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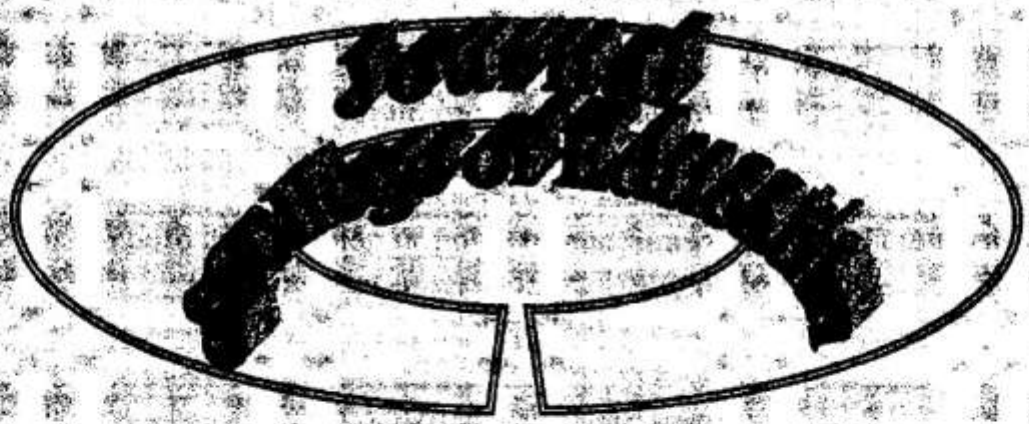

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اعتماد درجة تاين السطح على درجة الحرارة باستخدام نظرية الالتصاق الكيميائي

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الخلاصة:

لتوضيح تاثير كل من المسافة ودرجة الحرارة على عمليات انتقال الشحنة التي تجري على سطوح المعادن، مثل مغادرة بعض الجسيمات من سطح المعدن، وذلك باستخدام نموذج اندرسون – كرملي – نيونز للالتصاق الكيميائي.

كذلك تمت معالجة تفاعل ذرة قلوية (ذرة صوديوم) على سطح احد المعادن (التنكستن (112)) بادخال درجة الحرارة في الصيغة الرياضية للشحنات المؤثرة (اعداد الاشغال) للذرة الملتصقة، وبعد ذلك تم تطبيق نتائج المعالجة على حالة التاين الموجب للسطح والذي تبين انها تحدث عند مسافات تتناقص تدريجياً عندما تزداد درجة حرارة السطح.

الكلمات المفاتحية: الشحنة المؤثرة، الذرة الملتصقة، الالتصاق الكيميائي، تاين السطح، درجة التاين.

The Dependence of Ionization Degree on Surface Temperature by using the Chemisorption Theory

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Abstract:

For explaining the distance and temperature dependent charge transfer involved in surface processes dealing with particles leaving a surface, the Chemisorption theory (Anderson – Gerimly – Newns model) has been used. Treating the interaction of an alkali atom (Sodium) on a metal surface (Tungsten (112)) and introduce the temperature in the expression for effective charges (occupation numbers) of the adsorbed atom. Then the treatment was applied to the positive surface ionization and shows that it occurs at distances slightly decreasing with increasing temperatures.

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

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 that is occurs between the adatom and the surface which has many practical applications such the as chemisorption.

Chemisorption (Chemical adsorption), the Chemical bond formed between the adatom and the surface and which includes redistribution and 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)[1].

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 a polarization potential affecting on the charged particle. This phenomenon was described by the use of concept of the image charge. The effects of the image charge play a very important role in the atom – surface interaction [2] such as chemisorption process or any process includes a charge exchange.

Thus, 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 [3]:

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

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 amount of S_o which is used in the theoretical treatments as an adjustable parameter.

By neglecting the dependence of Γ on adatom energy level, one can describe the dependence of the broadening Γ on the distance S by [4]:

$$\Gamma(S)=\Gamma_o\, e^{-\alpha S} \qquad \text{---------- (2)}$$

This relation is independent on the spin of electrons whereas Γ_o represents the half width of the adatom energy level at the surface (S=0) and its practical value is between (0.3 – 1.5 eV), α is a dynamical parameter is given by [4]:

$$\alpha=\sqrt{2V_i} \qquad \text{---------- (3)}$$

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 [5]:

$$U = V_i - V_A \qquad \text{---------- (4)}$$

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 caused by the electron – electron interaction [6]. The treatment of U as its formula and its dependence on the distance is considered as one of the problems that meet the researchers. Generally, it is either taken as a constant equal to (V_I- V_A) or neglected [7].

