PUBLICATIONS OF
COLLEGE OF EDUCATION
UNIVERSITY OF BASRAH

JOURNAL OF BASRAH RESEARCHES
(Sciences)

Volume : 34
Number : 5
2008

Journal Basrah Researches (Sciences) Vol. 34 , No. 5, 15 October 2008

Ionization Degree - Surface Work Function Dependence in the Chemisorption of Li atom on Ni surface

Haider Q. Al-Edany

Physics department – College of education - University of Basrah - Basrah – Iraq

ISSN -1817 -2695

(Received 11/5/2008, Accepted 24/8/2008)

Abstract:

The aim of this paper is to explaining the effect of the distance and work function on the processes of charge transfer at the metal surfaces, such as the some of particles leaving a metal surface (surface ionization process), by using the AGN chemisorption theory .

The interaction of an alkali atom (Lithium) on a transitional metal surface (polycrystalline nickel surface) is treated by introduce the work function into the expression of atomic energy level on the adsorbed atom. Then the treatment was applied to the surface ionization and shows that it occurs at distances that increase rapidly with the increasing work function according to changing the face of surface.

Key words: chemisorption, adsorbed particle, ionization degree, surface ionization.

Introduction:

The adsorption of the atoms (ions) on solid surface is considered as one of the complex subjects, because it needs to understand many basic interactions that occur on the surface. One of these interactions is the interaction between the adatom and the surface for it has many practical applications.

The adsorption process (which is the adsorption of the atomic particles on a metal surface) differs from the absorption process (which is the absorption of the atomic particles by the metal). However, there are two kinds of the adsorption depending on the nature of bond formed between the adatom and the surface; these kinds are [1]:Physical adsorption (Physisorption), here the Van der Waales bond is dominated where there is no redistribution for the electronic density on adatom and on the surface.

Chemical adsorption (Chemisorption), the Chemical bond formed between the adatom and the surface and which includes redistribution and the rearrangement of the electronic density and its nature is restricted between the ionic bond and the covalent bond. The ionic bond is considered the dominated bond in the chemisorption of alkalis on the transitional metal (W, Mo, Ni, Ta) and its value is between (1.5 – 2.5 eV)[2].

According to the Anderson – Grimly – Newns (AGN) of the chemisorption, when a charged particle approaches to the surface then an electronic response of the metal leads to a polarization potential affecting on the charged particle. This phenomenon was described by the use of concept of the image charge [3]. The effect of the image charge plays a very important role in the atom – surface interaction [4] such as chemisorption process or any process that includes the charge exchange.

Theoretical Considerations:

If the adatom approaches to the surface, the adatom energy level will be shifted because the effect of the polarized charges on the surface. This is given by the image shift [5]:

$$\Delta E(S)=\frac{e^2}{4\sqrt{(S^2+S_o^2)}} \quad \text{---- (1)}$$

Where e represents the charge of electron, S_o is the location of image plane (screening length) which is explained on the basis of surface plane (S=0) is pushed into a metal by an amount of (S_o) which is used in the theoretical treatments as an adjustable parameter.

The wave functions of electrons in the adatom and the metal intersect with each other at the closest approach distance from the surface and this leads to resonant transitions that occur throughout the potential barrier that existed between the metal and the adatom, then the adatom energy level is broadened by 2Γ.

By neglecting the dependence of Γ on adatom energy level, one can describe the dependence of the broadening Γ on the distance S by [6]:

$$\Gamma^{\pm\sigma}(S)=\frac{(q_a^{\pm\sigma})^2}{16V_o(S+r_i)}\sqrt{2V_o-(q_a^{\pm\sigma})^2}\left(1+\frac{1}{2(S+r_i)q_a^{\pm\sigma}}\right)e^{-2Sq_a^{\pm\sigma}} \qquad \text{------------ (2)}$$

This relation is dependent on the spin of electrons whereas r_i represents the ionic radius and $V_o=\phi+|u_o|$, whereas ϕ is the surface work function, $|u_o|$ is the metal band width and $q_a^{\pm\sigma}$ is given by:

$$q_a^{\pm\sigma}=\sqrt{2E_a^{\pm\sigma}} \qquad \text{------- (3)}$$

where $E_a^{\pm\sigma}$ represents the energy of the atomic level whose spin ±σ of the adatom.

