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**VACANCY MODEL OF MELTING AND CHANGE
IN THE ACTIVATION ENERGY FOR SELF-DIFFUSION
IN RARE GASES
ON PASSING FROM THE SOLID TO THE LIQUID STATE**

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The fundamental assumptions of the vacancy model of melting, proposed by Górecki and coworkers [1,2], have been used as the starting point for deriving an expression for the activation energy of self-diffusion in rare gases (RGS) on passing from the solid to the liquid state. The result of these calculations indicates that the ratio of the activation energy in the solid state Q_s to that in the liquid state, Q_l , is for all the RGS the same:

$$Q_s/Q_l = 4,14.$$

This prediction agrees well with the experimental data available in the accessible literature, thus corroborating the validity of the vacancy model of melting.

Key words: rare gases, self-diffusion, melting.

Investigation of diffusion processes in liquids are of great interest from both the purely scientific and technological points of view. A correct theoretical interpretation of the diffusion coefficients would allow us to draw conclusions about the nature of ionic and electronic motions and interparticle interactions in materials. Also, a method of estimating their values would be of great use in the design of all the diffusion – limited metallurgical, chemical and other industrial processes.

It is generally accepted and supported by considerable experimental evidence that in a large number of solids, particularly in fcc metals, alkali halides and solidified rare gases, self-diffusion occurs by a vacancy mechanism and the temperature dependence of self-diffusion coefficient is represented by the Arrhenius equation

$$D = D_0 \exp(-Q_s/RT) \quad (1)$$

where the activation energy for self-diffusion in the solid state, Q_s , is the sum of the energies of formation energy, E_f , and migration, E_m , of vacancies. In the case of impurity

diffusion this simple picture is only slightly complicated by the vacancy-impurity interactions.

The understanding of diffusion processes in liquids is one of the fundamental subjects attracting the attention of many investigators. In spite of considerable effort the present situation is, however, much less satisfactory than that achieved for solids. This results from the fact that our understanding of the liquid state is still in an embryonic state. Many different models of the structure of liquids were proposed, but none of them has been commonly accepted. Consequently, there is no commonly accepted picture of atomic motions in liquids and different relations are proposed by theoreticians for describing the temperature dependence of the diffusion coefficient in melts [1, 2]. Many of the models of the structure of melts picture a liquid as a highly defective crystal. All these models suggest that the temperature dependence of the diffusion coefficient obeys the Arrhenius relation with an activation energy for diffusion in the liquid state, Q_l , much smaller than in the solid state, Q_s . Experimentalists also prefer the representation of their data in the diffusion in liquids with the use of the Arrhenius formula, although very often under the stipulation that this does not imply belief in the applicability of this formula to the diffusion in liquids.

In a series of papers [3–7] it has been shown that many physical properties of materials change in a systematic way on passing from the solid to the liquid state. All of the observed regularities are easily explainable in the framework of the vacancy model of melting in the version proposed by the present authors. Among others, it has been revealed [3,4] that for both the self- and impurity diffusion in metals and alkali halides the Q_s/Q_l ratio is nearly the same and approaches the value of 5. The purpose of the present communication is to draw attention to the hitherto unnoticed regularity in the changes of the activation energies for self-diffusion in condensed rare gases treated as representatives of the class of substances bounded by weak Van der Waals forces, on passing through the melting point.

The basis for derivation of the relation between the activation energies of self-diffusion in the solid and liquid phases of condensed rare gases is the vacancy model of melting of these substances [6], according to which:

- melting starts when the concentration of vacancies (Shottky defects) in the solid phase reaches a critical value of 0.37% at.,
- the melting process is the process of creation of additional vacancies at the expense of the heat of melting. The increase Δc of vacancy concentration on passing from the solid to the liquid phase amounts 18.5% at.

As it has been shown in [5], the value of the ratio of the vacancy formation energy to the vacancy migration energy is for all the fcc metals the same, $E_f/E_m=1$. Consequently, the activation energy for self diffusion, being the sum of the formation and migration energies of vacancies, $Q_D=2\cdot E_f=2\cdot E_m$. It could be expected that similar relations hold also for monoatomic rare gases, all crystallizing in the fcc structure. In order to check this supposition, in the table I the available in the literature [8–16] experimental data on the activation energies for formulation of vacancies as well as on the activation energies for diffusion in both the liquid and solid phases of rare gases were collected. In the column 4 of this table the values of vacancy migration energies, calculated as the difference between activation energy of self-diffusion in solid and the vacancy formation energy, are given.

