CALCULATION OF ACTIVATION ENERGY OF DIFFUSION AND SELF-DIFFUSION

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The methodology is given for the evaluation of activation energy of diffusion and self-diffusion based on the application of spatial-energy parameter (*P*-parameter). The corresponding calculations are made for 57 structures. The calculation results are in accordance with the experimental data.

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Introduction

Activation energy is one of the basic characteristics of diffusion processes. A lot of works are dedicated to theoretical calculations and experimental evaluations of this value.[1-10] However the comparison of reference data reveals rather contradictory results on many systems. For instance, a significant discrepancy between theoretical and experimental data of activation energy was obtained even for such well-investigated process as silicon self-diffusion (3.2 eV and 4.76 eV, respectively).[3-5]

It is customary to distinguish between several types of main diffusion mechanisms in crystals viz., diffusion by internodes, vacancy mechanism, replacement mechanism, etc. The diffusion activation energy equals the value of the potential barrier that has to be overcome by the atom to take a new balanced position in the neighboring node or internode.

Theoretical calculations of activation energy are very difficult. Therefore different authors tried to correlate it with some other values that can be calculated or defined theoretically. Thus according to Frenkel[11] during self-diffusion process the activation energy should be close to the value of crystal evaporation heat. However, as a rule, lower values are experimentally observed. Braune[5] tried to correlate the activation energy with melting temperature of crystals. However the correlation proposed by him is useful only for rough estimation of activation energy since the criterion for selecting the empirical constant of initial equation is missing.

A well-known Arrhenius equation is widely used for energy estimation of diffusion processes.

$$\Lambda = \Lambda_0 exp\left(-\frac{E_a}{RT}\right) \qquad (1)$$

where

Λ=coefficient of diffusion,

Λ_0= pre-exponential factor,

E_a = activation energy of diffusion,

R = gas constant and

T = thermodynamic temperature.

The dependence of initial parameters upon the temperature and pressure, the presence of pre-exponential factor in the equation rather complicate the issue of rational objectivity of data being obtained, in particular, when comparing diffusion mechanisms near the surface and inside the crystal.

In this research there is an attempt to numerically calculate the activation energy of diffusion based on initial spatial-energy characteristics of free atoms (methodology of *P*-parameter).

Spatial-energy parameter

The comparison between multiple regularities of physical and chemical processes allows assuming that in many cases the principle of adding inverse values of volume energies or kinetic parameters of interacting structures is fulfilled. Some examples are ambipolar diffusion, total rate of topochemical reaction, change in the light velocity when moving from vacuum to the given medium, resulting constant of chemical reaction rate (initial product – intermediary activated complex – final product).

Lagrangian equation for relative motion of isolated system of two interacting points with masses m_1 and m_2 in coordinate x with acceleration α can look as follows:

$$\frac{1}{\frac{1}{\frac{1}{m_1 a\Delta x}}+\frac{1}{m_2 a\Delta x}} \approx -\Delta U \qquad (2)$$

$$\frac{1}{\Delta U} \approx \frac{1}{\Delta U_1}+\frac{1}{\Delta U_2} \qquad (3)$$

where

ΔU_1 and ΔU_2 are the potential energies of material points on elementary portion of interactions and

ΔU is the resulting (mutual) potential energy of these interactions.

The atom system is formed of differently charged masses of nucleus and electrons. In this system the energy characteristics of sub-systems are orbital energy of electrons and effective energy of nucleus taking into consideration the screening effects. At the same time the bond energy of electrons or ionization energy of atom (E_i) can be used as orbital energy. Therefore, assuming that the resulting interaction energy in the system orbital-nucleus (responsible for inter-atom interactions) can be calculated following the principle of adding inverse values of some initial energy components, the introduction of P-parameter[12] as an averaged energy characteristics of valence orbitals based on the following equations can be substantiated.

$$\frac{1}{\frac{q^2}{r_\mathrm{i}}}+\frac{1}{E_\mathrm{i}}=\frac{1}{P_\mathrm{E}} \qquad (4)$$

$$P_\mathrm{E}=\frac{P_0}{r_\mathrm{i}} \qquad (5)$$

$$\frac{1}{P_0}=\frac{1}{q^2}+\frac{1}{(Er)_\mathrm{i}} \qquad (6)$$

$$q=\frac{Z^*}{n^*} \qquad (7)$$

where

E_i is the atom ionization energy,[13]

r_i is the orbital radius of i–orbital,[14]

and Z^* and n^* are effective charge of nucleus and effective main quantum number, respectively.[15,16]

P_0 will be called a spatial-energy parameter and P_E an effective P-parameter. Effective P_E parameter has a physical sense of some averaged energy of valence electrons in an atom and is measured in energy units, e.g. in electron-volts (eV).

