No Analytical crib available
August 23, 2014
Written by Professor Cooks
Ph# 45263

No Organic crib available
August 23, 2014
Written by Professor Ramachandran
Ph# 45303
### Amino Acid pKa Table

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<thead>
<tr>
<th>Amino Acid</th>
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**Question 1. (10 Points)**

Draw the peptide CSHADYK at pH 7.4. Don’t worry about stereochemistry for this one.

![Peptide Structure](image-url)
**Question 2. (10 Points)**

Explain the action of an enzyme on a simple Substrate → Product chemical reaction that is thermodynamically favorable. To do this, draw a labeled free energy versus reaction progress diagram. In this diagram use a solid line to show the uncatalyzed reaction trajectory. Use a dashed line to show the catalyzed reaction trajectory.

![Free Energy vs Reaction Progress Diagram](image)

**Question 3. (10 Points)**

In one sentence or less describe:

a) How does an enzyme affect the forward and backward reaction rates? **Accelerate**

b) How does an enzyme affect the reaction equilibrium? **No change**

**Question 4. (20 Points)**

In analyzing the kinetics for a general enzyme reaction: \( E + S \xrightleftharpoons[k_{-1}]{k_1} ES \xrightarrow{k_2} E + P \)

a) Write the Michaelis-Menten equation for the rate of product formation.

\[
\nu = \frac{V_{\text{max}} \cdot [S]}{K_M + [S]} = \frac{k_{\text{cat}} \cdot [E_{\text{total}}] \cdot [S]}{K_M + [S]}
\]

b) Explain the Michaelis-Menten assumption about the enzyme-substrate equilibrium. **E & S associate reversibly to form ES in rapid equilibrium (pre-equilibrium assumption)**

c) Explain the Briggs-Haldane assumption about the enzyme-substrate complex. **[ES] quickly reaches steady-state (steady-state assumption)**

d) As written, explain what implicit assumption is made about the chemistry step in this reaction to simplify analysis (think back to question 3). **Rate of the reverse reaction \( E + P \rightarrow ES \) (k_2) is negligible.**

e) How does this assumption constrain how you experimentally measure reaction rates?
Forward reaction rates should be estimated from initial velocity measurements.

f) Define the Michaelis constant $K_M$ in terms of the rate constants above and explain what it is.

$$K_M = \frac{(k_{-1} + k_2)}{k_1}$$

Substrate concentration for half-maximal velocity

g) Explain when $K_M$ is approximately equal to the enzyme-substrate dissociation constant $K_D$. $k_2 \ll k_{-1}$, chemistry step is slow

h) Explain what $k_{cat}$ is and be sure to talk about substrate concentration.

$$k_{cat} = k_2 = \frac{V_{max}}{[E_{total}]}$$

$k_{cat}$ is the turnover number or maximal catalytic activity. It is the number of substrate molecules converted to product per enzyme molecule per time when the enzyme is saturated with substrate.

i) If you could only know one measurement from someone else’s experiment, explain whether you would want to know $k_{cat}$ or $V_{max}$ to compare kinetic efficiency of two enzymes. $k_{cat}$, $V_{max}$ depends on $[E_{total}]$ which may vary from experiment to experiment.

k) Explain why $k_{cat}/K_M$ is more useful than $k_{cat}$ as a measure of catalytic efficiency under physiological conditions.

$k_{cat}/K_M$ is the catalytic efficiency under more physiologically realistic conditions when $[S] \ll K_M$ so that $[E_{total}]$ is approximately equal to free enzyme concentration $[E]$ and the Michaelis-Menten equation for rate of product formation simplifies to

$$v = \frac{k_{cat}}{K_M} \cdot [E] \cdot [S]$$

where $k_{cat}/K_M$ is the apparent second-order rate constant. Specificity parameter that allows you to discriminate between different substrates binding to the same active site.

