

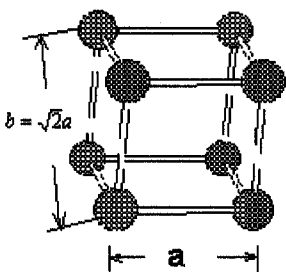
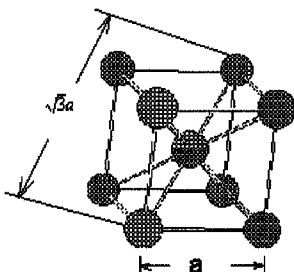
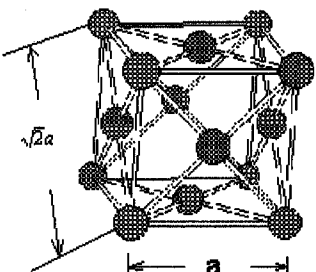
# **CHEM820 SURFACE ANALYSIS HOMEWORK**

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**Professor: Thomas P. Beebe, Jr.**  
**Department: Materials Science & Engineering**  
**Date: May 2<sup>nd</sup>, 2003**

1.) Showing your work and using clear diagrams, calculate the following parameters for the simple cubic, body-centered cubic, and face-centered cubic crystal structures. Make a table similar to the one in the lecture notes. Express your answers in terms of the lattice constant  $a$ .

- nearest-neighbor distance
- next-nearest-neighbor distance
- hard-sphere volume per conventional unit cell
- fraction of hard-sphere volume per unit volume of bulk material

**Solution:**

	simple cubic	body-centered cubic	face-centered cubic
Crystal Structure			
Nearest-neighbor distance	$a$	$\frac{\sqrt{3}}{2}a$	$\frac{\sqrt{2}}{2}a$
Next-nearest-neighbor distance	$b = \sqrt{2}a$	$b = a$	$b = a$
Hard-sphere volume per conventional unit cell	$V_{SC-primitive} = V_{SC-convention} = a^3$ $2r = a, r = \frac{a}{2}$ $V_{hard-sphere} = \frac{4}{3}\pi r^3 = \frac{\pi a^3}{6}$ There is one atom per Simple Cubic unit cell, so the hard-sphere volume is $\frac{\pi a^3}{6}$ .	$V_{BCC-primitive} = \frac{1}{2}V_{BCC-convention} = \frac{1}{2}a^3$ $4r = \sqrt{3}a, r = \frac{\sqrt{3}a}{4}$ $V_{hard-sphere} = \frac{4}{3}\pi r^3 = \frac{\sqrt{3}\pi a^3}{16}$ There are 2 atoms per BCC unit cell, so the hard-sphere volume is $\frac{\sqrt{3}\pi a^3}{8}$ .	$V_{FCC-primitive} = \frac{1}{4}V_{FCC-convention} = \frac{1}{4}a^3$ $4r = \sqrt{2}a, r = \frac{\sqrt{2}a}{4}$ $V_{hard-sphere} = \frac{4}{3}\pi r^3 = \frac{\sqrt{2}\pi a^3}{24}$ There are 4 atoms per FCC unit cell, so the hard-sphere volume is $\frac{\sqrt{2}\pi a^3}{6}$ .
Fraction of hard-sphere volume per unit volume of bulk material	$V_{hard-sphere} = \frac{\pi a^3}{6}$ $= \frac{\pi}{6}V_{SC-primitive}$ $fraction: \frac{\pi}{6} = 52.4\%$	$V_{hard-sphere} = \frac{\sqrt{3}\pi a^3}{16}$ $= \frac{\sqrt{3}\pi}{8}V_{BCC-primitive}$ $fraction: \frac{\sqrt{3}\pi}{8} = 68.0\%$	$V_{hard-sphere} = \frac{\sqrt{2}\pi a^3}{24}$ $= \frac{\sqrt{2}\pi}{6}V_{FCC-primitive}$ $fraction: \frac{\sqrt{2}\pi}{6} = 74.0\%$

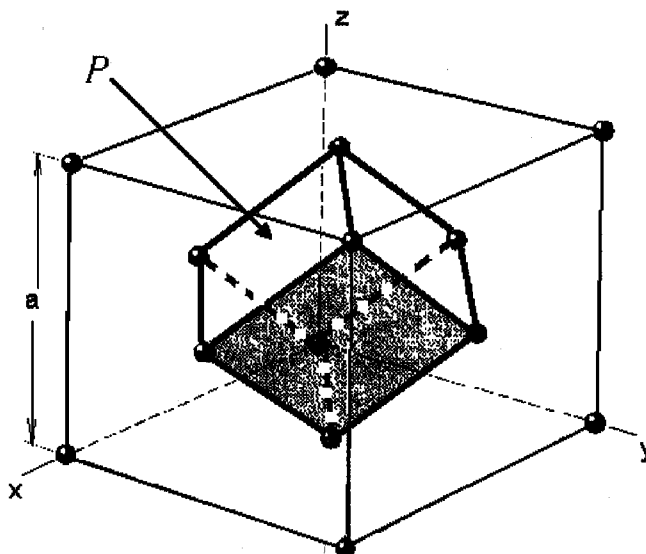
2) The following problem refers to the element gold, Au.