It is well-known that there is an energy difference between the adatom energy levels (the ionization level V_i and the affinity level V_A) which are far from the surface because of the electron – electron interaction which is called by intra atomic Coulomb interaction U whose value is equal to [7]:

$$U=V_i-V_A \qquad \text{—— (4)}$$

When the adatom approaches to the surface, the ionization and affinity levels will be shifted by ΔE which is given by equation(1). That means the value of effective U (U_{eff}) will decrease as the adatom approaches to the surface because of the correlation interaction which is caused by the electron – electron interaction [8]. The treatment of U as its formula and its dependence on the distance is considered one of the problems that meet the researchers. Generally, it is either taken as a constant equal to (V_I - V_A) or neglected.

Since the subject of this review concerns the chemisorption of alkali atom (which is adsorbing on the surface of the transitional metal as a positive ion), in this case, the correlation effects do not play a main role (that is, it cannot be neglected) to describe the positive ionization process of the alkali adatom, whereas it contains zero or one electron on its covalent shell. Therefore, the correlation effects were taken through the following relation [9]:

$$U_{eff}(S)=V_i-V_A-2\Delta E(S) \qquad \text{--- (5)}$$

The U_{eff} does not depend on the spin but it depends on the distance S through the image shift ΔE(S).

By taking the effects of the image shift and the correlation into account, the energy of the atomic level $E_a^{+\sigma}$ ($E_a^{-\sigma}$) whose spin up +σ (spin down –σ) of adatom is given by [10]:

$$\mathrm{E}_a^{\pm\sigma}(\mathrm{S})=(\phi-\mathrm{V}_i)+\Delta\mathrm{E}(\mathrm{S})+\mathrm{U}_{eff}\,\mathrm{n}_a^{\mp\sigma} \qquad \text{----- (6)}$$

$n_a^{+\sigma}$ ($n_a^{-\sigma}$) represents the effective charge (occupation number) of the $E_a^{+\sigma}$ ($E_a^{-\sigma}$) level. In this work, the measurements of energy will be with respect of the Fermi energy level ($E_f=0$) and the selection of spin is randomly.

The effective charge on the adatom energy level at any temperature T will be given by [11]:

$$\mathrm{n}_a^{\sigma}=\frac{1}{\pi}\left[\begin{gathered}2a_2k_BT\Gamma-\tan^{-1}\left(\frac{u_0-E_a^{\sigma}}{\Gamma}\right)+a_2\Gamma E_a^{\sigma}\ln\frac{(k_BT-E_a^{\sigma})^2+\Gamma^2}{(k_BT+E_a^{\sigma})^2+\Gamma^2}\\ +B_1^{\sigma}\tan^{-1}\left(\frac{-k_BT-E_a^{\sigma}}{\Gamma}\right)+B_2^{\sigma}\tan^{-1}\left(\frac{k_BT-E_a^{\sigma}}{\Gamma}\right)\end{gathered}\right] \qquad \text{------------ (7)}$$

Where k_B is the Boltzmann's constant, Γ is the half width of the atomic energy level and:

$$B_1^{\sigma}+B_2^{\sigma}=1$$

$$B_2^{\sigma}=a_o+a_2(E_a^{\sigma})^2+a_2\Gamma^2 \qquad \text{---- (8)}$$

a_o and a_2 are numerical constant.

The surface ionization process is an ionization process of a neutral species when it interacts with a solid surface with an appropriate work function and temperature [12]. Also, it is a macroscopically well known process, described by the Saha – Langmuir law, which expresses the ionization degree α , i.e. the ratio of the numbers of ions and neutrals desorbing from a surface with work function ϕ at temperature T bombarded by thermal atoms [13]:

$$\alpha=\frac{q_+}{q_o}\exp[(\phi-V_i)/k_BT] \qquad \text{-- (9)}$$

where q_+ and q_o respectively the partition functions of the ion and atom. In case of the alkalis, which have not low energy excited states, this ratio reduces to the ratio of the spin degeneracy of ion and atom, i.e 0.5 [14].This law has first been established by studying the thermodynamic equilibrium of plasma near a metallic surface [15]. However, the surface ionization has only been described in a thermodynamic way. Remy and Rassar [13] intended to describe it in a microscopic way by studying the quantum interaction giving rise to the charge exchange between the incident particles and the surface and emission of ions from this heated surface.A particle approaching a surface with thermal kinetic energy experiences the chemisorption forces leading to chemisorption at the equilibrium distance. The surface work function differs according to the face which is chosen to the adsorption process. Consequently the energy level, effective charge and the width of the level vary, and this level tends to become again discrete at a certain distance S_i , beyond which the chemisorption forces are no more acting and the particle to be desorbed, must overcome an additional potential barrier [16]. And the ionization degree at infinity is [13]:

$$\alpha_\infty = \left(\frac{1}{n_a^\sigma} - 1\right) \exp\left(-\frac{\Delta E(S)}{k_B T}\right) \qquad \text{—(10)}$$

