formula $\nu = \eta/\rho$ (ρ — melt density), because of very weak dependence of density on temperature (several percent in all range of liquid state) in comparison with 3–4 multiple change of viscosity in the same range [4], it is possible to change directly in the equation (3) apparent viscosity η to kinematic viscosity ν, having respectively corrected parameters A to $A^{/}$ and activation energy E_a to estimated value $E_a^{/}$

$$\nu = A^{/}\exp\left(\frac{E_a^{/}}{RT}\right). \quad (4)$$

Table 2 shows the activation energy values obtained from the modified Fraenkel equation (4) based on experimental (information) and calculated on cluster-associate model (1) data for 28 metals of D.I. Mendeleyev periodic system.

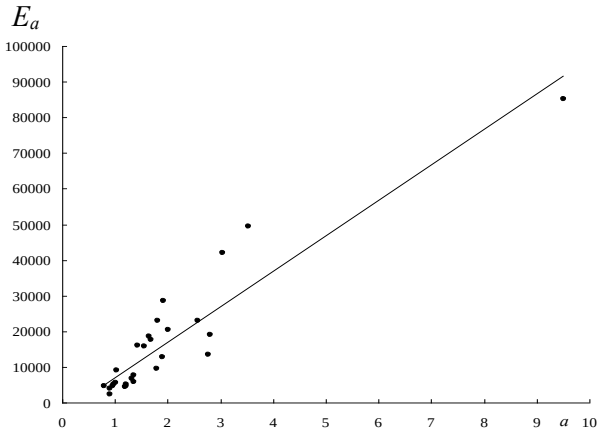
The activation energy values for the calculated data range from 2868 J/mole (mercury) to 128017 J/mole (beryllium). The correlation coefficient for the calculated activation energy values $E_a^{/}$ (calc) in comparison with experimental E_a(inf) comprised 0.8580 with its signification t_R = 16.6> 2 including beryllium. At its exception the correlation coefficient is much higher than $-R$ = 0.9552 with its signification t_R = 55.6 > 2.

Table 2

Activation energy values for experimental (Ea (inf)) and calculated on cluster-associate model (1) (E_a' (calc)) data for 28 metals

Element	E_a(inf), J/mole	E_a' (calc), J/mole	Element	E_a(inf), J/mole	E_a' (calc), J/mole
Li	5463	5920	Rb	4548	5055
Be	85231	128017	Sr	20453	22723
Na	5803	6485	Ag	22981	21684
Mg	22915	22150	Cd	9487	10867
Al	9029	8871	In	4681	5629
K	5138	5812	Sn	5155	5496
Ca	17635	20171	Te	13478	21476
Fe	49404	55540	Cs	4498	5072
Co	41971	46835	Ba	15889	17543
Ni	28610	29757	Au	16038	17294
Cu	18450	22133	Hg	2262	2868
Zn	12713	14134	Tl	6652	9154
Ga	3850	4074	Pb	4714	4448
Ge	19098	31004	Bi	7649	8447

Figures 3 and 4 show the comparison of the obtained range of activation energy data for experimental and calculated on cluster-associate pattern viscosity with the degree of cluster association for the metals under investigation, $E_a = f(\bar{a})$.



E_a is the activation energy, J/mole; $\bar{a}$ is the average degree of cluster association.
Points are experimental data, line is approximation of experimental data by equation $E_a = A + B\bar{a}$

Figure 3. Dependence of activation energy for experimental data on the degree of clusters association for 28 metals

As can be seen from the figures, the activation energy data obtained by processing the calculated values from the generalized pattern are described better by the approximate dependence.

The approximate equation for experimental data on viscous flow activation energy is expressed as:

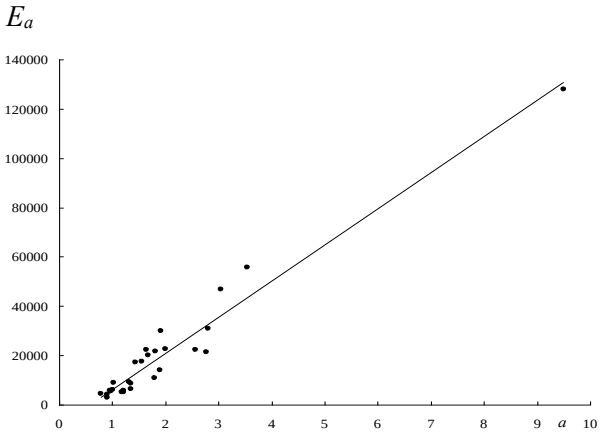
$$E_a(\text{inf}) = B\bar{a} + A = 9957\ \bar{a} - 2731. \quad (5)$$

For calculated on cluster-associate model (1):

$$E_a'(\text{calc}) = B'\bar{a} + A' = 14695\ \bar{a} - 8525. \quad (6)$$

The approximation dependability value for the information data on viscous flow activation energy depending on the degree of cluster association gives 0.9277, for the calculated from the model (1) — 0.9754.

Virtually, the coefficient B in equation (5) and B' in equation (6) make up the value of the activation energy corresponding to one cluster and are expressed as J/(mole·cluster). For experimental data, this coefficient is equal on average to ~10 kJ/(mole·cluster), and for calculated values is equal to ~15 kJ/(mole·cluster).



E_a is the activation energy, J/mole; $\bar{a}$ is the average degree of cluster association. Points are experimental data, line is approximation of data calculated according to the model (1) by equation $E_a^{/} = B^{/}\bar{a} + A^{/}$

Figure 4. Dependence of activation energy calculated on model (1) on the degree of clusters association for 28 metals

Shown above calculations confirm the functional nature of the cluster-associate pattern, taking into account the degree of clusters association from crystal mobile particles, which are the basis of a single model, and allow to consider the obtained approval as another proof of objectivity of chaotized particles concept.