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 can not be neglected) to describe the positive ionization process of the alkali adatom, whereas it contains zero or one electron on its covenant shell. Therefore, the correlation effects were taken through the following relation[8]:

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

The U_{eff} dose not depend on the spin but it depends on the distance S through the image shift $\Delta E(S)$.

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 [9]:

$$E_a^{\pm\sigma}(S) = (\phi_o - V_i) + \Delta E(S) + U_{eff}\, n_a^{\mu\sigma} \qquad \text{---------- (6)}$$

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

In increasing of surface temperature above 0°K leads the Fermi distribution function (equation (7)) decreases in all energy levels less than E_f ($E < E_f$), i.e., some of these full energy levels will discharge some of its charge and a new values of Fermi function will appear for the energy levels that are above Fermi level ($E > E_f$) and these levels will be filled after it has been empty [10].

$$f(E,T)=\frac{1}{1+\exp[(E-E_f)/k_BT}$$ ---------- (7)

Whereas k_B is the Boltzmann constant. Therefore, the work function value will be changed accordingly and the variation of work function with the temperature will be given by [11]:

$$\phi=\phi_o-(1.6x10^{-4})T$$ ---------- (8)

The effective charge of the adatom energy level for any temperature will given by [12]:

$$n_a^\sigma=\frac{1}{\pi}\left[\begin{array}{c}2a_2k_BT\Gamma-\tan^{-1}\left(\frac{u_0-E_a^\sigma}{\Gamma}\right)+a_2\Gamma E_a^\sigma\ln\frac{(k_BT-E_a^\sigma)^2+\Gamma^2}{(k_BT+E_a^\sigma)^2+\Gamma^2}\\+B_1^\sigma\tan^{-1}\left(\frac{-k_BT-E_a^\sigma}{\Gamma}\right)+B_2^\sigma\tan^{-1}\left(\frac{k_BT-E_a^\sigma}{\Gamma}\right)\end{array}\right]$$ ---------- (9)

Where u_o is the metal band width, Γ is the half width of the atomic energy level and:

$$B_1^\sigma+B_2^\sigma=1$$
$$B_2^\sigma=a_o+a_2(E_a^\sigma)^2+a_2\Gamma^2$$ ---------- (10)

a_o and a_2 are numerical constant.

Application to thermal positive surface ionization:

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 [13], 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 at temperature T bombarded by thermal atoms [14]:

$$\alpha=\frac{q_+}{q_o}\exp[(\phi-V_i)/k_BT]$$ ---------- (11)

Where q_+ and q_- respectively the partition functions of the ion and atom. In case of the alkalis, which have not low energy exited states, this ratio reduces to the ratio of the spin degeneracy of ion and atom, i.e. 0.5

Remy and Rassar [14] intended to describe the Saha – Langmuir law 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. If the surface is heated up to a temperature T, the adsorbed particle is thermally

excited and can move away from the surface. Consequently the energy, 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. At this distance S_i , the effective charge n_a^σ determines the probability for the adsorbed particle to be in an atomic state. The non - occupation probability of the level, which is the probability for the adsorbed particle in an ionic state, is $(1-n_a^\sigma)$. The ratio of the ionic and atomic states probabilities is the ionization degree α_{S_i} at the distance S_i [14]:

$$\alpha_{S_i} = \frac{1-n_a^\sigma}{n_a^\sigma} \qquad \text{---------- (12)}$$

Beyond this distance, the particle, to be desorbed, must overcome an additional potential barrier. And the ionization degree at infinity is [14]:

$$\alpha_\infty = \left(\frac{1}{n_a^\sigma} - 1\right) \exp\left(-\frac{\Delta E(S)}{k_B T}\right) \qquad \text{---------- (13)}$$

This expression containing the temperature 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 has been done on the system Na/W (112) for various temperature, where $\emptyset_o$ =4.8 eV [15], u_o=11.35 eV [8], V_i=5.14 eV , V_A=0.54 eV and r_i=0.97 A^0 [10] to check the general features of the calculation model.