**Question 5. (20 Points)**

A serine protease similar to chymotrypsin uses a catalytic triad of residues H, D, and S to cleave substrates after a tyrosine residue ($R_1$ and $R_2$ below are the peptide chains adjacent to the tyrosine):

$$R_1 - Y - R_2 + H_2O \rightarrow R_1 - Y + R_2$$

a) Explain what type of catalytic mechanism the S residue is involved in. **Covalent catalysis.**

b) Explain what type of catalytic mechanism the H residue is involved in. **General base then general acid catalysis.**

c) Explain what role the D residue plays. **$D$ can form a low barrier hydrogen bond to stabilize and enhance basicity of $H$.**
d) Draw a proposed mechanism for the enzyme catalyzed peptide bond hydrolysis.  
*See attached*

**Question 6. (10 Points)**
An unknown enzyme hydrolyzes the substrate p-nitrophenylacetic acid.

![Chemical Reaction](image)

The reaction progress can be followed by monitoring the absorbance of the nitrophenolate at 400 nm, as shown in the pre-steady state experiment shown below.

![Absorbance vs Time](image)

a) Explain what the shape of this plot suggests about the complexity of the mechanism. 
*Multistep mechanism, apparent fast 1st and slow 2nd step; evidence for acyl-enz. intermediate*

b) What can pre-steady state experiments determine that steady-state generally cannot?  
*Pre-steady state experiments can determine primary rate constants in a proposed kinetic reaction mechanism. Steady-state experiments determine $k_{cat}$ and $K_M$.*

c) Draw a diagram of a stopped-flow instrument and explain how it is used.

![Stopped-Flow Instrument](image)
**Question 7. (10 Points)**

Below is the pH rate profile, \( k_{cat}/K_M \) vs. pH, for an enzyme exhibiting Michaelis-Menten kinetics.

![Graph showing \( k_{cat}/K_M \) vs. pH](image)

a) Explain what two amino acids you might expect are in the active site.

*histidine; cysteine*

b) A different enzyme has a similar pH rate profile, but an active site cysteine has been associated with the left/rising half of the curve. Explain what this suggests about how the active site environment affects the cysteine.

*perturb cysteine pKa, maybe through electrostatic interactions*

c) In the enzyme in (b), a residue far from the active site has been associated with the right/falling half of the curve. Explain what this might suggest about how this protein regulates its enzyme activity.

*Conformational change*

**Question 8. (10 Points)**

A kinetic isotope effect (KIE) can be observed as the difference in reaction rates between different isotope-labeled species, usually expressed as a ratio. A primary KIE is observed when the isotope-substituted atom is involved in a bond being formed or broken. For example, C – H bond breakage during hydride transfer from NADH. When either atom is substituted by its isotope, a KIE can result from a change in the vibrational stretching frequency.

a) Given this brief description, explain whether you expect KIE’s for hydrogen-deuterium (\( k_H/k_D \)) or hydrogen-tritium (\( k_H/k_T \)) substitution to be greater. Explain whether you expect KIE’s for hydrogen-deuterium (\( k_H/k_D \)) or carbon-12–carbon (\( k_{12C}/k_{13C} \)) substitution to be greater.

\( k_H/k_T > k_H/k_D \); \( k_H/k_D > k_{12C}/k_{13C} \)

b) A maximum KIE value for \( k_H/k_D \) of \( \sim 6.9 \) at 25°C can be approximated by considering the difference in zero point energies (ZPE) of the C – H and C – D bonds. For elements in the first and second periods, ZPEs are the primary contribution to the isotope effect. In the figure below (Fig. 2-9A from Frey and Hegeman, 2007), the transition state is symmetrical, and there is negligible difference between the C – H and C – D transition state energies.
In the ground state, $ZPE = \frac{hv}{2}$. From IR spectroscopy, the C–H stretch is at $\tilde{v} \sim 2900 \text{ cm}^{-1}$ and the C–D stretch is at $\tilde{v} \sim 2100 \text{ cm}^{-1}$. Derive the max value for $k_H/k_D$. (Planck’s constant $h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s}$; gas constant $R = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; Avogadro’s constant $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$; $c = 3 \times 10^8 \text{ m} \cdot \text{s}^{-1}$)

$ZPE = \frac{hv}{2}$ and $\tilde{v} = v/c$ so $ZPE = hc \tilde{v}/2$

$ZPE_H = (6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3 \times 10^8 \text{ m/s})(2900 \text{ cm}^{-1})(100 \text{ cm/m})(6.022 \times 10^{23} \text{ mol}^{-1}) = 17357 \text{ J/mol}$

$ZPE_D = (6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3 \times 10^8 \text{ m/s})(2100 \text{ cm}^{-1})(100 \text{ cm/m})(6.022 \times 10^{23} \text{ mol}^{-1}) = 12569 \text{ J/mol}$