- Draw a unit cell of the bulk material
- Answer all of the questions to problem 1 for the element gold, and this time express your answers numerically ( $\text{\AA}$ ,  $\text{\AA}^3$ , etc.)
- Draw the Au (111), (110) and (100) surfaces using a neat stencil or computer
- Calculate the surface atom densities of the three surfaces in part (c.)
- Calculate the nearest-neighbor distance on each surface
- Calculate the next-nearest-neighbor distance on each surface and name it in terms of the unit cell dimension

**Solution:**

Au is FCC structure, according to the table of "Crystal Structures of the Elements", and its lattice constant  $a$  is  $4.08\text{\AA}$ .

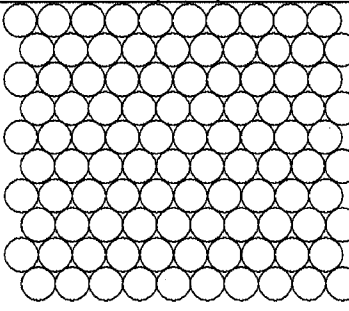
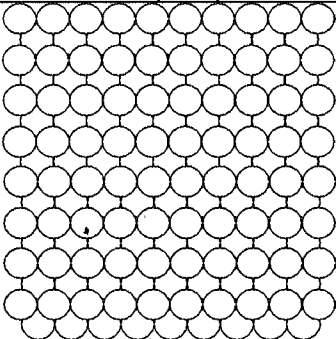
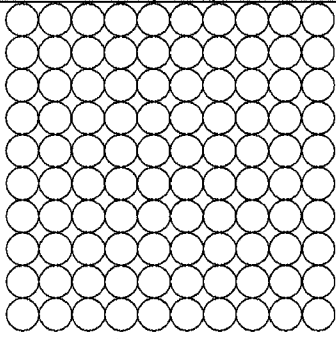
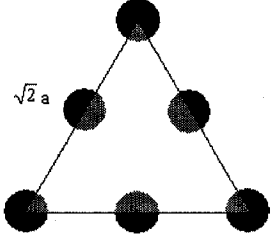
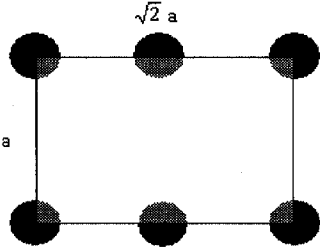
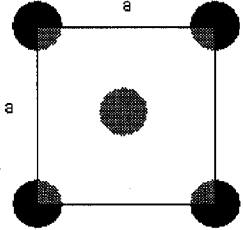
a) The unit cell in Au FCC bulk material:



b)

	FCC Au, $a=4.08\text{\AA}$
Nearest-neighbor distance	$\frac{\sqrt{2}}{2}a = 2.885\text{\AA}$
Next-nearest-neighbor distance	$b = a = 4.08\text{\AA}$
Hard-sphere volume per conventional unit cell	$4V_{hard-sphere} = \frac{16}{3}\pi r^3 = \frac{\sqrt{2}\pi a^3}{6} = 50.24\text{\AA}^3$
Fraction of hard-sphere volume per unit volume of bulk mate	$V_{hard-sphere} = \frac{\sqrt{2}\pi}{6}V_{FCC-primitive} = 74.0\%V_{FCC-primitive}$

c) &amp; d) &amp; e)