Table 1

Experimental values of activation energies of vacancy formation, self-diffusion and vacancy migration in condensed rare gases, and calculated values of the ratios of these quantities

Element	Values of the activation energies [kJ/mol]				$\frac{Q_{Ds}}{E_f}$	$\frac{Q_{Dl}}{E_f}$	$\frac{Q_{Ds}}{Q_{Dl}}$
	Vacancy formation E_f	Self – diffusion in solid Q_{Ds}	Vacancy migration $E_m = Q_{Ds} - E_f$	Self – diffusion in liquid Q_{Dl}			
1	2	3	4	5	6	7	8
Ne	2,00 [8]	3,96 [12]	1,96	0,88 [12]	1,98	0,44	4,49
Ar	5,40 [9]	15,07 [13]	9,67	2,93 [16]	2,79	0,54	5,15
Kr	7,45 [10]	20,10 [14]	12,64	3,89 [16]	2,70	0,52	5,16
Xe	10,38 [11]	21,98 [15]	11,60	5,05 [16]	2,12	0,49	4,35

An inspection of the data presented in table 1 shows that, in a rough approximation, the activation energy for self diffusion in the solid phase is proportional to the vacancy formation energy (see Fig. 1):

$$Q_{Ds} \cong 2,40E_f \quad (2)$$

Therefore

$$E_m = Q_{Ds} - E_f = 1,4E_f \quad (3)$$

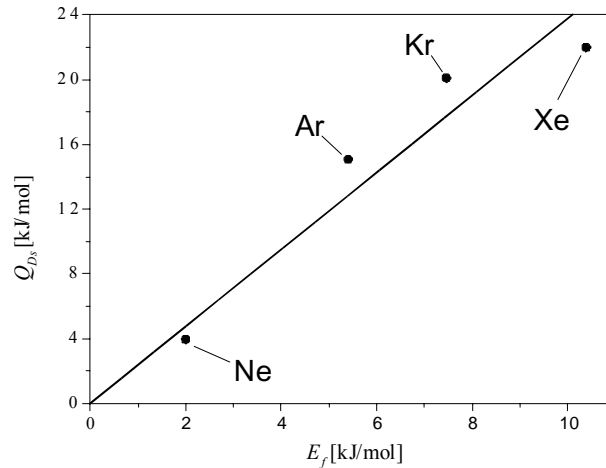


Fig. 1. Correlation between the activation energies for vacancy formation, E_f , and self-diffusion, Q_{Ds} in rare gas solids

According to the second postulate of the vacancy model of melting, approximately 18,5% of the lattice sites in the liquid phase are empty. Therefore, the value of the vacancy formation energy, being directly proportional to the binding energy [6], is in the liquid phase by 18,5% lower than that in the solid phase. Consequently, according to the eq. (3) the value of the migration energy of vacancies in the liquid phase diminishes also by 18.5% with respect to the solid phase:

$$E_{ml} = 0,815E_m = 1,14E_f. \quad (4)$$

The intensity of diffusion in the solid phase is limited by the number of vacancies in the nearest neighbourhood of migrating atom. In the liquid phase, at the vacancy concentration of 18,5% at. there are at least two vacancies in the first coordination sphere of each atom. The liquid state is “saturated” with vacancies, and the probability of jumping of an atom to the neighbouring site depends only on the vacancy migration energy. It is difficult, however, to interpret the diffusion in the liquid state as the migration of single vacancies (monovacancies). At concentration of 18,5% at. the aggregation of vacancies – formation of bi- and trivacancies must occur. The process of formation of bivacancies is observed already in the solid phase at temperatures close to the melting point. The presence of bivacancies causes the appearance of the “fast” component of diffusion stream, resulting from a large mobility of bivacancies. The experimental investigations [3] show, that in metals the migration energy of bivacancies is at least two times lower than for monovacancies.

Assuming the bivacancy mechanism of diffusion in liquid rare gases and the value of the bivacancy migration energy (similarly as in metals) two times lower than for monovacancies, one comes to the conclusion, that the activation energy for self-diffusion in the liquid phase of rare gases should be:

$$Q_{Dl} = \frac{1}{2}E_{ml} = \frac{1}{2} \cdot 1,14E_f = 0,57E_f. \quad (5)$$

The correctness of the above considerations is confirmed by the experimental facts (see column 7 in Table 1 and Fig. 2).