$E_a^H = E^f - ZPE_H$

$E_a^D = E^f - ZPE_D$

$k_H/k_D = \exp(-E_a^H/RT)/\exp(-E_a^D/RT) = \exp[(E_a^H + E_a^D)/RT] = \exp[(ZPE_H - ZPE_D)/RT]$

$= \exp[(17357 \text{ J/mol} - 12569 \text{ J/mol})/(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \cdot 298\text{K})]$

$= \exp[7]$  

c) As discussed above, semiclassical transition state theory predicts a maximum KIE value of \sim 6.9 for $k_H/k_D$. However, there are examples of enzymes, such as methane monooxygenase, in which KIE values of \sim 100 have been measured. What quantum mechanical phenomenon could a KIE\gg 7 suggest about a catalytic mechanism?

Tunneling
Figure 14.21 A detailed mechanism for the chymotrypsin reaction. Note the low-barrier hydrogen bond (LBHB) in (c) and (g).
Section 1: Electronic Configurations (13 points)

1. Give the ground state electronic configurations beyond the Noble Gas core and the number of electrons for:
   a. Cu $[Ar] 3d^{10} 4s^2$ b. Gd$^{2+}$ $[Xe] 6s^2 5d^{10} 4f^{14} 2 - 4f^{14} 5d^1$ c. Po $[Xe] 4f^{14} 5d^{10} 6s^2 6p^4$ d. Th$^{2+}$ $[Xe] 6d^2$

2. Give the ground state term symbols for each of the following free ion electronic configurations:
   a. Ni$^{2+}$ $5D$ b. Cr $3S$ c. $f^6p^2$ $9G$

Section 2: Quantum Numbers (10 points)

1. For a “6d” orbital, give the number of radial and planar nodes. $\text{Radial} = 3 \text{ planar} = 2 + 2$

2. How many electrons are in a filled “6h” subshell? $22 + 2$

3. Assuming a regular filling order, what orbital will accept the “next” electron after the “5g” subshell is filled in building up the electronic structure of an atom? 6f

4. What are two elements in their +3 oxidation states that possess five unpaired electrons having n = 4 and l = 3? Sm, Dy $+4$

Section 3: Bonding (25 points)

1. Draw the bonding interaction between a transition metal d-orbital and the appropriate orbitals on NO$^-$, showing both the $\sigma$ and $\pi$ interactions. $+4$

2. Upon reduction of the metal to a lower oxidation state, what will happen to the NO$^-$ bond length? What trend would you expect to observe by infrared spectroscopy? $\text{Length will increase}. \quad \text{IR frequency will decrease}$

3. Draw the structure of XeF$_5^-$, clearly showing the geometry and the positions of any lone pairs. Also, indicate the point group symmetry. $+4$

4. Draw the structures showing the mechanism for F exchange in HPF$_4$ by a Berry pseudorotation mechanism. $\leftarrow \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F}$
5. Consider the following point groups: $D_2d$, $T_d$, $C_{3v}$, $C_5$. List the point groups in which the molecules can’t be polar.

6. For a square planar metal complex ML$_4$, sketch the sigma antibonding molecular orbital for d$_{x^2-y^2}$.

Section 4: Nomenclature (8 points)

1. Name or provide the formula of, as appropriate, for each of the following:
   a. potassium dioxopentafluorouranate (VI)  $K_2[UF_5O_2]$  
   b. cyclopentadienidotetracarboxylniobium(I) $[Nb(C_5H_5)(CO)_4]$  
   c. [Cr(NH$_3$)$_3$(OH$_2$)$_2$(CH)] (NO$_3$)$_2$ - hydroxodiethylenecarboxylchromium(III) nitrate  
   d. K$_2$[Co(NCS)$_4$] - potassium tetraisothiocyanato cobaltate (II)  

Section 5: Coordination Chemistry (23 points)

1. Given [CoF$_6$]$^{3-}$, $\Delta_0 = 13,000$ cm$^{-1}$, $E_p = 21,000$ cm$^{-1}$ ($E_p$ = pairing energy)
   a. Is it high or low spin?  high spin  +2  
   b. How many unpaired electrons does it have? Show your work.  unpaired  +4  
   c. What is the crystal field stabilization energy?  -5200 cm$^{-1}$  +4  
   d. Predict the spin only magnetic moment.  9.90 $\mu$B  +3  

2. How many unpaired electrons are in K$_2$[Fe(CN)$_4$]? Show your work.  4  

3. Which of the following would be expected to undergo a LARGE Jahn-Teller distortion:  $t^6_2$, $t^6_2$, $t^6_2 e^3_2 t^6_2 e^3_2$  Explain your answer.  