This expression containing the work function and the microscopic parameter of the quantum interaction Γ included in n_a^σ connects the macroscopic parameters of the chemisorption process n_a^σ .

Results and discussion:

The calculations of occupation numbers have been done on the system Li/Ni for multi faces of Nickel surface, where u_o=14 eV [17], V_i=5.35 eV , V_A=0.62 eV and, r_i=0.68 A^0, r_i(Ni) =1.25 A^0 [18] at T=300 °K to check the general features of the calculation model.

The image shift has been calculated according to equation (1) with various values of S_o while the atomic half width has been calculated for the ionization V_i and affinity V_A levels according to equation (2). The equations (6) and (7) were solved by the self consistently way by using the formula of the correlation effect U_{eff} which was given by equation (5), to find the values of the occupation numbers ($n_a^{+\sigma}$,$n_a^{-\sigma}$) as a function of distance (S) and the surface work function (ϕ) as shown in figure(1) which explains two kinds of solutions, they are: a nonmagnetic solution $n_a^{+\sigma} = n_a^{-\sigma}$ for the distance $0 \le S \le 5.7 A^o$ with ϕ(110)=5.04 eV ($0 \le S \le 14.35 A^o$ for ϕ(001)=5.22 eV). For the larger distances, the solution is a magnetic state $n_a^{+\sigma} \ne n_a^{-\sigma}$. However, the distance S_{ch} , that the type of solution changes at it, varying according to the variety of work function and as it is shown in table(1).

So, noticing figure (1) and table (1) one can get the following:

1- The difference between $n_a^{+\sigma}$ *and* $n_a^{-\sigma}$ values at far distances is clear which can be understood throughout the weakness of the interaction (coupling) with the surface.
2- The values of the occupation numbers $n_a^{\pm\sigma}$ at the surface are small, that reflect the charge state of the Li atom on the surface of Ni which emphasizes the positive ionic state dominants at the surface.
3- The greater values of work function lead to smaller probability to charge transfer from the metal band to adatom level and vice versa. Table (1) shows that the occupation numbers decrease with increasing the values of work function.
4- The distance S_{ch} increases with the increasing work function, where the nonmagnetic solutions are reinforced by approaching the ionization level V_i (affinity level V_A) closer (farther) below (above) the Fermi energy level.

Concerning with the surface ionization degree, according to the occupation numbers calculations which had been used to determine the ionization degree of the Li/Ni system at various faces (work function values) through the equation(10), as shown in figure(2) and tables(1-2) that explain the following results:

i- The ionization degree α_∞ at the surface increases with the increasing of the work function, because the increasing of screening length S_o which leads to decreases in the image shift effects ΔE(S) and increases of the occupation number $n_a^{\pm\sigma}$, so the ionization degree α_∞ increases according to equation (10). The behavior of ionization degree agrees with the values of ionization degree α_{SL} , which are calculated according to Saha – Langmuir law (equation (9)). That is emphasizes that the alkali atom is adsorbing on the transitional metal surface as a positive ion
ii- The distance S_i increases with the increasing of the work function, with notification that

the similarity between the values of S_{ch} with S_i. This distance determines the state of desorbed atom as the atomic state or ionic state.

iii- The ionization degree α_∞ increases with the increasing the work function for all distance S as shown in figures (3 and 4).

Conclusion:

A model derived from the chemisorption theory to determine the occupation numbers of an alkali atom (Li) is adsorbed on a metallic surface (Ni). It has been explained that the occupation numbers are very sensitive to the atom – surface distance and work function, especially at the distances larger than $5a_o$. This is a great interest for various atoms – surface interaction processes involving the variation of the surface work function.