As it is seen, the ratio of the experimental values of activation energy, for self-diffusion to the vacancy formation energy in the solid phase is for all the rare gases nearly the same and amounts:

$$Q_{Dl}/E_f \cong 0,50. \quad (6)$$

The experimental value of Q_{Dl}/E_f only slightly differs from that predicted on the basis of vacancy model of melting and given by equation (5).

From equations (2) and (5) it follows that

$$Q_{Ds}/Q_{Dl} = 4,14 \quad (7)$$

This prediction stemming from the vacancy model of melting also agrees satisfactory with the experimental data, represented in Fig. 3 and in the column 8 of table 1, according to which the experimental value of the ration Q_{Ds}/Q_{Dl} is for all the condensed rare gases nearly the same, approaching the value of 4,74.

It is worth to note, that the value $Q_{Ds}/Q_{Dl}=4,14$, predicted by equation (7) is only the lower limit for this ratio, derived under assumption that the bivacancy migration energy is at least two times lower than that for migration of monovacancies. In this situation the

agreement between the predictions of the vacancy model of melting and experimental facts presented in table 1 and in Fig. 2 and 3 is very satisfactory.

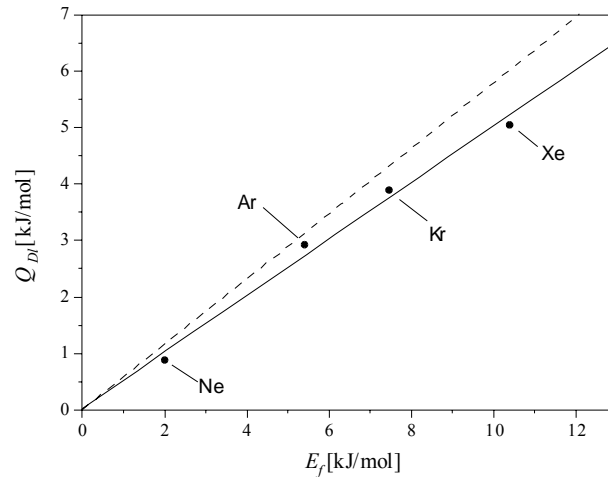


Fig. 2. Correlation between the activation energy for vacancy formation energy in the solid phase, E_f , and activation energy for self-diffusion, Q_{Dl} , in the liquid phase of rare gases

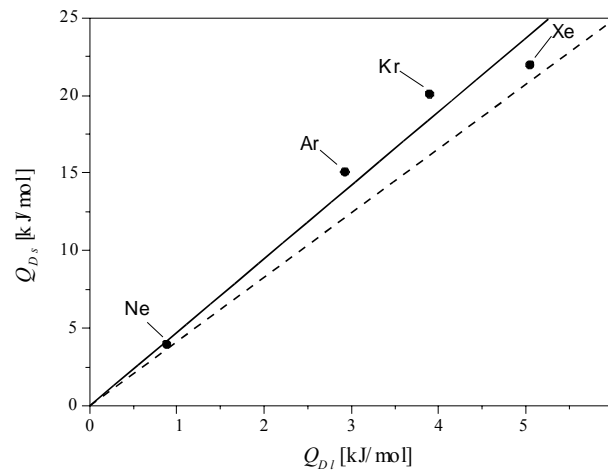


Fig. 3. Correlation between the activation energy for self-diffusion in the liquid, Q_{Dl} , and in the solid phase, Q_{Ds} , of rare gases

The results presented in the present work indicate that the vacancy model of melting not only predict correctly the changes in many physical properties on passing through the melting point, but also may be the source of valuable information on the mechanism of transport phenomena in liquids.

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**ВАКАНСІЙНА МОДЕЛЬ ПЛАВЛЕННЯ ТА ЗМІНИ ЕНЕРГІЇ АКТИВАЦІЇ
САМОДИФУЗІЇ ІНЕРТНИХ ГАЗІВ ПІД ЧАС ПЕРЕХОДУ З ТВЕРДОГО У
РІДКИЙ СТАН**

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Фундаментальні припущення, викладені авторами в попередніх працях стосовно вакансійної моделі плавлення використано як вихідні дані для отримання виразів для енергії активації самодифузії інертних газів під час переходу з твердого стану у рідкий. Результати розрахунків свідчать, що відношення величини енергії активації в твердому стані до її значення у рідкому становить 4,14 і є однаковим для всіх інертних газів.

Отриманий висновок підтверджується літературними експериментальними даними, що обґрунтовує вакансійну модель плавлення.

Ключові слова: інертні гази, самодифузія, плавлення.

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