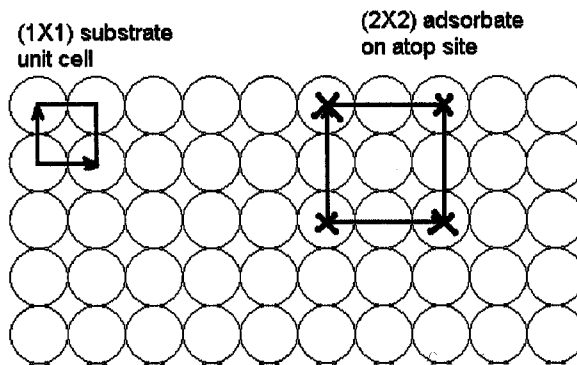
	Au(111)	Au(110)	Au(100)
Surface Structure			
Surface Density	 <p>FCC (111)</p> $\frac{(3 \times 60/360 + 3 \times 1/2) \text{ atoms}}{\frac{1}{2} \times \sqrt{2}a \times \sqrt{2}a \times \sin(60^\circ)}$ $= \frac{2 \text{ atoms}}{\frac{\sqrt{3}}{2} a^2}$ $= \frac{2 \text{ atoms}}{\frac{\sqrt{3}}{2} \times (4.08 \times 10^{-8})^2} \text{ cm}^{-2}$ $= 1.387 \times 10^{15} \text{ atoms} \cdot \text{cm}^{-2}$	 <p>FCC (110)</p> $\frac{(4 \times 1/4 + 2 \times 1/2) \text{ atoms}}{\sqrt{2}a^2}$ $= \frac{2 \text{ atoms}}{\sqrt{2}a^2}$ $= \frac{2 \text{ atoms}}{\sqrt{2} \times (4.08 \times 10^{-8})^2} \text{ cm}^{-2}$ $= 8.494 \times 10^{14} \text{ atoms} \cdot \text{cm}^{-2}$	 <p>FCC (100)</p> $\frac{(4 \times 1/4 + 1) \text{ atoms}}{a^2}$ $= \frac{2 \text{ atoms}}{a^2}$ $= \frac{2 \text{ atoms}}{(4.08 \times 10^{-8})^2} \text{ cm}^{-2}$ $= 1.201 \times 10^{15} \text{ atoms} \cdot \text{cm}^{-2}$
Nearest neighbor distance	$\frac{\sqrt{2}}{2} a = 2.885 \text{ \AA}$	$\frac{\sqrt{2}}{2} a = 2.885 \text{ \AA}$	$\frac{\sqrt{2}}{2} a = 2.885 \text{ \AA}$
Next nearest neighbor distance	$b_{(\sqrt{3} \times \sqrt{3})R30^\circ} = \frac{\sqrt{3}}{2} \times \sqrt{2}a$ $= \frac{\sqrt{6}}{2} \times 4.08 \text{ \AA} = 4.996 \text{ \AA}$	$b_{(1 \times 1)} = a = 4.08 \text{ \AA}$	$b_{(1 \times 1)R45^\circ} = a = 4.08 \text{ \AA}$

3.) Draw the following substrate-adsorbate structures, and calculate the adsorbate coverage. Show the (1 X 1) substrate unit cell. Use the provided surface templates.

- (2 X 2) on Rh(100) with adsorbate on atop sites
- $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$  on Rh(111) with adsorbate on atop sites
- $p(3 \times 3)$  on Rh(100) with adsorbate on atop sites
- (2 X 2) on Rh(110) with adsorbate on atop sites
- $\begin{pmatrix} 1 & 1 \\ -1 & 2 \end{pmatrix}$  on Rh(111) with adsorbate on atop sites
- $\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$  on Rh(100) with adsorbate on atop sites
- $\begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix}$  on Rh(110) with adsorbate on atop sites

**Solution:**

a)

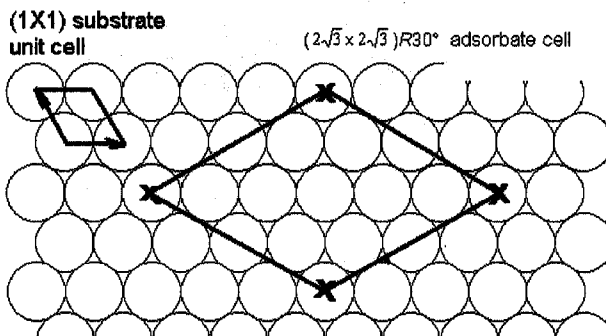


**Surface coverage:**

In every (2X2) adsorbate cell, there are 4 adsorbate molecules and everyone has  $\frac{1}{4}$  molecule involved. So the number of adsorbates is:  $4 \times \frac{1}{4} = 1$ ; while, there are one whole Rh molecule inside the cell, four  $\frac{1}{2}$  Rh molecules in and another four  $\frac{1}{4}$  in, so the total substrate molecules are:  $1 + 4 \times \frac{1}{2} + 4 \times \frac{1}{4} = 4$

$$\text{coverage} = \theta = \frac{\# \text{ of adsorbate}}{\# \text{ of substrate}} = \frac{1}{4} \text{ monolayer}$$