According to the calculations[12] the values of P_E parameters are numerically equal (in the range of ± 2 %) to the total energy of valence electrons (U) by atom statistic model. Using the known relation between the electron density (β) and intra-atomic potential by atom statistic model, it is possible to obtain the direct dependence of P_E parameter on the electron density at the distance r_i from nucleus by Eqn. (8).

$$\beta_\mathrm{i}^{\frac{2}{3}}=\frac{AP_0}{r_\mathrm{i}}=AP_\mathrm{E} \qquad (8)$$

where A is a constant.

The reliability of this equation was confirmed experimentally by determining the electron density using wave functions by Clementi and comparing it with the value of electron density calculated via the value of P_E-parameter.

Modifying the rules of adding inverse values of energy magnitudes of subsystems as applied to complex structures, the equation (Eqn. 9) for calculating P_S-parameter of complex structure can be obtained

$$\frac{1}{P_\mathrm{S}}=\left(\frac{1}{NP_\mathrm{E}}\right)_1+\left(\frac{1}{NP_\mathrm{E}}\right)_2+\cdots \qquad (9)$$

where N_1 and N_2 are a number of homogeneous atoms in the subsystem.

The same electron density should be fixed during the formation of solution and other structural interactions in the spots of contact between atoms-components. This process is followed by the redistribution of electron density between valence zones of both particles and transition of part of electrons from one external sphere to adjoining ones. Apparently, the frame electrons of atoms do not participate in such an exchange.

Obviously, the proximity of electron densities in free atoms-components results in the minimization of transition processes between boundary atoms of particles, thus favouring the formation of a new structure. Therefore, the task of estimating the degree of structural interactions in many cases means a comparative estimation of electron density of valence electrons in free atoms (on averaged orbitals) participating in the process.

The less is the difference (P'_0/r'_i - P''_0/r''_i), the more energetically favourable is the formation of a new structure or solid solution.

The estimation of mutual solubility for structural interactions of isomorphic type in many (over one thousand) simple and complex systems[12] was carried out based on this technique. Isomorphism as a phenomenon is considered as applied to crystalline structures. But, apparently, analogous processes can also proceed between molecular compounds where their role and value are none the less than in purely Coulomb interactions. It seems diffusion processes, replacement in particular, can also be estimated via the methodology of P-parameter.

Calculation methodology

It is established that during self-diffusion the activation energy often equals the total of enthalpies of formation and transition of vacancies. Obviously, in any actual situation different diffusion mechanisms can act simultaneously, but the activation energy must always be defined by inter-atom interactions in structures.

Thus, the task of estimating the activation energy is to define the actual energy of paired inter-atom interaction of diffusion atom and atoms of diffusion medium, for each specific type of interactions.

Earlier the diffusion coefficients of some refractory oxides were calculated using initial spatial-energy notions[17] via total P-parameter of interacting diffusion atoms and diffusion medium.

Let us now demonstrate that with the help of P-parameter it is possible to rather reliably and easily estimate the activation energy during the transfer of atoms in solids.

For this we use the tabulated values of P_0-parameters calculated via the ionization energy (Table 1) based on the Eqns. 4-7. In diffusion processes, with the prevalence of ionic structures, it is preferable to use the energy of atom ionization (E_i) as the orbital energy.

