Spring '05 **CH370** (51995) / **CH387D** (52080) Name ____________________

Hackert **Exam III** ID ____________________

$R = 8.314 \times 10^7$ g-cm^2 /(sec^2-mol-K) = 8.314 J/mol-K ; $\eta = 0.01$ g/(cm-sec)

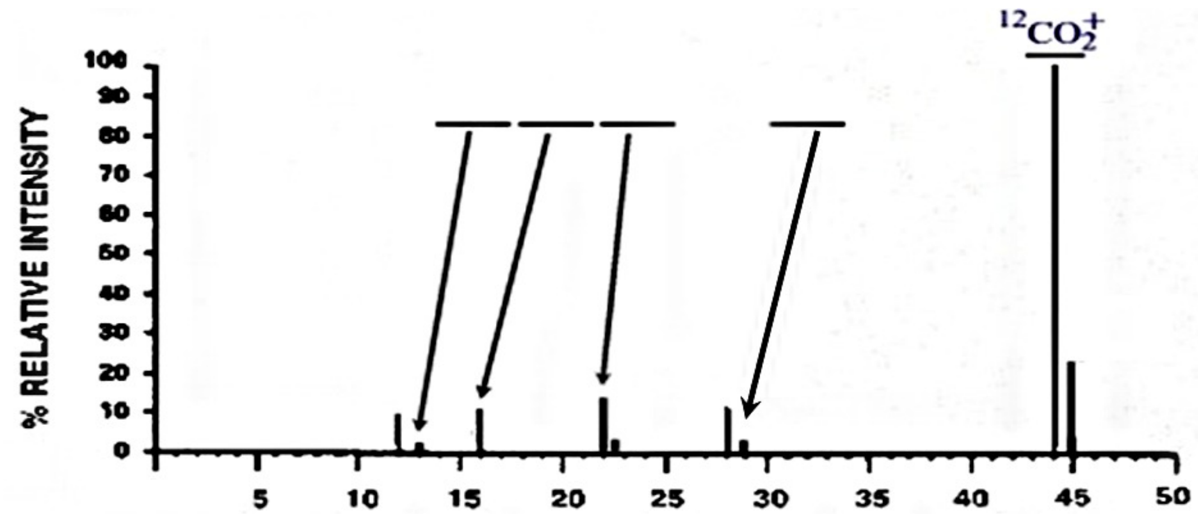
$n\lambda = 2d\sin\theta$; $k = 1.38 \times 10^{-23}$ J/K; $h = 6.63 \times 10^{-34}$ J-sec; $E = (\gamma\, h\, m\, H)/2\pi$;

γ for ^{1}H = 26.7×10^7 rad/sec-T ; $\theta = [S]/(Kd + [S])$; $\nu = n - \nu Kd/[S]$;

1. **Mass Spec:**

a) Consider the following mass spec obtained from CO_2 gas given off by a microorganism that had been grown with media enriched with ^{13}C glucose. Identify the **four** ion peaks shown by placing a label (ion composition and charge as illustrated) for the corresponding **cations** on the blank lines provided.

(8)



b) Identify what is meant by each of these mass spec developments **and** list **one advantage** of each method:

(6)

MALDI –

ESI –

c) Consider a time-of-flight experiment. If it takes 28 microsec for a triply charged ion of mass 55,000 Da to reach the detector, estimate the time of arrival for the same particle carrying four charges to reach the detector? ____________________

(6)

2. Ligand Binding:

a) Consider the problem of multiple binding equilibria. The Scatchard Equation is often given as: $\nu/[S] = (1/Kd)(n - \nu)$.

What is the meaning of the "n" and "ν" terms in this equation, **and** illustrate on the figure how plotting ν vs. $\nu/[S]$ can yield information on the number of binding sites and the value of Kd.

"n" =

ν

"ν" =

(6)

____________________ ν / [S]

b) Consider the binding of a ligand to a single, noncooperative site on a very large protein with 1063 amino acids of which 25 are tryptophans and 37 are tyrosines . If the experiment is done on a Thursday at 8:00 a.m. of the day the Spurs rebounded by beating the Denver Nuggets to the night before, and if K_d = 0.20 μM and $[E]_o$ = 0.20 μM, and $[S]_{total}$ = 2μM, calculate the % occupancy of the ligand sites under these conditions.