Section 6: Solid State Chemistry (20 points)

1. Calculate the lattice energy of AlCl$_3$ (per mole) using the following data:

   $\Delta H_{\text{sub}}$ of [Al (g)] = +291 kJ / mol  
   $\Delta H_{\text{diss}}$ of [Cl$_2$ (g)] = +243 kJ / mol  
   IE$_1$ (Al) = +578 kJ / mol  
   IE$_2$ (Al) = +1817 kJ / mol  
   IE$_3$ (Al) = +2745 kJ / mol  
   $\Delta H_{\text{EA}}$ (Cl) = -349 kJ / mol  
   $\Delta H_{r}$ of [AlCl$_3$ (s)] = -704 kJ / mol  

   (IE = ionization energy, EA = electron affinity, sub = sublimation, diss = dissociation)

2. The structure of $\alpha$-tin (Atomic Weight = 118.71) is shown to the right. If the length of an edge of the unit cell is 650 pm (1 pm = 10$^{-12}$ m), calculate the density of the metal.

   \[ 5.74 \text{ g/cm}^3 \]
P-Chem Cume, August 2014
Announced topic: Diatomic Molecules

Solutions

This course is focused on the bonding, spectroscopy, quantum mechanics, statistical mechanics, and thermodynamics of the prototypical homonuclear diatomic molecule \( \text{H}_2^+ \).

Potentially helpful equations.

\[ E = mc^2, \text{ 1 gross} = 144 \text{ units}, \text{ 1 acre} = 0.4047 \text{ hectare}. \]

\[ q = \frac{N_1}{N} q_{\text{outer}} q_{\text{inner}} q_{\text{val}} \]

\[ E_{\text{rot}} = N k_B T \left( \frac{\partial \ln q_{\text{rot}}}{\partial T} \right); C_V \left( \frac{\partial E}{\partial T} \right) \]

RigidRotor: \( \hat{H} \psi = E \psi = -\frac{\hbar^2}{2I} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial \psi}{\partial \theta}) \right] + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \)

(10)

1. In atomic units, the Hamiltonian describing \( \text{H}_2^+ \) is given by the following equation:

\[ \hat{H} = \frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \]

\[ \langle \psi | \hat{H} | \psi \rangle = \int \left( \phi_{1sA}^* \pm \phi_{1sB}^* \right) \left( -\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) \left( \phi_{1sA} \pm \phi_{1sB} \right) \, d^3 r \]

Perturbation theory suggests that the molecular orbitals for \( \text{H}_2^+ \) can be generated from a basis set consisting of linear combinations of atomic orbitals \[ \psi_c = N \left( \phi_{1sA} + \phi_{1sB} \right) \]

describing the sum of the two hydrogenic 1s orbitals, in which \( N \) is a normalization constant.

a. Explain either qualitatively or mathematically the meaning and role of the exchange, correlation, and overlap integrals that collectively combine to generate the potential energy surface for \( \text{H}_2^+ \).

\[ \text{Exchange: } T = \int \Psi_{1sA}^* \frac{1}{r_B} \Psi_{1sA} \, d^3 r \]

\[ \text{Overlap: } S = \int \Psi_{1sA}^* \Psi_{1sB} \, d^3 r \]

b. What are the driving interactions that result in bond formation?