The alkali atom can be adsorbed on a metal surface as a positive ion and cannot be adsorbed as a negative ion.The previous results applied to study the positive surface ionization at thermal equilibrium (T=300 °K). The expression of the ionization degree has been expressed in terms of the occupation number n_a^σ that is the characteristic parameter of the quantum interaction between the adatom and the metal surface. The values of this ionization degree are the same manner agreement with those evaluated by the Saha – Langmuir law, and allows to determine the distance at which, the surface ionization occurs. This distance is increasing rapidly with the increases of the work function.

Table (1): characterizes the chemisorption functions and ionization degree at the surface as a function of work function.

Li / Ni , $V_i = 5.39$ eV , $V_A = 0.62$ eV , $r_i = 0.68$ A° , r_i (Ni) = 1.25 A° , T=300 °K , S = 0											
Face	ϕ (eV)	S_o(A°)	n_a	E_a(eV)	U_{eff}(eV)	Γ (eV)	S_{ch}(A°)	S_{ch}	α_∞	S_i(A°)	S_i
110	5.04	0.8972	0.2064	1.2462	2.6865	1.1964	5.7	10.78 a_o	1.5596×10^{-21}	6	11.34 a_o
001	5.22	1.1400	0.1945	1.3535	2.8199	1.2109	14.35	27.13 a_o	8.2625×10^{-20}	14.5	27.41 a_o
111	5.35	1.2244	0.1853	1.4445	2.8612	1.2231	50	94.52 a_o	2.9529×10^{-19}	50.3	95.09 a_o

a_o is the Bohr radius

Table (2): characterizes the ionization degree at different distances from the surface as a function of work function.

Li / Ni , $V_i = 5.39$ eV , $V_A = 0.62$ eV , $r_i = 0.68$ A° , r_i (Ni) = 1.25 A° , T=300 °K				
Face	ϕ (eV)	α_∞ (S=0.2 A°)	α_∞ (S=5 A°)	α_{SL}
110	5.04	6.1541×10^{-20}	2.0307×10^{-6}	6.5926×10^{-7}
001	5.22	2.0704×10^{-18}	1.6715×10^{-5}	6.9664×10^{-4}
111	5.35	6.5564×10^{-18}	4.6866×10^{-5}	1.0641×10^{-1}

Note: α_∞ **was calculated according to equation (10) whereas the values of n_a and ΔE are taken at the distances 0.2 and 5 A°.**

While α_{SL} was calculated according to equation (9) with $\frac{q_+}{q_o} = 0.5$, T=300 °k , k_B is the Boltzmann's constant, V_i is defined above and ϕ varies with each face.

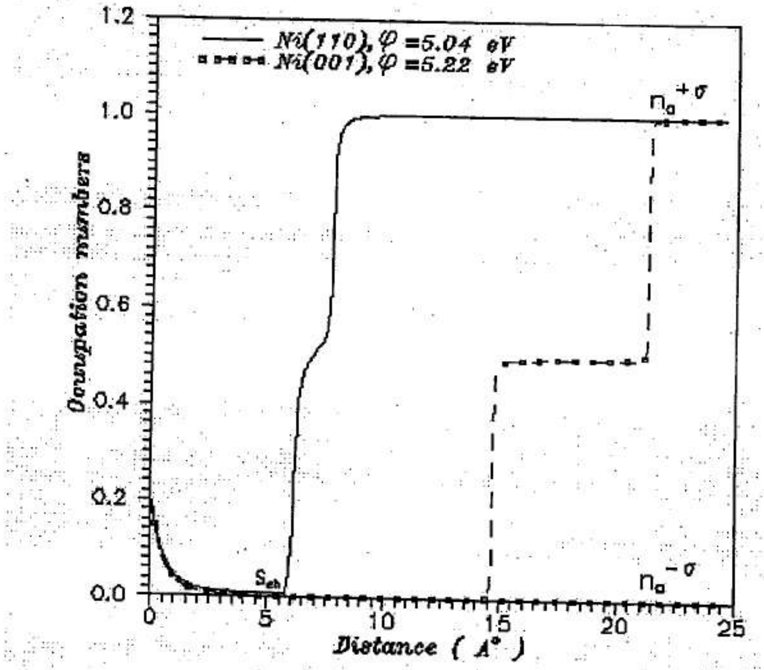

Figure (1): shows the occupation numbers as a function of distance and surface work function for the system Li/Ni