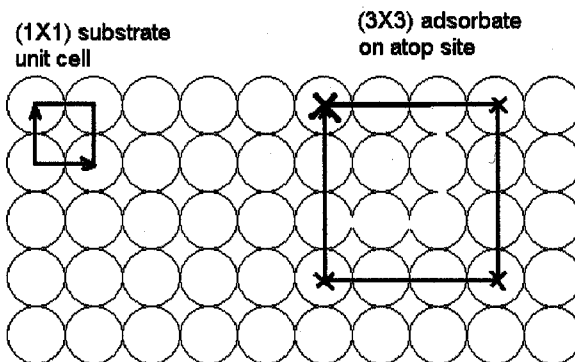
b)

Surface coverage:

In every  $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$  adsorbate unit cell, there are 2 adsorbate molecules, which have  $\frac{1}{3}$  molecule involved for each; and there are another two, each of which has  $\frac{1}{6}$  molecule inside the unit cell. So the number of adsorbates is:  $2 \times \frac{1}{3} + 2 \times \frac{1}{6} = 1$ ; while, there are 9 whole Rh molecules inside the cell, four  $\frac{1}{2}$  Rh molecules in and another two  $\frac{1}{3}$  in, two  $\frac{1}{6}$  in, so the total substrate molecules are:  $9 + 4 \times \frac{1}{2} + 2 \times \frac{1}{3} + 2 \times \frac{1}{6} = 12$ .

$$\text{coverage} = \theta = \frac{\# \text{ of adsorbate}}{\# \text{ of substrate}} = \frac{1}{12} \text{ monolayer}$$

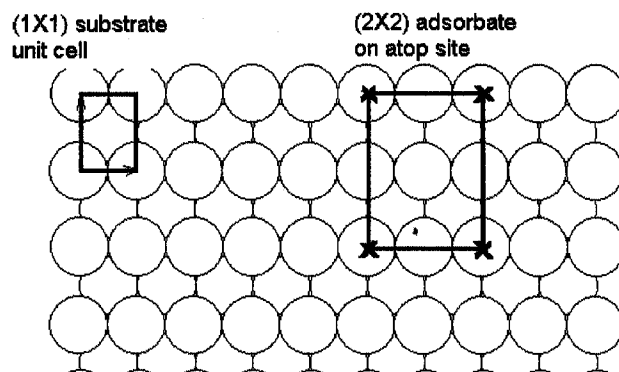
c)

Surface coverage:

In every  $(3 \times 3)$  adsorbate cell, there are 4 adsorbate molecules and everyone has  $\frac{1}{4}$  molecule involved. So the number of adsorbates is:  $4 \times \frac{1}{4} = 1$ ; while, there are four whole Rh molecule inside the cell, eight  $\frac{1}{2}$  Rh molecules in and another four  $\frac{1}{4}$  in, so the total substrate molecules are:  $4 + 8 \times \frac{1}{2} + 4 \times \frac{1}{4} = 9$

$$\text{coverage} = \theta = \frac{\# \text{ of adsorbate}}{\# \text{ of substrate}} = \frac{1}{9} \text{ monolayer}$$

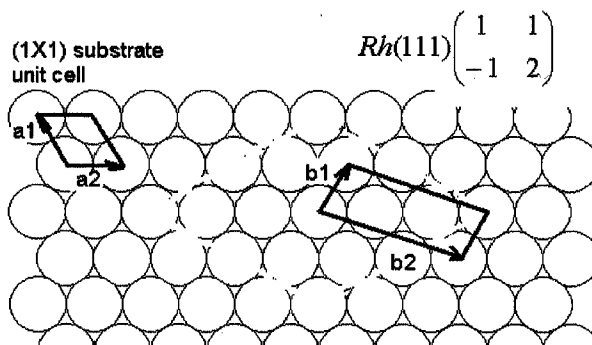
d)

Surface coverage:

In every (2X2) adsorbate cell, there are 4 adsorbate molecules and everyone has  $\frac{1}{4}$  molecule involved. So the number of adsorbates is:  $4 \times \frac{1}{4} = 1$ ; while, there are one whole Rh molecule inside the cell, four  $\frac{1}{2}$  Rh molecules in and another four  $\frac{1}{4}$  in, so the total substrate molecules are:  $1 + 4 \times \frac{1}{2} + 4 \times \frac{1}{4} = 4$

$$\text{coverage} = \theta = \frac{\# \text{ of adsorbate}}{\# \text{ of substrate}} = \frac{1}{4} \text{ monolayer}$$