Now, with the help of P-parameter, we cab determine the averaged effective energy of paired inter-atom interaction in the system M'-M". Having summed up P_0 by valence electrons and divided the value of $P_0/2r_i$ by a number of effective valence electrons (n), we obtain some effective energy of atom falling at one valence electron (Eqn. 10).

$$Q = \frac{P_0}{2r_i n} \tag{10}$$

Applying the previously stated principle of adding inverse values of P_E-parameters (Eqn. 9), we obtain the resulting value of effective energy of paired interaction of atoms 1 and 2 during diffusion and self-diffusion.

$$\frac{1}{E_a} = \frac{1}{Q_1} + \frac{1}{Q_2} \tag{11a}$$

or

$$\frac{1}{E_a} = 2\left[\left(\frac{r_i n}{P_0}\right)_1 + \left(\frac{r_i n}{P_0}\right)_2\right] \tag{11b}$$

where E_a = activation energy.

If during self-diffusion $n_1 = n_2$ and $Q_1 = Q_2 = Q$, then

$$E_a = \frac{Q}{2} = \frac{P_0}{4r_i n} \tag{12}$$

Table 1. P_0-parameters of valence orbitals of neutral atoms in basic state (calculated via the ionization energy of atoms).

Atom	**Valence orbitals**	E_i **(eV)**	r_i **(Å)**	q^2_i **(eVÅ)**	P_0 **(eVÅ)**	ΣP_0 **(eVÅ)**
H	$1s^1$	13.595	0.5295	14.394	4.7985	4.7985
Li	$2s^1$	5.390	1.586	5.890	3.487	3.487
Be	$2s^1$	9.323	1.040	13.159	5.583	13.347
	$2s^1$	18.211	1.040	13.158	7.764	
C	$2p^l$	11.260	0.596	35.395	5.641	51.739
	$2p^1$	24.383	0.596	35.395	10.302	
	$2s^1$	47.86	0.620	37.243	16.515	
	$2s^1$	64.48	0.620	37.243	I9.281	
O	$2p^1$	13.618	0.414	71.380	5.225	17.304
	$2p^1$	35.118	0.414	71.380	12.079	
Na	$3s^1$	5.138	1.713	10.058	4.694	4.694
Mg	$3s^1$	7.469	1.279	17.501	6.274	15.436
	$3s^1$	15.035	1.279	I7.50I	9.I62	
Al	$3p^1$	5.986	1.312	26.443	6.055	31.624
	$3s^1$	18.829	1.044	27.119	11.396	
	$3s^1$	28.44	1.044	27.119	14.173	
Si	$3p^1$	8.152	1.068	29.377	6.716	54.394
	$3p^1$	16.342	1.068	29.377	10.948	
	$3s^1$	33.46	0.904	38.462	16.932	
	$3s^1$	45.13	0.904	38.462	19.799	
P(III)	$3p^1$	10.487	0.919	38.199	7.696	35.996
	$3p^1$	19.73	0.916	38.199	12.268	
	$3p^1$	30.16	0.9I6	38.199	16.038	
S(II)	$3p^1$	10.360	0.808	48.108	7.130	20.682
	$3p^1$	23.35	0.808	48.108	13.552	
K	$4s^1$	4.339	2.162	10.993	5.062	5.062
Ca	$4s^1$	6.113	1.690	17.406	6.483	15.803
	$4s^1$	11.871	1.690	17.406	9.320	
Ti(II)	$4s^1$	6.82	1.477	20.879	6.795	17.026
	$4s^1$	I3.58	1.477	20.879	10.231	
Ti(III)	$3d^1$	28.14	0.489	106.04	12.184	29.210
Ti(IV)	$3d^1$	43.24	0.489	106.04	17.629	46.839
V(II)	$4s^1$	6.74	1.401	22.328	6.6362	17.162
	$4s^1$	14.21	1.401	22.328	10.525	
V(III)	$3d^1$	29.699	0.449	129.09	12.097	29.249
V(V)	$3d^1$	48.0	0.449	129.09	18.468	71.579
	$3d^1$	65.2	0.449	129.09	23.863	
Cr(III) $4s^I3d^5$	$4s^1$	6.765	1.453	23.712	6.949	25.835
	$3d^1$	16.498	0.427	152.29	6.734	
	$3d^1$	31.00	0.426	52.29	12.152	
Cr(III) $4s^23d^4$	$4s^1$	6.765	1.453	23.712	6.949	31.048
	$4s^1$	16.498	1.453	23.712	11.920	
	$3d^1$	31.00	0.426	152.29	12.152	
Mn(II)	$4s^1$	7.435	1.278	25.118	6.895	18.025
	$4s^1$	154640	1.278	25.118	11.130	
Mn(III)	$3d^1$	33.69	0.3885	177.33	12.200	30.225
Fe(II)	$4s^1$	7.893	1.227	26.57	7.098	18.462
	$4s^1$	16.183	1.227	26.57	11.364	
Fe(III)	$3d^1$	30.64	0.365	199.95	10.564	29.026
Fe(II)	$4s^1$	7.893	1.227	26.57	7.098	12.835
	$3d^1$	16.183	0.365	199.95	5.7372	
Fe(III)	$3d^1$	30.64	0.365	199.95	10.564	23.399
Co(II)	$4s^1$	7.866	1.181	27.983	6.973	18.687
	$4s^1$	17.057	1.181	27.983	11.7I4	
Co(III)	$3d^1$	33.49	0.343	224.85	10.929	29.615
Ni(II)	$4s^1$	7.635	1.139	29.348	6.708	18.838
	$4s^1$	18.153	1.139	29.348	12.I30	
Cu(I) $4s^13d^{10}$	$4s^1$	7.726	1.191	30.717	7.081	7.081
Cu(II) $4s^13d^{10}$	$3d^1$	20.922	0.312	278.78	6.191	13.272
Zn′	$4s^1$	9.394	1.065	32.02	7.623	19.599
	$4s^1$	17.964	1.065	32.02	11.976	
Zn″	$4s^1$	9.394	1.065	32.02	7.623	12.798
	$3d^1$	17.964	0.293	308.13	5.175	
Se(II)	$4p^1$	9.752	0.918	61.803	7.819	22.614
	$4p^1$	21.19	0.918	61.803	14.795	
Zr(II)	$5p^1$	6.835	1.593	23.926	7.483	18.547
	$5p^1$	12.92	1.593	23.926	11.064	
Zr(IV)	$4d^1$	24.8	0.790	153.76	17.378	58.773
	$4d^1$	33.97	0.790	153.76	22.848	