Conclusions

1. The interconnection of clusters association degree in cluster-associate pattern of metals viscosity with their ionization potentials for all periods of D.I. Mendeleyev element system reveals their regular relation similar to the previously proposed [2] three separated patterns. This confirms the functional nature of the new pattern, which retains clusters from crystal mobile particles as a physical basis, with additional consideration of their association.

2. Analysis of activation energy values obtained from the modified Fraenkel equation on the basis of experimental (information) and calculated on cluster-associate pattern data for 28 metals showed their adequate straight-line dependence, moreover the description of their interconnection with the degree of clusters association on the basis of the calculated from the proposed pattern activation energy values is more accurate.

3. The obtained data based on the new cluster-associate pattern can be considered as another confirmation of the concept fruitfulness of chaotized particles.

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А.Ш. Қажикенова, Д.Б. Алибиев, А.Б. Сейтимбетова, Ж.М. Тентекбаева

Кластерлік-ассоциативті модель бойынша металдардың иондың потенциалының ассоцирленген кластерінің дәрежесінің өзара байланысы

Мақалада сұйық металдардың кинематикалық тұтқырлығының кластерлік-ассоциаттық моделі қарастырылған. Бұл модель хаотизирленген бөлшектер тұжырымдамасының негізінде алынды. Ұсынылған үлгіге сәйкес авторлар сұйық металдағы кластерлердің ассоциациялану дәрежесінің орташа мәндерін есептеді. Есептеу үшін Д.И. Менделеевтің элементтері кестесінің екінші — алтыншы кезеңдерінің 28

металдары зерттелген. Авторлардың жұмысында металдарды иондаудың бірінші әлеуетін кластерлердің ассоциациялану дәрежесінің алынған мәндерімен салыстыру келтірілген. Бұл салыстыру бірінші иондау әлеуетінің өзгеруімен тығыз байланыста кластерлер қауымдастығы дәрежесінің заңды өзгеруін көрсетті. Френкель теңдеуімен біріктірілгенде активтендіру энергиясын есептеу үшін аппроксимирлеуші теңдеуі алынды. Тұтқырлықтың температуралық тәуелділігінің кластерлік-ассоциаттық моделі үшін алынған теңдеу жиырма сегіз металл үшін балқыманың тұтқыр ағысын активтендіру энергиясын есептеу кезінде пайдаланылған. Активтендіру энергиясы бойынша алынған нәтижелерді авторлар эксперименталды мәліметтермен салыстырды. Бұл салыстыру ұсынылған модель бойынша алынған белсендіру энергиясы бойынша деректер аппроксимациялық тәуелділіктен жақсы сипатталатынын көрсетті. Алынған нәтижелерді көрнекі растау үшін жұмыста кестелер мен суреттер келтірілген. Осылайша, Д.И. Менделеев элементтері жүйесінің барлық кезеңдері бойынша металдарды иондаудың бірінші әлеуетін кластерлер ассоциациясының дәрежесімен салыстыру кезінде олардың заңды байланысы анықталды. Бұл байланыс кластерлік-қауымдасқан модельдің функционалдық сипаты туралы бекітуге мүмкіндік береді.

Кілт сөздер: тұтқырлық, ретсізделген бөлшектер, ассоцирленген кластердің дәрежесі, кластерлі-ассоциативті модел, сұйық металдар, активтендіру энергиясы, кристалл қозғалысты бөлшектер, иондау әлеуеті, Френкельдің модификацияланған теңдеуі.

А.Ш. Кажикенова, Д.Б. Алибиев, А.Б. Сейтимбетова, Ж.М. Тентекбаева

Взаимосвязь степени ассоциированности кластеров с потенциалами ионизации металлов по кластерно-ассоциатной модели

В статье рассмотрена кластерно-ассоциатная модель кинематической вязкости жидких металлов. Модель была получена на основе концепции хаотизированных частиц. Авторами, согласно предложенной модели, были рассчитаны средние значения степени ассоциированности кластеров, содержащихся в жидком металле. Для расчета были исследованы 28 металлов второго – шестого периодов таблицы элементов Д.И. Менделеева. Кроме того, приведено сопоставление первого потенциала ионизации металлов с полученными значениями степени ассоциированности кластеров. Данное сопоставление показало закономерное изменение степени ассоциации кластеров в тесной связи с изменением первого потенциала ионизации. В комбинации с уравнением Френкеля получено аппроксимирующее уравнение для расчета энергии активации. Уравнение для кластерно-ассоциатной модели температурной зависимости вязкости использовано при расчете энергии активации вязкого течения расплава для двадцати восьми металлов. Полученные результаты по энергии активации авторы сравнили с экспериментальными данными. Результаты сопоставления показали, что данные по энергии активации, полученные по предлагаемой модели, описываются лучше аппроксимирующей зависимостью. В работе для большей наглядности полученных результатов приведены таблицы и рисунки. Таким образом, при сопоставлении первого потенциала ионизации металлов по всем периодам системы элементов Д.И. Менделеева со степенью ассоциации кластеров выявлена их закономерная связь, которая позволяет утверждать о функциональном характере кластерно-ассоциатной модели.

Ключевые слова: вязкость, хаотизированные частицы, степень ассоциированности кластеров, кластерно-ассоциатная модель, жидкие металлы, энергия активации, кристаллоподвижные частицы, потенциал ионизации, модифицированное уравнение Френкеля.

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