**Name:**_____

**Affirmation: If I make use of my laptop during this exam,**
**I will not resort to any online information beyond that available at the 243A website**

**Signature:**_____

**[1] (15 points)** Suppose that the sticking probability for oxygen <u>molecules</u> ($O_2$) incident on a W(110) surface at 298 K and an ambient pressure of 1 x 10(-8) torr is constant at 1.0 until a coverage of <u>atomic</u> oxygen of 0.5 monolayers (as measured relative to the W atom surface density of $1.41 \times 10^{15}$ atoms/cm$^2$) is reached. Above this coverage, assume that the sticking probability drops to 0.1. Calculate the time variation of the coverage of atomic oxygen on the surface, make a qualitative plot of coverage versus time, and determine how long it will take to reach a full coverage of 1.0 monolayer.

**[2] (25 points)** A Hartree-Fock calculation for the CO molecule yields a <u>total</u> energy for the system of - 112.75 atomic units (1 a.u. = 27.211 eV) and one-electron eigenvalues $\varepsilon_{C1s}$ = -20.65 a.u. and $\varepsilon_{O1s}$ = -11.30 a.u. The distance between C and O in the calculation was set to be the equilibrium distance of 1.18 A.

**5 pts** (a) Estimate the O 1s and C 1s binding energies <u>in eV</u> from this data.

**5 pts** (b) What additional theoretical <u>total</u> energies would you need to be able to calculate the relaxation energies involved with the O1s and C 1s binding energies? Specify these as precisely as you can.

**5 pts** (c) After photoelectron ejection from the C 1s orbital, what *other* molecule's outer electron orbitals would best represent the final outer electron orbitals of the resulting ion?

**10 pts** (d) Write down the equations for the coulomb and exchange integrals between the C 1s and O 1 s ...en provide numerical estimates for *both* of these integrals, using a simple classical ......... appropriate. Note that these two core orbitals are on two different centers and so overlap negligibly. Also, it may be convenient to note that two classical electron point charges separated by a distance of 1 Å have a repulsive potential of 14.4 eV.

**[3] (20 points)** Consider KLL Auger emission from Cu metal, with some relevant binding energies being:

| Cu: | Z = 29 | Zn: Z = 30 |
|-----|--------|------------|
| M4,5 | ?.? | 10.2 |
| M3 | 75.1 | 88.6 |
| M2 | 77.3 | 91.4 |
| M1 | 122.5 | 139.8 |
| L3 | 932.5 | 1021.8 |
| L2 | 952.3 | 1044.9 |
| L1 | 1096.7 | 1193.6 |
| K1 | 8980.5 | 9660.8 |

**5 pts** (a) What will be the most energetic Auger electron in this series? Make the most accurate estimate you can of its energy, indicating the type of formula you have used.

**10 pts** (b) After the Auger transition in (a), what type of hole state will be left behind? If we now want to estimate the effect of this hole state on the surrounding valence electrons, we might treat the final

state as an "impurity atom" in the Cu lattice.  What would be the atomic number of the atom we would choose for the impurity in this case?

5 pts  (c) Derive the energy of the Cu $K\alpha_1$ x-ray from binding energy tables, and compare your answer to the tabulated value of 8047.78.

[4]  (40 points)  This problem consists of several independent parts.  Answer each part briefly.

(a) (10 points) If a bulk alloy of 40% Ru and 60% Mo were prepared, would the composition of an atomically clean surface of this alloy be expected to be different from that in the bulk?  Why or why not?

(b) (15 points) Consider an idealized two-dimensional material whose "surfaces" are the one-dimensional lines or curves describing its boundaries.  Assume that the material has a simple cubic crystal structure and that the "surface tension", now in units of energy/length, is smallest along <100> type directions parallel to the cube directions, where it has a normalized value of 1.00.  The surface tension is next smallest along <110> directions at 45° with respect to <100>, where it has a value of 1.25, and it is <u>much larger</u> along any other direction.  From this information, use the Wulff construction to predict the shape of a sample of this material at equilibrium, including in particular, the fraction of surface of {100} type and the fraction of {110} type.