Nb(III) $5s^14d^4$	$5s^1$	6.882	1.589	20.191	7.093	34.587
	$4d^1$	14.320	0.747	113.64	9.776	
	$4d^1$	28.1	0.747	113.64	17.718	
Mo(II) $5s^14d^5$	$5s^1$	7.10	1.520	21.472	7.182	17.475
	$4d^1$	16.155	0.702	110.79	10.293	
W′(II)	$6s^1$	7.98	13.60	38.838	8.483	20.689
	$5d^1$	17.70	0.746	161.43	12.206	
W″(II)	$6s^1$	7.98	1.360	38.838	8.483	23.344
	$6s^1$	17.70	1.360	38.838	14.861	
Ag(I) $5s^14d^{10}$	$5s^1$	7.576	1.286	26.283	7.108	7.108
Sn(II)	$5p^1$	7.332	1.240	47.714	7.637	20.761
	$5p^1$	14.6	1.240	47.714	13.124	

The results of calculations based on Eqn. 11 and 12 are given in table 2. An example of calculations for self-diffusion of carbon atom (as shown in table 2) is given below.

$$\frac{1}{E_a} = 2\times\left(\frac{0.596\times2}{51.739}+\frac{0.596\times4}{51.739}\right) = 7.23eV \qquad (13)$$

The activation energy of diffusion of various elements in germanium has been calculated (Table 3). Here for hydrogen atom the ion radius equal to 1.36Å has been used. As an example the calculation of activation energy of diffusion of aluminium in germanium is shown. $1/E_a = 1/Q_1 + 1/Q_2$; $1/Q = (2 \times 1.312 \times 3)/31.24 + (2 \times 1.90 \times 4)/61.76$, $E_a = 2.55$ eV, $E_{a\,(}$exp) = 2.70 eV.

Table 2. Calculation of activation energy of volume self-diffusion.