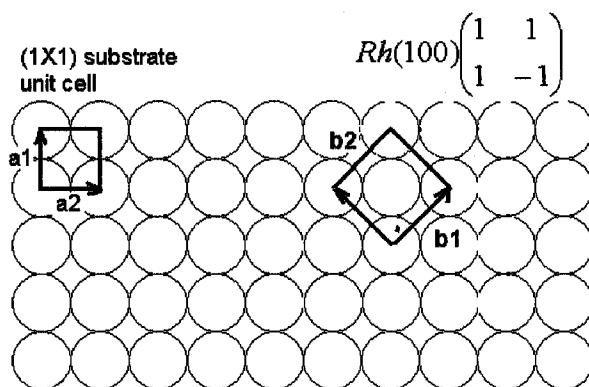
e)  $Rh(111) \begin{pmatrix} 1 & 1 \\ -1 & 2 \end{pmatrix}$

Surface coverage:

In every  $Rh(111) \begin{pmatrix} 1 & 1 \\ -1 & 2 \end{pmatrix}$  adsorbate cell, there are 4 adsorbate molecules, parts of each of them compensate with each other to form one whole adsorbate molecule. While, different parts of the substrate molecules form 3 whole substrate molecules.

$$\text{coverage} = \theta = \frac{\# \text{ of adsorbate}}{\# \text{ of substrate}} = \frac{1}{3} \text{ monolayer}$$

$$f) Rh(100) \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$$

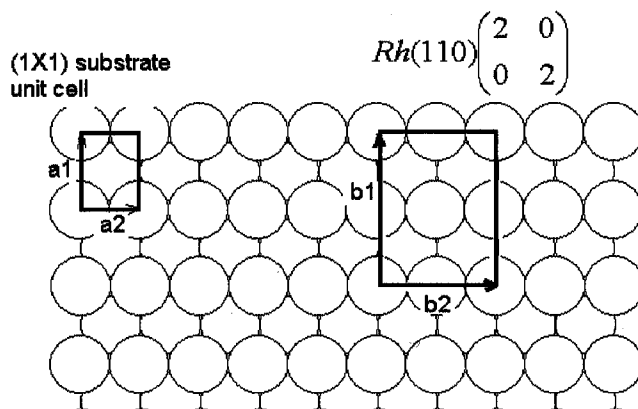


Surface coverage:

In every  $Rh(100) \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$  adsorbate cell, there are 4 adsorbate molecules, parts of each of them compensate with each other to form one whole adsorbate molecule. While, different parts of the substrate molecules form 2 whole substrate molecules.

$$coverage = \theta = \frac{\#ofadsorbate}{\#ofsubstrate} = \frac{1}{2} monolayer$$

$$g) Rh(110) \begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix}$$



Surface coverage:

In every  $Rh(110) \begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix}$  adsorbate cell, there are 4 adsorbate molecules, parts of each of them compensate with each other to form one whole adsorbate molecule. While, different parts of the substrate molecules form 4 whole substrate molecules.

$$coverage = \theta = \frac{\#ofadsorbate}{\#ofsubstrate} = \frac{1}{4} monolayer$$

- 4.) Use a computer spreadsheet to complete the following problem. Using the Morse potential (see lecture notes), plot the 2-dimensional potential energy curves for both chemisorbed and physisorbed molecules on a surface. Select the appropriate parameters so as to approximately reproduce the figure in the lecture notes, showing both an activated and non-activated transition from the physisorbed to the chemisorbed state. Show the formulae and parameter values, as well as the final plots of the curves, in what you hand in.

**Solution:**

Morse potential is used to describe adsorption thermodynamics:

$$V_{Morse} = D_e (1 - e^{-a(R-R_e)})^2$$

$D_e$  = chemisorption well-depth

$R$  = interatomic distance of adsorbate & surface

$R_e$  = equilibrium distance

$a$  = adjustable parameter (typically = 2)

From the curve in the lecture notes, for the chemisorption (W-O) of oxygen on tungsten,  $D_e \approx 610(\text{kJ/mol})$ ,  $R_e \approx 2.3\text{Å}$ ,  $a_1 = 2.0$ ,  $a_2 = 2.5$ ; for the physisorption (W+O<sub>2</sub>),  $D_e \approx 20(\text{kJ/mol})$ ,  $R_e \approx 3.3\text{Å}$ , and  $a_1 = 2.0$  was taken.