The atomic half width has been calculated for the ionization V_i and affinity V_A levels according to equation (3). The image shift was chosen to put $\Delta E(S)$ at the surface (S=0) into the experiment values of $\Delta E(S)$ [9] for the chemisorption of alkali atoms on tungsten surface.

Equations (6) and (9) 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 temperature (T) as shown in figure (1) which explains two kinds of solutions, they are: a non – magnetic solution $n_a^{+\sigma} = n_a^{-\sigma}$ for the distance $0 \le S \le 5.1\,A^o$ at T=300 K ($0 \le S \le 1.25\,A^o$ at T=2000 K). For the distances S > 5.01 A^0 at T=300 K (S > 1.25 A^0 at T=2000 K), the solution is a magnetic state $n_a^{+\sigma} \neq n_a^{-\sigma}$.

However, the distance S_{ch} , that the type of solution changes at this distance, varying according to the variety of the temperature 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 Na atom on the surface of W (112) which emphases the positive ionic state dominants at the surface.

3- The occupation number increases to all distance S with increasing temperature, because of the occupied energy levels of the metal band above Fermi level increases, that leads to increasing the number of energy levels which resonant or qusiresonant with these on the adatom.

4- It well known that, the formation of negative ions on the surface at certain temperature is reinforced when $k_BT > U_{eff}$, whereas the metal electrons which their energy at the range of energy k_BT below Fermi energy level can be thermally excited.

The thermal energy can be used to pass the potential barrier of U_{eff} by another electron when the adatom approaches to the surface [16]. According to table(1), the values of U_{eff} are greater than k_BT for all temperature T. that assures the adsorption of the alkali atoms on the tungsten surface can not be as a negative ions.

5- The distance S_{ch} decrease with the increasing temperature T, where the magnetic solutions are reinforced by keeping the ionization level V_i (affinity level V_A) closer (farther) below (above) the Fermi energy level.

According to the occupation numbers calculations which had been used to determine the ionization degree of the Na/W(112) system at various temperatures through the equation(13), as shown in figure(2) and table(2) that explain the following results:

i- The behavior of ionization degree α_∞ at all different a temperature in figure (2) is agrees with the behavior of results from the reference [14] and as shown in figure (3).

ii- The distance S_i decreases gradually with increasing of the temperature, from 4.16 a_o to 0.76 a_o when the temperature varies from 1000 K to 3000 K, as shown n table(2). This distance determines the state of desorbed atom as the atomic state or ionic state. This fact corresponds with the

results in reference [14], whereas in which, the ionization degree was calculated to Na/Rh and found that S_i varies from $17a_o$ to $13a_o$ when temperature varies from 1000 K to 3000 K.

iii-The values of ionization degree α_{SL} , which are calculated according to Saha – Langmuir law (equation (11)), in table (2) are gives approximately values of S_i by matching α_{SL} with figure (2).

Conclusion:

A model derived from the chemisorption theory, which determines the effective charges of an alkali atom adsorbed on a metallic surface. It has explained that the effective charge is very sensitive to the atom – surface distance and the temperature, especially at the distances larger than 5 a_o . This is of a great interest for various atoms –surface interaction processes involving high temperatures.

The previous results applied to study the positive surface ionization at thermal equilibrium. The expression of the ionization degree has been expressed in terms of the effective charge (occupation number n_a^σ), that is the characteristic parameter of the quantum interaction is between the adatom and the metal surface. The values of this ionization degree are nearly agree with those given by the Saha – Langmuir law and allows to determine the distance at which, the surface ionization occurs. This distance is slightly decreases when the temperature increases.

Table (1): characterize the chemisorption functions as a function of temperature.

T(K)	$\emptyset$(eV)	k_BT (eV)	n_a	E_a (eV)	S_{ch} (A°)	S_{ch}
300	4.75	2.5851×10^{-2}	0.17246	1.6040	5.1	9.64 a_o
1000	4.64	8.6171×10^{-2}	0.18486	0.98063	2.75	5.20 a_o
1500	4.56	1.2926×10^{-1}	0.19463	0.92603	1.85	3.50 a_o
2000	4.48	1.7234×10^{-1}	0.20521	0.87355	1.25	2.36 a_o
2500	4.40	2.1543×10^{-1}	0.21664	0.82327	0.95	1.80 a_o
3000	4.32	2.5851×10^{-1}	0.22893	0.77521	0.7	1.32 a_o

Table (2): characterize the ionization distance and ionization degree (Saha – Langmuir law) as a function of temperature.

