CH448/548 Surface Chemistry 2009

Midterm Exam

Name : Key **Score :** 80 / 80

SHOW WORKING WHERE APPROPRIATE TO ENSURE PARTIAL CREDIT

Possibly useful information :

$\lambda = [150 / E(eV)]^{1/2}$ Å

$h = 6.626 \times 10^{-34}$ J s

$k = 1.381 \times 10^{-23}$ J / K

$R = 8.314$ J / mol K

$m_e = 9.109 \times 10^{-31}$ kg

$N_A = 6.022 \times 10^{23}$

1 atm = 760 torr = 101,325 Pa

WARM-UP QUESTIONS

1 pt 1. Circle the most appropriate answer after taking the exam (Any answer = 1 pt).

Taking this exam was a St. Valentine's Day present / punishment / massacre

4 pts 2. Spell out the name of the surface science technique represented by the following acronyms:

LEED = low energy electron diffraction

STM = scanning tunneling microscopy

AFM = atomic force microscopy

TDS = themal desorption spectroscopy

NOW FOR THE REAL STUFF

In a dungeon lab in Gilbert Hall, Dr. Watson and his faithful assistant, Igor, have recently claimed the discovery of the new superheavy element Watsonium (Wa) (atomic number 666) with some very unusual properties. Despite some skepticism from the rest of the scientific community, they have pursued the surface chemistry of this element.

Watsonium crystallizes in two allotropic forms. One allotrope (α-Wa) crystallizes in the face-centered cubic structure, while the other (β-Wa) crystallizes in the body-centered cubic structure. Both allotropes have one atom at each lattice point. Interestingly, both structures have the same lattice constant a_0 = 500 pm.

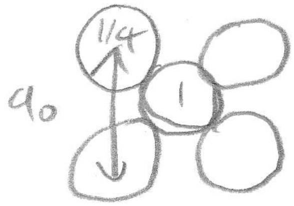
Answer the following question about this remarkable substance.

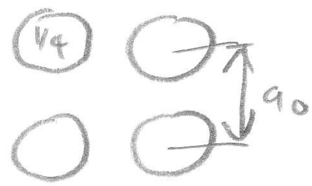
13 pts 3. a) Both allotropes of Wa cleave easily to expose a $(\bar{1}03)$ surface. This means that the surface plane intercepts a set of Cartesian axes at (in units of a_0) : (3 pts)

x-intercept = -1 y-intercept = ∞ z-intercept = $1/3$

b) If we compare the atom density (atoms/area) in the α-Wa(100) and β-Wa(100) surfaces we find that the relative atom density α-Wa(100) : β-Wa(100) is : (5 pts)
(MAKE SKETCHES FOR PARTIAL CREDIT – 2 pts for a correct guess)

fcc α-Wa(100) bcc β-W(100)





2 atoms / a_0^2 1 atom / a_0^2

Pick one 3 : 1 **(2 : 1)** 1 : 1 1 : 2 1 : 3

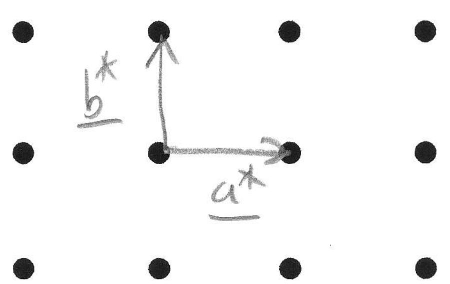
(c) What is the atomic radius of a Wa atom? (5 pts)
(SHOW WORKING)

For fcc (100)

$$4r = \sqrt{2}\,a_0$$

$$r = \frac{\sqrt{2}}{4} \times 500\,\text{pm} = 177\,\text{pm}$$

14 pts 4. We have found that the clean bcc (β-Wa)(100) surface has an ideal surface structure. It also adsorbs O atoms. LEED patterns of the clean and the O-covered surface look as below :



Clean

O-covered

a) the LEED patterns were taken with electrons of 100 eV energy. What wavelength will these electrons have? (2 pts)

$$\lambda(\text{Å}) = \left(\frac{150}{100}\right)^{1/2} = 1.22\ \text{Å}$$

b) what are the lengths of the reciprocal mesh vectors ($\underline{a}^*_s$, $\underline{b}^*_s$) for the O-covered surface in terms of those for the clean surface reciprocal mesh vectors ($\underline{a}^*$, $\underline{b}^*$)? (6 pts)

$$|\underline{a}^*_s| = \frac{\sqrt{2}}{2}|\underline{a}^*| \qquad |\underline{b}^*_s| = \frac{\sqrt{2}}{4}|\underline{b}^*|$$

so $|\underline{a}^*_s| / |\underline{a}^*|$ = $\frac{\sqrt{2}}{2}$ or $1/\sqrt{2}$ $|\underline{b}^*_s| / |\underline{b}^*|$ = $\frac{\sqrt{2}}{4}$ or $1/2\sqrt{2}$

c) What is the angle of rotation between ($\underline{a}^*_s$, $\underline{b}^*_s$) and ($\underline{a}^*$, $\underline{b}^*$)? 45 ° (2 pts)

d) Write the notation that specifies the adsorbate structure in the form (p × q)Rα° (4 pts)

$$p = \frac{|\underline{a}_s|}{|\underline{a}|} = \frac{|\underline{a}^*|}{|\underline{a}^*_s|} = \sqrt{2}$$

$$q = \frac{|\underline{b}_s|}{|\underline{b}|} = \frac{|\underline{b}^*|}{|\underline{b}^*_s|} = 2\sqrt{2}$$

$(\sqrt{2} \times 2\sqrt{2})R45°$

10 pts 5. Igor thinks that we should use scanning probe microscopies to study Wa surfaces.