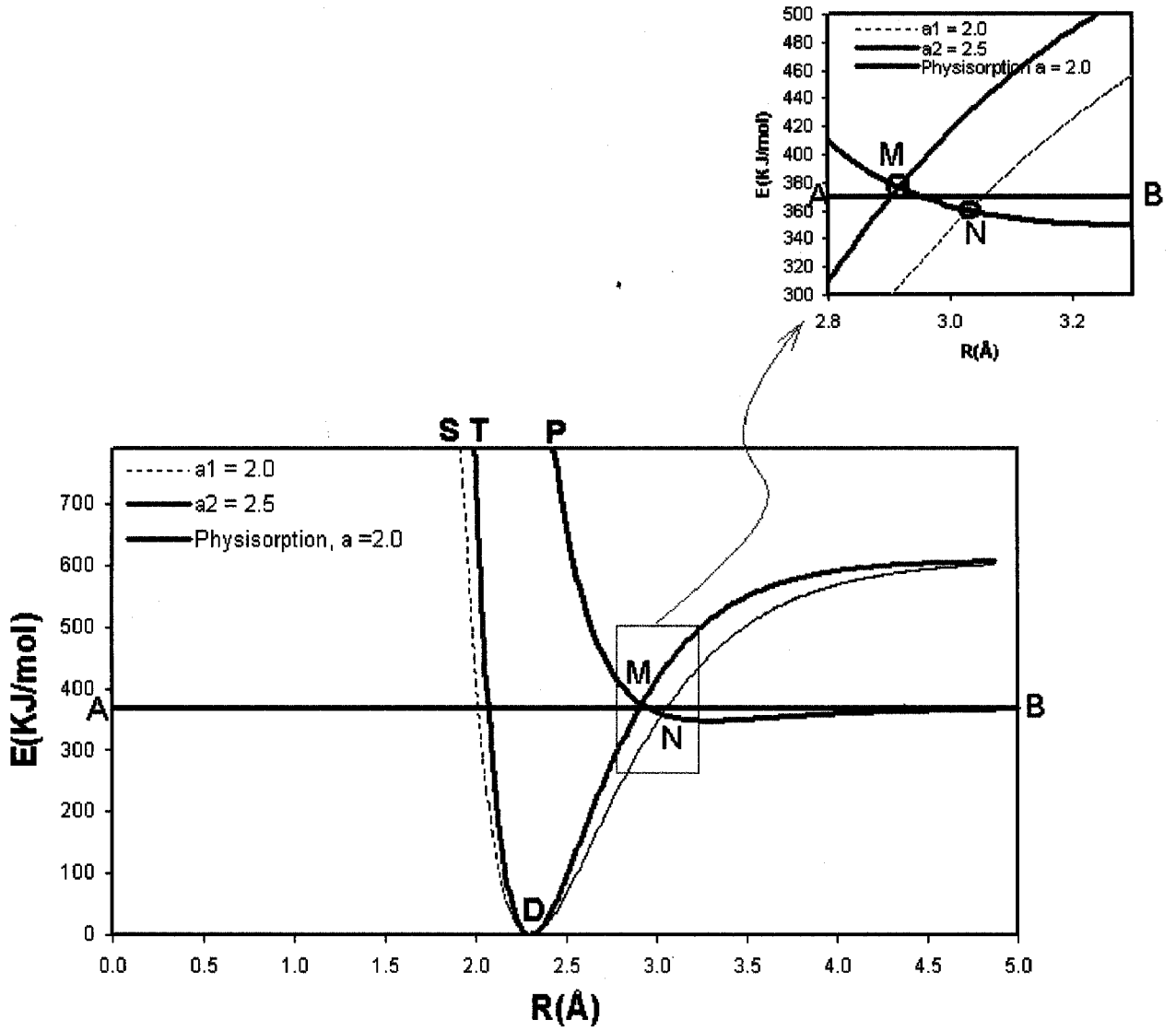
So the formulas used in the plots are:

$$V_{Morse-chemi-1} = 610(1 - e^{-2.0(R-2.3)})^2$$

$$V_{Morse-chemi-2} = 610(1 - e^{-2.5(R-2.3)})^2$$

$$V_{Morse-physi} = 350 + 20(1 - e^{-2.0(R-3.3)})^2$$

When  $a_1 = 2.0$ , starting from the physisorbed curve, it doesn't need to overpass any energy barrier, oxygen chemically adsorbs onto tungsten, which is curve B→N→D→S; When  $a_2 = 2.5$ , it needs to get extra energy to go to chemisorption mode, so the path is B→N→M→D→T. The former mode is chemisorption non-activated, and the later is chemisorption activated. For some cases, chemisorption will never happen, and only physisorption exists, which is B→N→M→P.