Atom	**Orbitals**	**P_0(eVÅ)**	**r_i (Å)**	**n_1-n_2**	**E_a (eV) (calcd.)**	**E_a (eV) (Exp.)**
Li	$2s^1$	3.487	1.586	1 – 1	0.55	0.57
Be	$2s^2$	13.347	1.04	2 – 2	1.60	1.70 – 1.63
C_1	$2p^2+2s^2$	51.739	0.596	4	7.23	7.07
C_2	$2p^2+2s^2$	51.739	0.596	2		
Mg	$3s^2$	15.436	1.279	2-2	1.51	1.40
Al_1	$3p^1+3s^2$	31.624	1.312	3	1.47	1.47
Al_2	$3p^1$	6.055	1.312	1		
Na	$3s^1$	4.694	1.713	1 – 2	0.457	0.45
Si_1	$3p^2+3s^2$	54.394	1.068	4	4.24	4.76
Si_2	$3p^2+3s^2$	54.394	1.066	2		
P	$3p^1$	7.696	0.919	5 – 5	0.419	0.408
K	$4s^1$	5.062	2.162	1 – 2	0.390	0.406
Cl	$3p^1$	8.125	0.728	7 – 7	0.399	–
Ca	$4s^2$	15.803	1.690	1 – 2	1.56	1.67
S_1	$3P^2$	20.682	0.808	4	2.13	2.03
S_2	$3P^2$	20.682	0.808	2		(monocrystal)
Zn	$4s^1$	7.623	1.065	2 – 2	0.896	0.885
Zn	$4s^I+3d^1$	12.798	1.065	2 – 2	1.50	1.34
Cd	$5s^1$	8.349	1.184	2 – 2	0.881	0.83
Ge	$4p^2+4sS^2$	61.175	1.090	4 – 4	3.508	3.15
Ge_1	$4p^2+4sS^2$	61.175	1.09	4	3.37	3.15
Ge_2	$4p^2$	19.361	1.09	2		
Se_1	$4p^2$	22.614	0.918	6		1.2 – 1.4
Se_2	$4p^2$	22.614	0.918	2	1.54	
α-Zr	$5s^2+4d^2$	58.773	1.593	4 – 4	2.30	2.25
	$5s^1+4d^1$	17.055	1.593	2 – 2	1.338	1.17
β-Zr	$5s^2+4d^2$	58.773	1.593	4	1.69	1.65
	$5s^1+4d^1$	17.055	1.593	2		
β-Ti	$4s^2$	17.026	1.435	2 – 2	1.48	1.52
V_1	$4s^2+3d^3$	71.579	1.401	5	4.26	4.08
V_2	$4s^2+3d^3$	71.579	1.401	1	4.26	
Jn	$5p^1$	6.999	1.382	3	0.606	0.810
	$5p^1$	6.999	1.382	1		
Sn	$5p^2$	20.761	1.240	4 – 4	1.05	1.01
Sb	$5p^3$	41.870	1.193	5 – 5	1.76	1.55 – 2.08
Te	$5p^4$	50.542	1.111	6 – 6	1.896	1.75 – 2.03
Hf	$6s^2$	19.828	1.476	2 – 2	1.68	1.68; 1.804

Table 3. Calculation of activation energy of volume self-diffusion in germanium. Initial data for germanium: Orbital $4p^1$: P_0 = 7.128, n=1, r_i = 1.090 Å. Orbital $4p^2$ P_0 = 19.361 eVÅ, r_i = 1.090 Å, n=2. Orbitals $4p^2 + 4s_2$: P_0 =61.17 eVÅ, n= 4, r_{max} 1.090 Å.