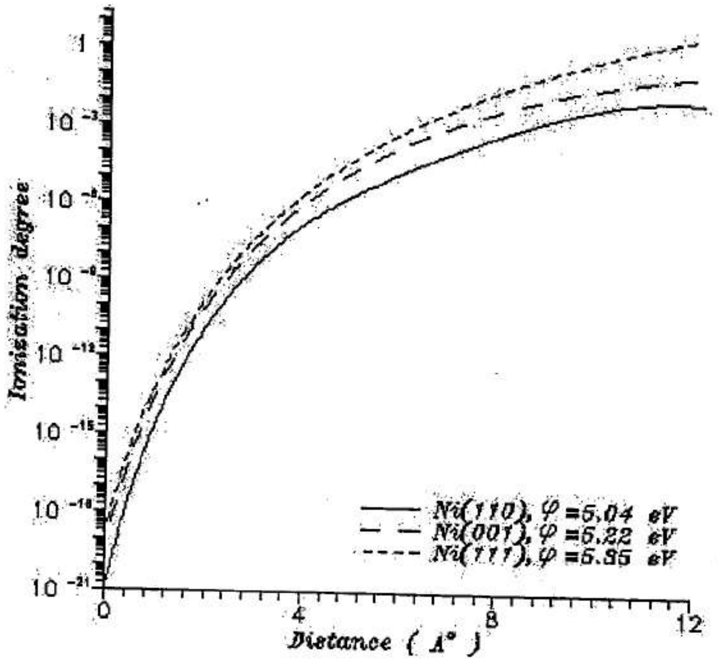

Figure (2): shows the behavior of ionization degree α_∞ as a function of distance and surface work function for the system Li/Ni

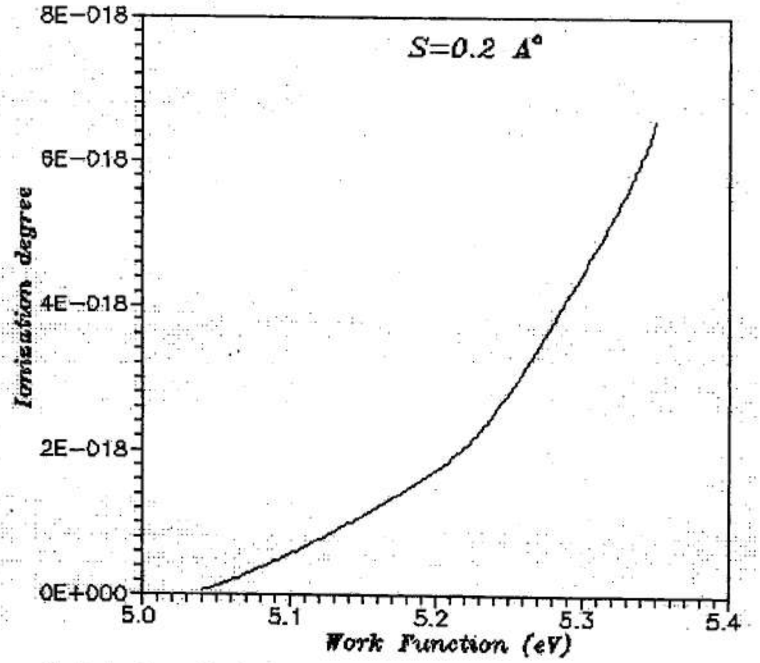

Figure (3): shows the behavior of ionization degree α_∞ versus the surface work function of the system Li/Ni at distance S=0.2 A° from the surface