- 5.) Use a computer spreadsheet to complete the following problem. Generate the plots shown in the lecture notes for Langmuir adsorption. In separate columns, calculate the rate of adsorption, the coverage and the exposure. Your final answer should show two plots: **one for the rate of adsorption versus coverage**, and **a second for the coverage versus exposure**. Select reasonable values for the time and pressure in order to achieve a monolayer coverage in a few minutes. In the second plot (coverage versus exposure), show four curves on the same graph for initial sticking coefficients of 1.0, 0.5, 0.1 and 0.01.

**Solution:**

- a) For first-order Langmuir adsorption, we take  $CO_{(g)} \leftrightarrow CO_{(ads)}$  as an example, the rate

of adsorption can be expressed as:  $R_a = \frac{d\theta}{dt} = S_0 F(1-\theta)$ . Here,

-  $S_0$  is the initial sticking coefficient;

-  $F$  is incident flux, and

$$F = P \left( \frac{1}{2\pi mkT} \right)^{1/2} = P \left( \frac{6.02 \times 10^{23} \text{ molec/mol}}{2\pi \times 3.8 \times 10^{20} \text{ molec/(cm}^2 \text{ Sec Torr)} \times 28 \text{ g/mol} \times 300 \text{ K}} \right)^{1/2} = \bar{F} P ;$$

$$\bar{F} = 0.434 \left( \frac{\text{cm}^2 \cdot \text{s} \cdot \text{Torr}}{\text{g} \cdot \text{K}} \right)^{1/2}, \text{ for CO}$$

-  $\theta$  is the fractional surface coverage, so  $1-\theta$  is the free sites remaining.

$$\text{So } R_a = \frac{d\theta}{dt} = S_0 \bar{F} P(1-\theta)$$

And  $\theta(t) = 1 - \exp(-S_0 \bar{F} P t)$ , here  $Pt$  is representing exposure.

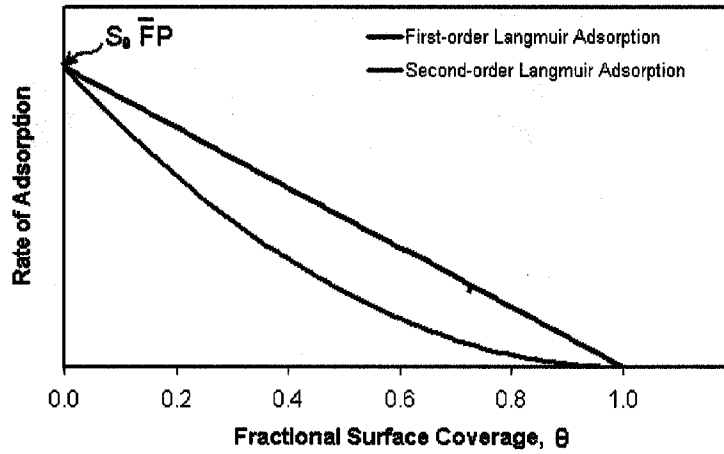
- b) For 2<sup>nd</sup>-order Langmuir adsorption, we take  $O_{2(g)} + 2\text{sites} \leftrightarrow 2O_{(ads)}$  as an example, the

rate of adsorption can be expressed as:  $R_a = \frac{d\theta}{dt} = S_0 \bar{F} P(1-\theta)^2$ , and

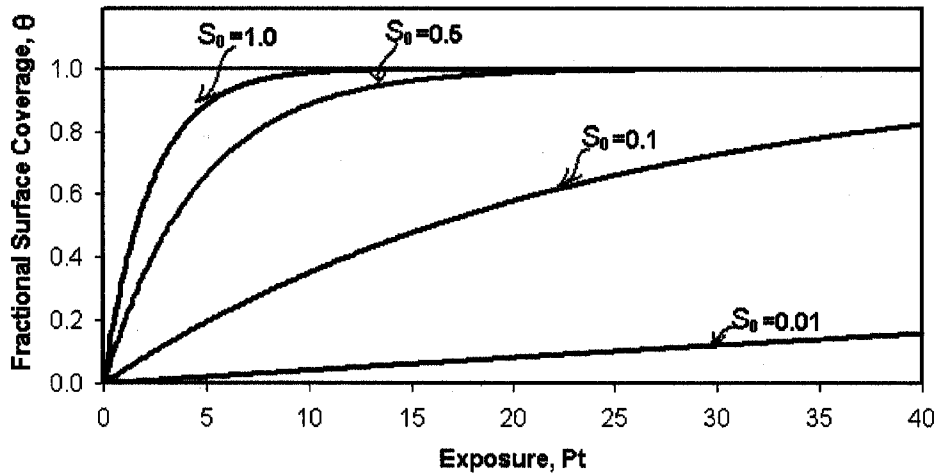
$$\bar{F} = 1.442 \left( \frac{\text{cm}^2 \cdot \text{s} \cdot \text{Torr}}{\text{g} \cdot \text{K}} \right)^{1/2}, \text{ for } O_2.$$