(7)

c) We discussed four methods of experimentally determining binding constants. Name them and then briefly describe the basis for the methodology for two of those methods.

(2) ____________________ ____________________ ____________________ ____________________

(6)

3. X-rays:

a) We discussed several ways of generating short wavelength radiation. Briefly state how such radiation is produced (or the defining characteristics of such radiation) by each of the following methods.

i) copper rotating anode generator

ii) synchrotron light

(6)

iii) a gamma radiation source

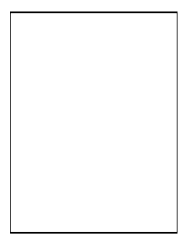
b) Write down the "Bragg Equation":

(2)

c) Consider the following illustrations of two unit cells. Sketch the "Bragg planes" that correspond to the Miller indices given below each cell. Assume the "**a**" axis is vertical and the "**b**" axis horizontal in each case.

(6)

(420)



(230)

d) Given that the reciprocal lattice shows three, orthogonal reciprocal lattice vectors belonging to a tetragonal space (Hint: a = b) and the following diffraction data, calculate the lattice constants and volume of this tetragonal unit cell. (Assume $\lambda = 1.5418$ Å).

(8)

hkl	***2θ***
5 5 0	18.47°
0 0 17	14.88°

a = ____________

b = ____________

c = ____________

V = ____________

e) Given the following equation for calculating the electron density function at a point with fractional coordinates (x,y,z) in the unit cell. 1) Draw a "box" around all parts of the electron density equation that correspond to experimentally measured quantities, and 2) draw a circle around all parts of the electron density equation that correspond to missing items that are supplied by "solving" the phase problem.

(4)

$$\rho(x,y,z) = (1/V)\Sigma\Sigma\Sigma\ |F_{hkl}|\ e^{i\alpha_{hkl}}\ e^{-2\pi i(hx + ky + lz)}$$

f) "Simulated annealing" is used in conjunction with the refinement of both X-ray and NMR structural models. Briefly describe what this process is and note how the use of simulated annealing differs for X-ray vs. NMR structural refinement?

(6)

4. NMR:

a) Is structure determination by multidimensional NMR methods a true "imaging" method like EM or X-ray determination? Why or why not? Include in your answer what great difficulties need to be overcome when using NMR techniques.

(8)

b) What is the equation describing the energy of interaction of the nucleus with an 21.2 Tesla magnetic field for a proton in this magnetic field?

(3)

c) What is the energy difference in the transition between two states for protons (gyromagnetic ratio for ^{1}H = 26.7 x 10^{7} rad/sec-T) with “m” = - ½ and + ½ if the nucleus is placed in a magnetic field strength (**H**) of 21.2 Tesla?

(4)

d) What is the **frequency** (in MHz) of a photon that has the energy required to induce a transition between two adjacent proton states in a magnetic field with a strength of 21.2 Tesla? The gyromagnetic ratio for ^{1}H = 26.7 x 10^{7} rad/sec-T .

(5)

e) Calculate the ratio of particles (n+ / n-) for these nuclei in a 21.2 Tesla magnetic field according to the Boltzmann distribution is T = 20 ^{o}C? (Note: the ratio is about 0.9999 for an 11.7 Tesla magnet that Dr. Hoffman routinely uses.)

(5)

f) What is the advantage of having bigger and more powerful magnets in NMR instrument?

(2)

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BONUS QUESTIONs: (no wrong answers – just need three responses)

(1) Do you like the current time slot for this class (T/Th 8:00)? Yes ____; No ____

(2) What times you would prefer that would probably fit your schedule: (***select two***)

TT 8:00 ___; TT 9:30 ___ ; TT 11 ___; TT 12:30 ___; TT 2:00 ___ ; TT 3:30 ___;

MWF 8 ___; MWF 9 ___; MWF 10 ___; MWF 11 ___;