(a) Circle the correct answers in the following statements. (1 pt each)

The scanning tunneling microscope (STM) measures repulsive forces / electrical current / gravitational attraction between a sharp tip and a surface. The signal increases / decreases by a factor of about 1 % / 10 / 10^6 for change in distance of 0.1nm.

either OK

should read "if tip gets closer by"

poorly worded

The atomic force microscope (AFM) measures repulsive forces / electrical current / gravitational attraction between a sharp tip and a surface. This technique can be used only in vacuum / only in air / in air, vacuum or liquid.

(b) Igor find that on α-W(100), the STM image appears to only show 3/4 of the number of atoms he expected. What could account for this? What change in the STM operating conditions could he try to see all the atoms? (5 pts)

1) the surface is reconstructed in such a way that 1/4 of the atoms are too low for the STM to "see"

2) the electronic nature of the surface is such that 1/4 of atoms are invisible because of a mismatch of the orbital symmetries between tip and surface.

Operating the STM at a different bias voltage may make the "missing" atoms visible.

18 pts 5. Igor finds that CO adsorption on β-W(100) is "Langmuirian".

(a) The Langmuir isotherm can be written generally as :

$$\theta = (bP)^{1/n} / (1 + (bP)^{1/n}) \qquad n = 1, 2$$

a) explain *in a few words* the significance of θ, b and n (6 pts)

θ = coverage , 0 → 1

b = k_{ads}/k_{des} = K for adsorption

n = order of adsorption (usually 1 or 2)

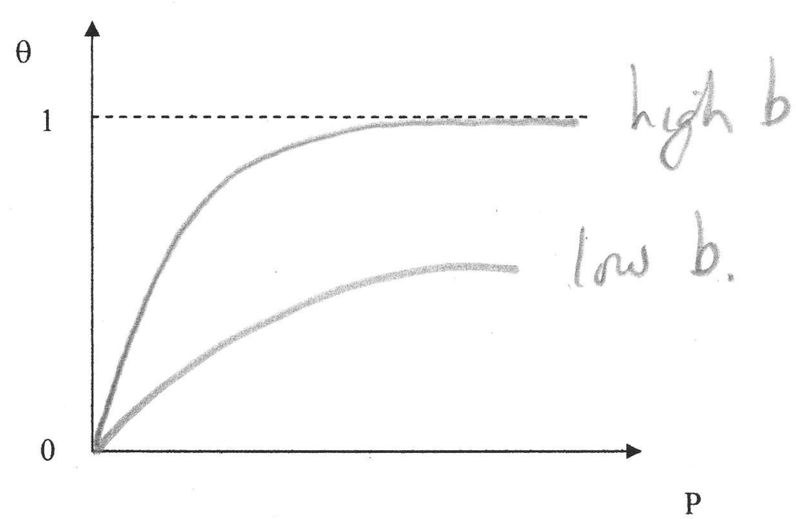
b) explain *very briefly* 3 approximations made in deriving this isotherm (6 pts)

i) only 1 type of site, all identical

ii) only 1 adsorbate / site

iii) ΔH_{ads} not f(θ)

c) sketch the approximate form of the isotherm for the cases where b is large and small. (6 pts)



20 pts 6. Finally, Igor has reported on some thermal desorption experiments on Watsonium.

(a) Fill in the blanks in the following statements. (2 pts each)

N_2 adsorbs on Wa(100) at 100K with an enthalpy of adsorption of 15 kJ/mol in a ___physi___ sorbed state. A TDS experiment starting at 100 K shows a symmetric peak at 200 K indicating that ___N_2 molecules___ are desorbing in a ___2nd___-order desorption process. When adsorption takes place above about 300K the coverage of adsorbate starts to increase with temperature in an ___activated___ adsorption process. Another TDS experiment on this system shows an asymmetric peak at 1000 K indicating that ___N atoms___ are desorbing in a ___1st___-order desorption process.

(b) if the attempt frequency for the desorption of Na adsorbed on Wa is 10^{13} s^{-1} and the activation energy for desorption is 800 kJ/mol what will be the ~~rate of desorption~~ surface lifetime of Na atoms at 500 K? (8 pts)

For desorption

$$\tau = \frac{1}{\nu} e^{E_a/RT}$$

E_a = activation energy for desorption /mole

$$= 10^{-13} e^{800\times10^3/8.314\times500}$$

$$= 3.78\times10^{70}\ s\ !$$