T (K)	S_i (A°)	S_i	α_{SL}
1000	2.2	4.16 a_o	1.5101×10^{-3}
1500	1.3	2.46 a_o	5.6260×10^{-3}
2000	0.8	1.51 a_o	1.0859×10^{-2}
2500	0.65	1.23 a_o	1.6112×10^{-2}
3000	0.4	0.76 a_o	2.0960×10^{-2}

Where a_o is the Bohr radius

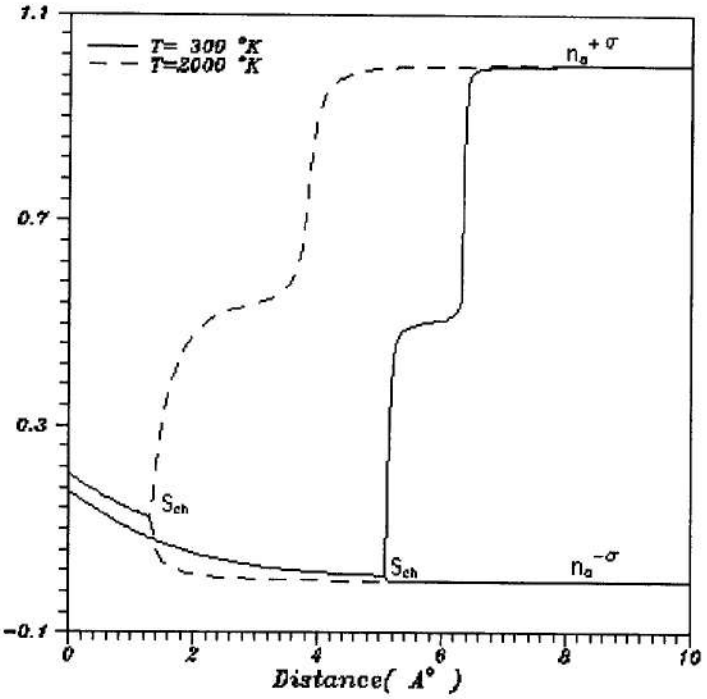

Figure (1): The occupation numbers as a function of distance and temperature for the system Na/W (112)

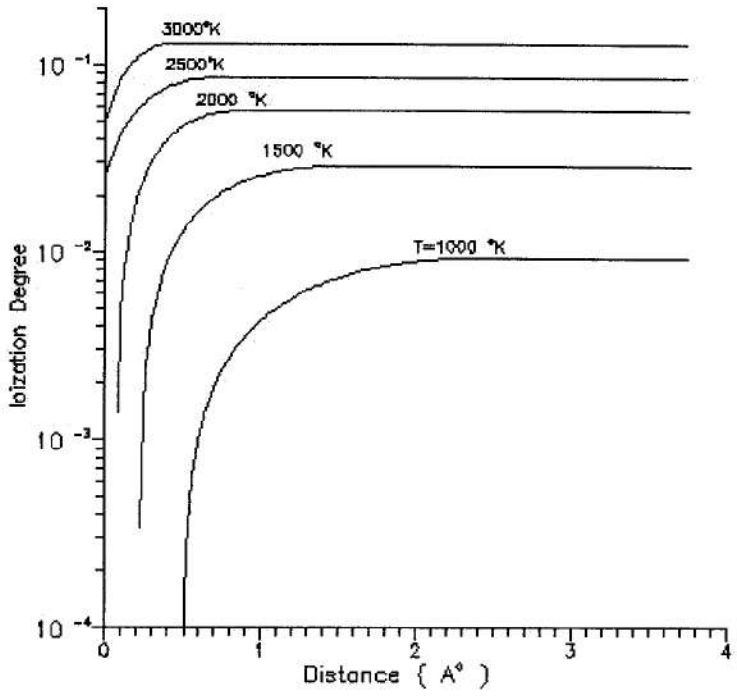

Figure (2): The behavior of ionization degree α_∞ as a function of distance and temperature for the system Na/W (112)

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