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The Effect of Surface Impurities on the Thermal Accommodation of Rare Gases on a Tungsten Surface

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A rather comprehensive experimental examination of the effect of surface impurities (potassium and cesium) on the thermal accommodation of rare gases on a tungsten surface has been made by Roach and Thomas. The present work examines these effects from a theoretical viewpoint with particular emphasis on the effect on the thermal accommodation of helium on a tungsten surface caused by the adsorption of cesium ions and/or atoms. For this examination, the theory of Allen and Feuer has been utilized using reasonable values of the interaction parameters for helium with the adsorbate as well as the force constant for the adsorbate-substrate bond. Resulting values of the accommodation coefficients are compared with experimental values.

§1. Introduction

Alkali metal adsorption on a clean tungsten substrate has been extensively investigated experimentally¹⁻⁵⁾ and theoretically.⁶⁻⁸⁾ Of particular interest here are the experimental measurements of the extent of energy transfer as expressed by the accommodation coefficient (hereafter AC in text and α in equations)⁹⁾ between the rare gases and a tungsten surface undergoing adsorption of cesium or of potassium made by Roach and Thomas.¹⁰⁻¹²⁾ The AC of each rare gas was determined under conditions such that coverages of adsorbate were established over a range between no adsorbate present to a monolayer and beyond. The general behavior observed is that the AC of a rare gas increases above the clean tungsten surface value as the first layer of adsorbate is forming, passes through a maximum and then decreases to a final constant value.

Roach¹⁰⁾ and Stickney¹³⁾ have discussed qualitatively these experimental data. Both workers viewed the accommodation in a simple manner; i.e., that the rare gas exchanges energy with the surface either via collision with bare tungsten (AC on these sites = α_w) or via collision with the adsorbate (AC on these sites = α_A). Thus for less than monolayer coverage it was suggested the observed AC could be written $\alpha = (1 - \theta)\alpha_w + \theta\alpha_A$, where θ = fraction of the total adsorption sites covered with adsorbate. From the experimental values of α , α_A may be evaluated if a correlation is made between

time of adsorption and coverage θ . Since α_A is larger than α_w for the system under consideration, the energy transfer by helium is more efficient on the adsorbate than on the bare substrate. This suggests that the effective temperature of reflected molecules differs accordingly depending on the segment of surface with which they have interacted. For consideration of the "out-of-equilibrium" implications for such systems, the reader is referred to the excellent review²⁴⁾ by Hurlbut. The observed non-linear dependence of α with θ results because of the dependence of α_A on coverage. Considering the changing nature of the adsorbed state of alkali metal as the coverage increases, this dependence of α_A on θ seems qualitatively reasonable. However, a quantitative explanation has not yet been made and indeed it is the purpose of this paper to present results of this nature.

§2. Theoretical Background and Procedure

Prominent among investigations to theoretically describe the effect of surface impurities on the thermal accommodation coefficient are those of Jackson,¹⁴⁾ Allen and Feuer,¹⁵⁾ Goodman¹⁶⁾ and McCarroll.¹⁷⁾ The latter two investigators employed classical mechanical approaches while the former two workers formulated quantum mechanical descriptions. The work of Allen and Feuer is of particular interest here as a first step toward a better understanding of the importance of the various factors affecting thermal accommodation of

rare gases on a tungsten surface with varying degrees of coverage by alkali metal atoms and/or ions.

Allen and Feuer, using a one dimensional model, obtained an expression for the AC as a function of temperature, mass of lattice atoms (M_L), mass of impurity atoms (M_A), force constant associated with the coupling of lattice atoms to each other (K_L), force constant associated with the coupling of the impurity to the lattice (K_A), and interaction parameter (a) for a simple exponential repulsive interaction between gas atom and surface. The total accommodation coefficient associated with the crystal with adsorbed impurity (α_A above) is given by the expression

$$\alpha_A = \alpha_B + \alpha_L \quad (1)$$

where α_B is the contribution associated with the band modes and α_L is due to a localized impurity mode which exists only under certain adsorbate-substrate conditions. For the system of particular interest here, namely cesium on tungsten, the condition for existence of the localized mode is not satisfied. Therefore the expression for α_B is of primary interest:

$$\alpha_B = \frac{4}{\pi} \frac{16\pi^3 M_g^2 \omega_m \beta^3}{h M_L a^2} \int_0^1 d\theta \frac{\theta^3 (1 - \theta^2)^{1/2}}{(e^{\theta^2} - 1) D(\theta)} \times \int_0^\infty dE e^{-\beta E} \frac{\sinh \pi \mu_i \sinh \pi \mu_f}{(\cosh \pi \mu_i - \cosh \pi \mu_f)^2} \quad (2)$$