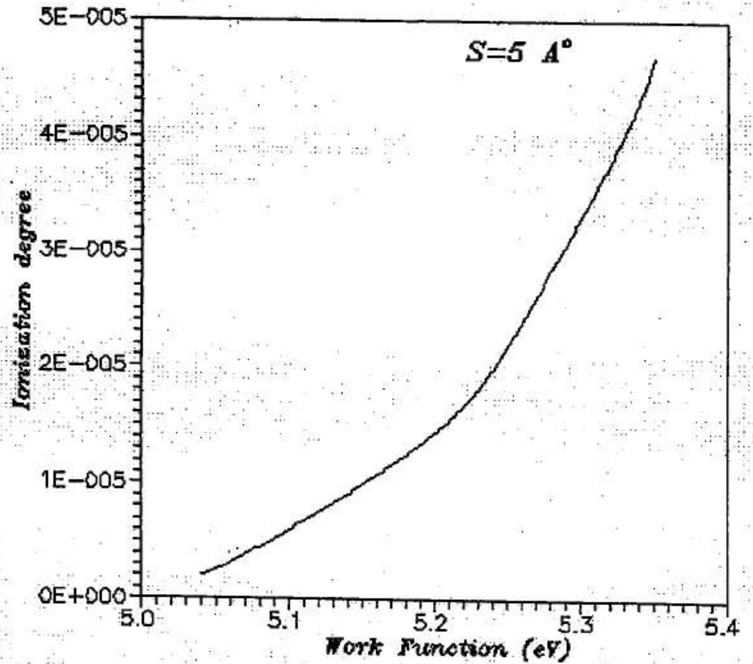

Figure (4): shows the behavior of ionization degree α_∞ versus the surface work function of the system Li/Ni at distance S=5 A° from the surface

References:

1- B. I. Lundqvist, Vacuum J., Vol. 33, No. 10-12,P. 639-649, 1983.

2- R. L. Gerlach and T. N. Rhodin, Surf. Sci., Vol. 19, P. 403, 1970.

3- J. D. Jackson, " Classical Electrodynamics " 2nd edn., New York: Willey, P. 54.

4- H. Winter, J. Phys., Condense Matter, Vol.8, P. 10149-10183, 1996.

5- A. J. Dekker, "Solid State Physics" edited by the Macmillan Press LTD, P.228-230, 1971.

6- M. A. Ibraheem, M. Sc. Thesis, Basrah University, Basrah, Iraq, 1990.

7- A. W. Wiess, Phys. Rev., Vol. 166, P. 70, 1968.

8- D. M. Newns and R. Brako, Rep. Prog. Phys, Vol. 52, P. 655-697, 1989.

9- H. Kawai, K. Makoshi and A. Yoshimori, Surface Science, Vol. 206, P. 525-532, 1988.

10- J. W. Jadzuk, J. K. Hartman and T. N. Rhodin, Phys. Rev., Vol. 14, No. 2, 1971.

11- H. Q. Al-Edany and J. M. Almukh, J. Basra Researches, Vol. 28, part 3, P. 136 - 145, 2002.

12- K. Murray, K. Boyd and Y. Naite, International union of pure and applied chemistry, p. 1-48, 2006.

13- B. Rasser and M. Remy, Surf. Scien. P. 223- 239, 1980.

14- M. J. Dresser, Journal of Applied Physics, Vol. 39, P. 338 – 339, 2007.

15- E. Ya. Zandberg and N. I. Ionov, Surface Ionization (IPST), Jerusalem, 1971.

16- A. Modinos, " Field Thermionic and Secondary Electron Emission Spectroscopy ", Plenum Press, New York, 1985.

17- N. V. Smith and S. T. Chen, Phys. Rev., Vol. B40, No. 11, P. 7565, 1989.

18- Kittel in "Introduction to Solid State Physics" 6th edn, 1986.

درجة التأين واعتمادها على دالة الشغل لسطح المعدن في الالتصاق الكيميائي للنظام Li atom on Ni surface

حيدر قاسم فاضل

قسم الفيزياء – كلية التربية – جامعة البصرة – البصرة – العراق.

الخلاصة:

ان الهدف من هذا البحث هو توضيح تأثير كل من المسافة ودالة الشغل على عمليات انتقال الشحنة التي تجري على سطوح المعادن، مثل مغادرة بعض الجسيمات من سطح المعدن (تأين السطح)، بالاستفادة من نموذج AGN للالتصاق الكيميائي.

تمت معالجة تفاعل ذرة قلوية (ذرة ليثيوم) على سطح معدن انتقالي (سطح النيكل متعدد السطوح(الاوجه)) بادخال دالة الشغل في الصيغة الرياضية لطاقة المستوي الذري للذرة الملتصقة، وبعد ذلك تم تطبيق نتائج المعالجة على حالة التاين الموجب للسطح والذي تبين انها تحدث عند مسافات تتزايد بشكل كبير عندما تزداد دالة الشغل مع تغير وجه السطح المشترك في التفاعل.

الكلمات المفتاحية: الالتصاق الكيميائي، الذرة الملتصقة ، درجة التأين ، تأين السطح.