$$\text{And } \theta(t) = 1 - \frac{1}{1 + S_0 \bar{F} P t}.$$

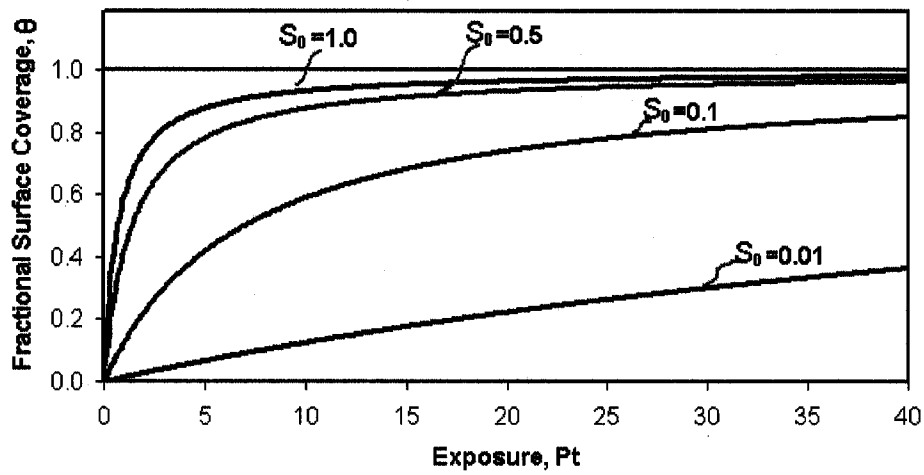
Because 1 Exposure = 1 Langmuir =  $10^{-6}$  Torr·sec, one monolayer forms in approximately 1 second when the pressure is  $10^{-6}$  Torr. In order to achieve a monolayer coverage in a few minutes, for example, 5 minutes (300 seconds), we need a pressure of  $\sim 3.3 \times 10^{-9}$  Torr.



First-order langmuir adsorption



Second-order langmuir adsorption



- 6.) On one side of a sheet of paper, double spaced and typed, explain the seminar of one of the following visiting scientists. Discuss their methods and their findings.

### **The Surface Chemistry of Biomaterials**

By - Kevin Healy – University of California Berkeley

In this talk, Dr. Kevin Healy, from U. C. Berkeley, talked mainly about three relative points of his research: 1) the methods they are using to modify the metal oxide surfaces into bioactive ones; 2) the design of IPN to make bioactive metal oxide surfaces less bioactive; 3) the method to control the nuclear shape and projected area of the growing cells.

- *Metal Oxide Surface Modification:* This is a simple three-step immobilization strategy (metal oxide + EDS + SMCC + peptides), which can not only control the surface density, but also be generally used to control molecular or cell behavior at interfaces, due to the ligand specific surface. XPS and ellipsometry data were collected to characterize the surface chemistry, thickness and density.
- *IPN Grafted to Oxide Surface:* The grafting an IPN of P(AAm-co-EG) onto oxide surfaces was introduced and the robust surface is non-protein binding and less adhesive than the silane modified one, which can be used for medical devices to prevent material fouling and non-specific protein adsorption. Contact Angle, XPS, ellipsometry were applied to study the robust surface wettability, chemistry as well as thickness, respectively.
- *Engineering Gene Expression by Modulation of Nuclear Shape:* Photolithography was used to form EDS pattern on the DMS substrate, and then cells grow onto the EDS patterns. The shape of the nuclei controlled by confining attachment and spreading of isolated cells on adhesive islands. And the gene expression is altered by changing nuclear shape – patterned cells are forced to cease dividing and differentiate at a significantly earlier time point than unpatterned cells. In this study, TOF-SIMS with imaging was used to confirm the spatial distribution of the substrate chemistry. Specially, reverse transcription (RT) *in situ* PCR was performed to observe intracellularly the osteocalcin mRNA cells growth, organization, and nucleation on homogeneously patterned EDS/ P(AAm-co-EG) surface.

In summary, Dr. Healy's research group is doing a wonderful job to solve the problems of the bio-devices by surface modification of the biomaterials.