where ω_m is the maximum band frequency, ω is a band frequency, $\beta = \hbar \omega_m / kT$, $\theta = \omega / \omega_m$, a is the parameter in the repulsive exponential interaction $V(x) = Ce^{-ax}$, $\mu_i = 2[2M_g W_i]^{1/2} / \hbar a$, $\mu_f = 2[2M_g (W_i + \hbar \omega)]^{1/2} / \hbar a$, W_i is the incident gas atom energy, $E = W_i / \hbar \omega_m$,

$$D(\theta) = 1 + [4M^2 + 4M - (8M/K)]\theta^2 + 16M^2[(1-K)/K^2]\theta^4,$$

$M = M_A / M_L$ and $K = K_A / K_L$. The above expression for α_B is the one dimensional analogue of the Jackson¹⁴⁾ and Devonshire¹⁸⁾ expressions for the AC for exponential repulsive interaction between gas and solid. It is clear from the above expressions that α_B is a function of M_g , M_L , M_A / M_L , ω_m , a , T and K_A / K_L . "Reasonable" values for all the parameters except the last are readily available. The force constant ratio can be approximated from the work of Gyftopoulos⁶⁾ and hence α_B can be calculated,

numerically evaluating the integrals.

It must be noted however that attractive forces have been neglected and for the system of interest here (i.e., cesium ions/atoms adsorbed and exchanging energy with helium gas atoms), the attractive forces play, we believe, an important role. Therefore to examine this effect, the quantity Q appearing in the integrals $\phi(\theta)$ and ϕ_L in the Allen and Feuer development¹⁵⁾ have been obtained from the earlier Devonshire work¹⁸⁾ for Morse potential interactions. The effect of this consideration is to replace in eq. (2) above the term $(\sinh \mu_i \pi \sinh \mu_f \pi) / (\cosh \mu_i \pi - \cosh \mu_f \pi)^2$ with $((\sinh 2\mu_i \pi \sinh 2\mu_f \pi) / (\cosh 2\mu_i \pi - \cosh 2\mu_f \pi)^2) (A_{\mu_i} + A_{\mu_f})^2 / (A_{\mu_i} A_{\mu_f})$ where $A_{\mu_i} = |\Gamma(-d + i\mu_i + \frac{1}{2})|^2$ and $A_{\mu_f} = |\Gamma(-d + i\mu_f + \frac{1}{2})|^2$ with $d = 2(2M_g D)^{1/2} / \hbar a$ and D is the well depth in the Morse expression.

Using eq. (2) above with the noted modification to include attractive interactions between gas atoms and adsorbate, calculations of the AC of helium with cesium adsorbed on a tungsten substrate have been made and are reported in the next section. The cesium-tungsten system was chosen for examination because much is known of the adsorbed state of cesium on tungsten as derived from FEM studies and as noted in the introduction the experimental AC data for this system must be correlated with adsorbate coverage to extract α_A .

§3. Results and Discussion

Equation (2) above was used to calculate α_A and α_w for several combinations of parameters of interest for helium interacting with a tungsten surface with varying amounts of cesium. Those results are shown in Tables I and II. For those calculations for the He-Cs-W system the parameters automatically fixed in eq. (2) are $M_g = 4.0026$, $M_L = 183.86$, $M_A = 132.91$ and $\kappa = a/2 = 1.3 \text{ \AA}^{-1}$, where the latter is the "reasonable" value for the repulsive constant suggested by Goodman.²⁰⁾ Two values of ω_m have been used and are indicated in the tables in terms of Debye temperatures, θ_D , of 380 and of 260. The former is the often used bulk value²¹⁾ and the latter has been suggested as appropriate for these systems.²²⁾

Table I shows, for $\theta_D = 260$, the variation of α_A over a wide range of force constant ratios

Table I. Calculated values of the thermal accommodation coefficient of helium on cesium adsorbed on tungsten with $\theta_D=260$ K and $\alpha_w=0.0729$.

$D=100$				
$K=K_A/K_L$.1	.2	.3	.4
α_A	0.1295	0.1279	0.1226	0.1169
α_A/α_w	1.78	1.75	1.68	1.60
$D=200$				
$K=K_A/K_L$.1	.2	.3	.4
α_A	0.1432	0.1483	0.1463	0.1421
α_A/α_w	1.96	2.03	2.01	1.95

 Table II. Calculated values of the thermal accommodation coefficient of helium on cesium adsorbed on tungsten with $\theta_D=380$ K and $\alpha_w=0.0572$.