Diffusing element					**Germanium**			**E_a (eV) Calculated**	**E_a (eV) Experimental**
Atom	**Orbitals**	**P_0(eVÅ)**	**r_i(Å)**	***n***	**Orbitals**	**P_0(eVÅ)**	**n**		
Li	$2s^1$	3.487	1.586	1	$4p^1$	7.128	1	0.469	0.46
Zn	$4s^2$	19.599	1.065	2	$4p^2+4s^2$	61.176	4	2.78	2.80
Al	$3p^1+3s^2$	31.624	1.312	3	$4p^2+4s^2$	61.176	4	2.55	2.70
In	$3p^1+5s^2$	40.749	1.328	3	$4p^2+4s^2$	61.176	4	2.96	3.2
Sn	$5p^2$	20.761	1.240	2	$4p^2$	19.361	2	2.15	1.90
Pb	$6p^2+6s^2$	71.221	1.215	4	$4p^2+4s^2$	61.176	4	3.58	3.60
H	$1s^1$	4.794	$R_{И}$=1.36	2	$4p^1$	7.128	4	0.44	0.38
As	$4p^3$	39.448	1.001	5	$4p^2+4s^2$	61.176	4	2.52	2.51
B	$2p^I+2s^2$	26.753	0.776	1	$4p^2+4s^2$	61.176	4	5.09	4.54
La	$4p^I+4s^2$	37.678	1.254	3	$4p^2+4s^2$	61.176	4	2.95	2.5-3.14
P	$3p^3$	35.996	0.919	5	$4p^2+4s^2$	61.176	4	2.51	2.49
Sb	$5p^3$	41.870	1.193	5	$4p^2+4s^2$	61.176	4	2.34	2.42
Be	$2s^2$	13.347	1.040	2	$4p^2+4s^2$	61.176	4	2.20	2.50
N	$2p^3$	33.664	1.578	3	$4p^2+4s^2$	61.176	4	2.36	2.58
Bi	$6p^3$	48.483	1.295	5	$4p^2+4s^2$	61.176	4	2.44	2.42

Table 4. Estimation of activation energy of diffusion and self-diffusion in metal systems

Solvent					**Diffusing element**					**E_a (eVB)**	
Atoms	**P_0, eVÅ**	**R_i, Å**	***n***	**P_0/R_in**	**Atoms**	**P_0, eVÅ**	**R_i, Å**	***n***	**P_0/R_in**	**Calcd.(eq.11, 12)**	**Expt.**
γ-Fe ($4s^23d^1$)	29.026	0.67	3	14.441	γ-Fe ($4s^2$)	18.462	0.80	2	11.539	3.207 self-diffusion	2.8–3.2
γ-Fe ($4s^23d^1$)	29.026	0.67	3	14.441	Cr ($4s^13d^2$)	25.835	0.64	3	13.456	3.483	3.468
γ-Fe ($4s^23d^1$)	29.026	0.67	3	14.441	C ($2p^3$)	32.458	2.60	3	4.1613	1.615	1.586
γ-Fe ($4s^23d^1$)	29.026	0.67	3	14.441	Mn ($4s^2$)	18.025	0.91	2	9.9038	2.937	2.71±0.04 2.861
γ-Fe ($4s^2$)	18.462	0.80	2	11.539	Mn ($4s^2$)	18.025	0.91	2	9.9038	2.665	2.419
γ-Fe ($4s^2$)	18.462	0.80	2	11.539	Ni ($4s^2$)	18.838	0.74	2	12.728	3.026	2.905
γ-Fe ($4s^2$)	18.462	0.80	2	11.539	Mo ($5s^14d^1$)	17.475	0.915	2	9.5492	2.613	2.557
γ-Fe ($4s^2$)	18.462	0.80	2	11.539	W ($6s^15d^1$)	20.689	0.98	2	10.821	2.792	2.709
γ-Fe ($4s^23d^1$)	29.026	0.80	3	14.441	Cu(I) ($4s^1$)	7.081	0.98	1	7.2255	2.408	2.309 2.558
γ-Fe ($4s^23d^1$)	29.026	0.80	3	14.441	Cu(II) ($4s^13d^1$)	13.272	0.80	2	8.295	2.634	2.644
α-Fe ($4s^13d^2$)	23.399	0.67	3	11.641	α-Fe ($4s^13d^1$)	12.835	0.80	2	8.022	2.375 self-diffusion	2.493–2.658
α-Fe ($4s^13d^2$)	23.399	0.67	3	11.641	Cr ($4s^13d^2$)	25.835	0.64	3	13.456	3.121	2.904 3.022
α-Fe ($4s^13d^1$)	12.835	0.80	2	8.0219	C ($2p^1$)	5.641	2.60	1	2.1696	0.854	0.867 0.833
α-Ti ($4s^2$)	17.026	0.78	4	5.4571	α-Ti ($4s^13d^1$)	13.044	0.78	4	4.1808	1.184 self-diffusion	1.270
β-Ti ($4s^2$)	17.026	0.78	4	5.4571	β-Ti ($4s^2$)	17.026	0.78	4	5.4571	1.304 self-diffusion	1.303
α-Zr ($5s^14d^1$)	17.055	0.925	2	9.2027	α-Zr ($5s^14d^1$)	17.055	0.925	2	9.2027	2.305 self-diffusion	2.25