(c) (15 points) The stereographic image below shows the structure of $C_{60}$ "buckyballs" adsorbed on a Cu(111) surface.
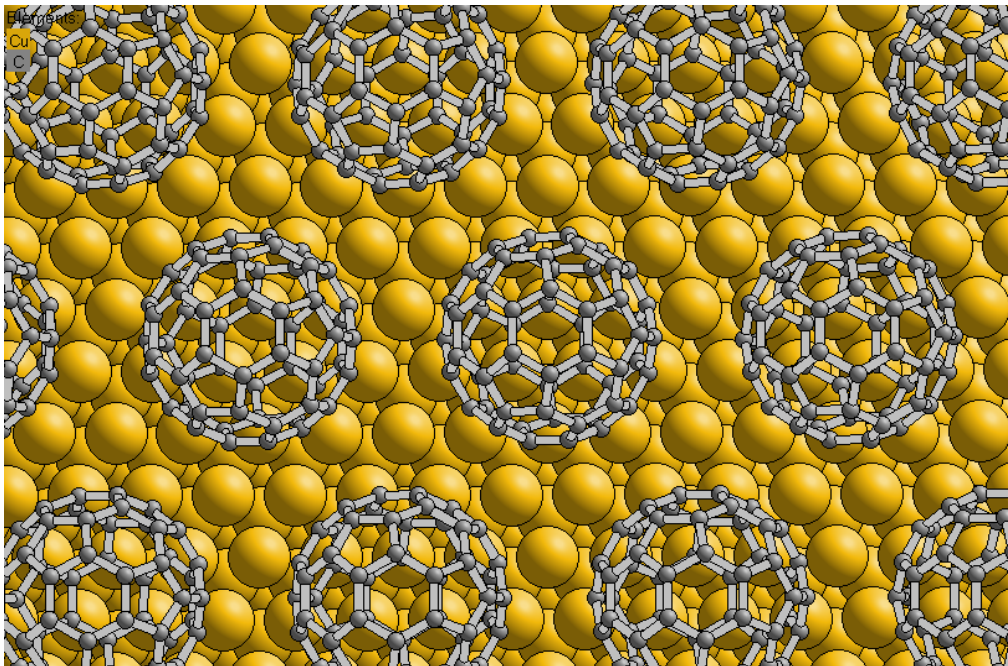


(i) What would you call this structure in Wood notation, treating the $C_{60}$ molecules as a single unit?

5 pts

(ii) What would the LEED pattern qualitatively look like for this surface, considering only the strongest spots from the top Cu layer and the $C_{60}$?  Indicate clearly which spots come from the Cu, the $C_{60}$, and from both of them.

5 pts

(iii) If the $C_{60}$ array were translated by 2.0 Å to the right relative to the Cu surface, would your answer to part (ii) change?  Explain why or why not.

5 pts

(#1) $\quad r = (3.51 \times 0^{22}) \dfrac{P}{\sqrt{TM}} = (3.51 \times 10^{22}) \dfrac{(1 \times 10^{-0} \text{ Torr})}{\sqrt{298 \text{ K} \cdot 32}} = 3.59 \times 10^{12}$

$$\dfrac{\text{molec}}{\text{cm}^2 \cdot \text{s}}$$

Atomic coverage $\quad \Theta = \dfrac{s'}{s} = 2 \dfrac{1}{s} \displaystyle\int_0^t r\, P_s(t')\, dt'$

where $\quad s = 1.41 \times 10^{15} \text{ atoms}/\text{cm}^2$

and $\quad P_s(t) = \begin{cases} 1 & \text{up to } \Theta = 0.5 \text{ at } t = t_{0.5} \\ 0.1 & \text{for } \Theta > 0.5 \text{ up to } t_{1.0} \end{cases}$
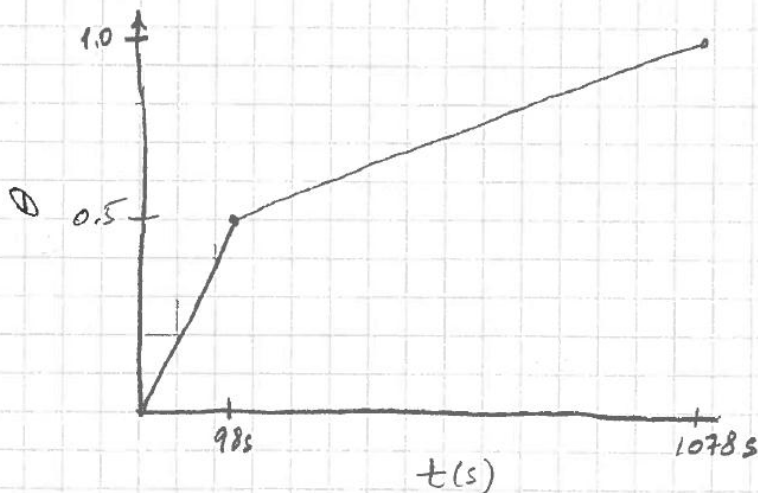
$\therefore \quad \Theta = 2 \dfrac{1}{(1.41 \times 10^{15})} \cdot (3.59 \times 10^{12}) \left( t_{0.5} + (t - t_{0.5})\, 0.1 \right)$