$D=100$				
$K=K_A/K_L$.1	.5	.75	1.0
α_A	0.1282	0.0879	0.0742	0.0656
α_A/α_w	2.24	1.54	1.30	1.15
$D=200$				
$K_A/K_L=0.1$	$\alpha_A=0.1500$	$\alpha_A/\alpha_w=2.62$		

and for two values of the attractive Morse parameter D . The two values of the attractive potential parameter D were chosen to encompass the values of 100–130 kcal/mole suggested by Goodman²⁵⁾ as appropriate for helium on tungsten from pairwise interaction considerations. Of course the values may be much too low for the helium-adsorbate interactions and indeed this is indicated by the calculated α_A values shown in Tables I and II. Also shown is the ratio of α_A/α_w where $\alpha_w=0.0729$, the calculated value of α for clean tungsten with $\theta_D=260$ and $D=100$. This ratio will be compared with experimental values rather than absolute values as there is always the uncertainty of scaling factors to account for the one dimensional model¹⁸⁾ and the distorted wave approximation error.¹⁹⁾ Of particular interest here are the α_A for K_A/K_L of about 0.1 as this appears to most nearly correspond to a realistic value for the Cs-W system, as will be discussed later. It should be noted that the effect of an increasing attractive interaction as evidenced by larger values of D has the expected effect of increasing α_A .

Table III. Experimental values of the thermal accommodation coefficient of helium or cesium adsorbed on tungsten.

Time ~ Min.	α	α_A	$(\alpha_A/\alpha_w)^*$
10	0.0258	0.0567	3.66
20	0.0350	0.0545	3.52
30	0.0398	0.0479	3.10
40	0.0413	0.0413	2.66
50	0.0400	0.0361	2.33
60	0.0370	0.0327	2.11
70	0.0350	0.0329	2.12
80	0.0341	0.0341	2.20

* $\alpha_w=0.0155$

Table II shows values of α_A and α_A/α_w for a Debye temperature of 380 K. With the increase of θ_D , $\alpha_w=0.0572$ and again we see α_A increasing as D increases.

For comparison of these α_A/α_w values with experimental data, Table III contains experimental values of the AC of helium on tungsten as the latter adsorbs cesium atoms/ions. The time elapsed after flashing the filament to remove all adsorbate is the indicator of surface coverage. The expression $\alpha=(1-\theta)\alpha_w+\theta\alpha_A$ was used to calculate α_A between zero time and time for maximum AC to be observed (at 240 K, $t_{\max}=40$ minutes). Beyond the maximum, an expression has been used but where now the two types of surfaces that helium interacts with are cesium adsorbed in an "optimal" arrangement and in close packed structure (see below). The values of α_A so calculated are shown in Table III as well as values of α_A/α_w . Although the α_A/α_w values calculated and shown in Tables I and II are only in good agreement with experimental values of Table III at coverages near and beyond maximum AC, they show the correct trend over the entire range and reflect that the attractive interaction between helium atoms and adsorbed cesium ions/atoms are indeed important.

As indicated above, comparison of experimental and theoretical values may be most appropriately made for K_A/K_L values of about 0.1. From the considerations of Levine and Gyftopoulos⁶⁾ and the experimental data of Langmuir and Taylor,²³⁾ K_A/K_L is found to be nearly 0.1 for cesium on tungsten.

The assignment of completion of a cesium layer at a coverage corresponding to maximum AC was made after consideration of the work

of Fedorus and Naumovets.¹⁾ Those workers found the minimum in work function on the 011 plane occurs at a concentration of 3.3×10^{14} atoms cm^{-2} . They attribute this concentration as "optimal" and beyond that concentration the cesium begins to form a close packed structure which is a complete "monolayer" at a concentration of 5.2×10^{14} atoms cm^{-2} . Roach and Thomas¹⁰⁾ have previously shown a parallel behavior between AC and work function changes for tungsten adsorbing potassium under the same experimental conditions. In view of these facts the assignment of completion of one type layer at the maximum AC and formation of a second type beyond the maximum seems reasonable.

The comparison of α_A/α_W in Tables I-III suggests that if larger values of the attractive parameter D were considered, good agreement would be obtained between this simple theory and experiment even at low coverages. Indeed such calculations are underway. The initial large values of α_A or α_A/α_W are physically attributable to the strong field associated with cesium ions adsorbed on the surface and as the coverage increases, the ions are depolarized and a decrease in α_A and α_A/α_W is observed. As noted earlier, experimental AC data are also available for potassium adsorption on tungsten and a similar analysis to that reported here will be completed later this year. Simultaneously research to make ab initio calculations of the effect of adsorption on the AC is planned.

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