β-Zr ($5s^2$)	18.547	0.925	4	5.0127	β-Zr ($5s^2$)	18.547	0.925	4	5.0127	1.253 self-diffusion	1.305
β-Zr ($5s^2$)	18.547	0.925	4	5.0127	β-Zr ($5s^1 4d^1$)	17.055	0.925	2	9.2027	1.623 self-diffusion	1.65
Ca ($4s^2$)	15.803	1.04	2	7.5976	C ($2p^2$)	15.943	2.60	2	3.066	1.092	1.010
Ca ($4s^2$)	15.803	1.04	2	7.5976	Fe ($4s^2$)	18.462	0.80	2x2	4.011	1.31	1.29

Table 5. Calculation of activation energy of diffusion of oxygen atoms

Oxygen	**Diffusion medium**						**E_a (eV) Calcd. eq. (8.9)**	**E_a (eV) Exp.**
Q_1(eV)	**Atoms**	**Orbitals**	**P_0(eV)**	**r_i (Å)**	**n**	**$P_0/2r=Q_2$ (eV)**		
3.1809	Si	$3p^2 3s^2$	54.394	1.068	2	12.733	2.545	2.494
3.1809	α-Ti	$4s^2$	17.026	1.477	2	2.8819	1.512	1.453
3.1809	V	$4s^1 3d^1$	12.716	1.401	2	2.269	1.324	1.258
3.1809	Fe (at T≈1900K)	$4s^2$	18.462	1.227	6	1.2539	0.899	0.846
3.1809	Cu (II)	$4s^2$	20.841	1.191	2	4.4877	1.861	1.857
3.1809	Ge	$4p^2$	19.361	1.090	4	2.2203	1.308	1.343
3.1809	α-Zr	$5s^1 4d^1$	17.055	1.593	2	2.677	1.454	1.293
3.1809	Nb	$5s^1$	7.093	1.589	1	2.2319	1.312	1.249
1.9210	Nb	$5s^1$	7.093	1.589	1	2.2319	1.032	1.080
1.9210	Ta	$6s^2$	22.565	1.413	2	3.992	1.297	1.258
1.9210	W (at T≈1973 K)	$6s^2$	23.344	1.360	4	2.1455	1.014	1.041

Analogous calculations for oxygen diffusion are shown in Table 5. In this Table for oxygen:

$$Q_1 = \frac{17.304}{21.361} = 3.1809\ eV \qquad \text{(orbital } 2p^2\text{)} \qquad (14)$$

$$Q_1 = \frac{5.215}{21.362} = 1.9210\ eV \qquad \text{(orbital } 2p^1\text{)} \qquad (15)$$

In all cases either the number of valence electrons of one sublevel or number of all valence electrons of the given main number of atom was used as the number n.

For hydrogen atom n=2, this corresponds to the realization number of all its possible bonds. For elements of groups 1 and 2n equals the group number, for groups 3a during self-diffusion n_1=3, n_2=1. For groups 4-a n_1=4, n_2=2. For *Na* and *K* n_1=1 and n_2=2, this reflects the possibility of generalizing valence electrons in inter-structural interactions.

The comparison of calculation and experimental values,[1-10,18] of activation energy of diffusion (Table 2-5) shows that these values are in satisfactory accordance (in the limits of experiment accuracy). Temperature factor, that can also have values in diffusion processes, was indirectly considered in this approach via selecting the most valence-active orbitals of the atom. Thus, for instance, for trivalent iron $4s^2 3d^1$ can usually be valence-active orbitals at lower temperatures, and $4s^1 3d^2$ at higher temperatures of the process.

Conclusion

Since the resulting value of P-parameter of a complex structure is quite easily calculated, this method can be applied for predicting the activation energy of diffusion and self-diffusion processes not only in simple but also in complex systems, in bio-systems as well.

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