$0.5 = 5.09 \times 10^{-3}\, t_{0.5}$

$\therefore \quad t_{0.5} = 98 \text{ s}.$

$t_{1.0} - t_{0.5} = 10 \times 98 = 980 \text{ s}.$

$\therefore \quad t_{tot} = 980_s + 98 = 1078 \text{ s}.$

(#2) a). According to Koopmans' Theorem,

$$E_b^V(k)^{KT} = -\epsilon_k \qquad (1\,a.u. = 27.21\,eV)$$

∴ $E_b(O1s) = -(-11.30\,au) = 307.47\,eV$ ✓

$E_b(C\,1s) = -(-20.65\,au) = 561.89\,eV$ ✓

b). We would need to know:

1). Total Energy of $CO^+$ ion with O1s hole ✓

2). Total Energy of $CO^+$ ion with C1s hole. ✓

c). **NO** √

d). $J = \iint \phi_{C1s}^*(\bar{r}_1)\,\phi_{O1s}^*(\bar{r}_2)\,\frac{1}{r_{12}}\,\phi_{C1s}(\bar{r}_1)\,\phi_{O1s}(\bar{r}_2)\,dV_1 dV_2$

$K = \iint \phi_{C1s}^*(\bar{r}_1)\,\phi_{O1s}^*(\bar{r}_2)\,\frac{1}{r_{12}}\,\phi_{O1s}(\bar{r}_1)\,\phi_{C1s}(\bar{r}_2)\,dV_1 dV_2$

$K \approx 0$   (almost no overlap) ✓

$J \approx \frac{1}{r_{12}}$ (in a.u)    $\approx 10\,eV$ ✓

(#3) a). $E_{kin}(K_j L_k L_i) = E_b^{Cu}(K_j) - \frac{1}{2}\left[E_b^{Cu}(L_k) + E_b^{Zn}(L_i) + E_b^{Zn}(L_k) + E_i\right.$

Most energetic Auger electron will correspond to:

K1  L3  L3

$E_{kin}(K1, M3, M3) = 8980.5\,eV -$

$\qquad -\frac{1}{2}\left[932.5eV + 1021.8eV + 1021.8eV + 932.5eV\right] = 7026.2\,eV$

b). The final state will be a **2-hole state** ($2\,2p_{3/2}$ holes).
The atomic number of the impurity atom would be **Z+2 = 31**

Deleted. Not on this year's exam

(c)  $E_{K\alpha1}(Cu) = E(K1) - E(L3) =$ 8979 – 932.7 = 8046.3
Compared to 8047.48 from table of x-ray energies

**[#4]** a). The surface tensions of Ru and Mo are very close to each other ($\sim 2200$ ergs/$m^2$), hence it takes about the same amount of energy to form a surface that is composed of Ru or Mo. Therefore, the composition of the clean surface s going to be close to bulk.

b).
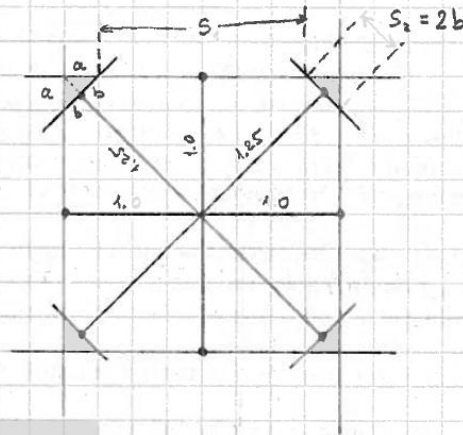


$b = \sqrt{2} - 1.25$

$a = \sqrt{2}\,b = \sqrt{2}\,(\sqrt{2} - 1.25)$

$s_1 = 2 - 2a = 2 - 2\sqrt{2}\,(\sqrt{2} - 1.25) = 1.536 \implies 4\,s_1 = 6.144$

$s_2 = 2b = 2(\sqrt{2} - 1.25) = 0.328 \qquad\qquad \implies 4\,s_2 = 1.314$

$S_{TOT} = 4\,s_1 + 4\,s_2 = 7.458$

$\implies f_{s_1} = \dfrac{4 s_1}{S_{TOT}} = \dfrac{6.144}{7.458} = 0.824$

and

$f_{s_2} = \dfrac{4 s_2}{S_{TOT}} = \dfrac{1.314}{7.458} = 0.176$

c). (i) $Cu(111)(4 \times 4)R0° - C_{60}$

(ii) LEED pattern would have 2 sets of spots :

1). Spots that are far apart, due to Cu.  (○)

2). Spots that cluster close together, due to $C_{60}$  (●)

(iii) There would be no change to the pattern, because the angular position of the LEED spots is determined by lateral spacing between atoms (units) in each layer.