Mathematically, the exchange integral provides the stabilizing interaction. Qualitatively, the \( e^- \) in \( \text{H}_2^+ \) can "spread" over a larger box by delocalizing over two protons instead of one.
2. a. Sketch an approximate potential energy surface for $\psi_+ = N(\phi_{1s} + \phi_{2s})$ and $\psi_- = N(\phi_{1s} - \phi_{2s})$ as a function of interatomic separation, labeling the sum and difference.

\[ \psi_+ \quad \psi_- \]

b. Include an order-of-magnitude estimate for the equilibrium bond length.

\[ 2 \text{Å} \quad (\text{actual value} = 1.34 \text{ Å}) \]

c. Sketch isosurfaces (i.e., contours of constant probability density) for the electronic molecular orbitals of H$_2^+$ produced from both the sum and difference of the two 1s orbitals at the equilibrium bond length (hint: $\phi_{1s} = N_r e^{-\frac{r}{a_0}}$).
3. a. Based on the sketches of the molecular orbitals corresponding to the sum and difference states, is the ground to electronic state electric dipole allowed or forbidden?

Allowed and polarized along the bond axis. The superposition of \( \Phi_+ + \Phi_- \) shifts density to the left of the ring over to the right as the phase between \( \Phi_+ \) and \( \Phi_- \) changes.

b. If it is allowed, in which direction is it polarized and why? If not, why not? Note – the explanation relating the sketches of the molecular orbitals to the electronic transition moment is worth more than the correct result.

polarized along the bond axis

4. Explain how you would recover the vibrational constant based on the calculated potential energy surface.

Second derivative of \( \Phi_+ \) evaluated about the minimum.

\[ F = -kx \quad \text{and} \quad k = \frac{d^2V}{dR^2} \quad \text{and} \quad \omega = \sqrt{\frac{k}{m}} \]

5. Explain how you would recover the rotational constant based on the calculated potential energy surface.

Moment of inertia, based on mass of \( \text{H}_2^+ \) bond length

\[ E_j = B J(J+1) \]

\[ B = \frac{k^2}{2I} = \frac{k^2}{2mR_0^2} \]
6. The solutions to the Schrödinger Equation for a rigid rotor are the spherical harmonics, which also describe the angular part of the electron motion in the H-atom.
   a. Prove that the following spherical harmonic wavefunction is also an eigenfunction of the angular moment operator; \( \hat{L}_z = -ih \frac{\partial}{\partial \phi} \).
   \[
   \psi(\theta, \phi) = N \sin \theta e^{i\phi}
   \]
   \[
   \hat{L}_z \psi = -i \hbar \frac{\partial}{\partial \phi} \left( N \sin \theta e^{i\phi} \right)
   \]
   \[
   = -i \hbar N \sin \theta e^{i\phi} \frac{\partial}{\partial \phi} e^{-i\phi}
   \]
   \[
   = -i \hbar N \sin \theta e^{-i\phi} = -\hbar \hat{L}_z \psi
   \]
   b. What are the corresponding eigenvalues?
   The eigenvalue is \(-\hbar\).

   c. Based on the eigenvalues, is the wave traveling clockwise or counterclockwise about the z-axis of \( H_2^+ \)?
   Angular momentum about \( \hat{z} \) has a negative eigenvalue. If right-handed motion corresponds to counterclockwise, the wave function is rotating clockwise.

   d. What are the H-nuclei doing during this process?
   The proton positions are really only described in terms of probability. The wave function describing proton positions are delocalized, mirroring the hydrogenic s, p, d, etc. orbitals.

7. The following wavefunction is also a solution to the Schrödinger equation describing the rotational motion of \( H_2 \).
   a. Prove that it is not an eigenfunction of the angular moment operator.
   \[
   \psi(\theta, \phi) = N \sin \theta (e^{i\phi} + e^{-i\phi}) = 2N \sin \theta \cos \phi
   \]
   \[
   \hat{L}_z \psi = -i \hbar \frac{\partial}{\partial \phi} N \sin \theta (e^{i\phi} + e^{-i\phi}) = -i \hbar N \sin \theta \frac{\partial}{\partial \phi} (e^{i\phi} + e^{-i\phi})
   \]
   \[
   = \hbar N \sin \theta e^{i\phi} - \hbar N \sin \theta e^{-i\phi} \neq \hbar \hat{L}_z \psi
   \]
   b. Sketch the orbital corresponding to the wavefunction above.
8. Explain how a wave can have rotational energy and be a solution to the Schrödinger equation, but not possess angular momentum.

Classically there is no way! A particle has to be rotating either clockwise or counterclockwise to possess rotational energy. However, for a wave half the amplitude can rotate clockwise and half counterclockwise to form a standing wave with rotational energy \( \mathcal{E} \) but \( \langle l_z \rangle = 0 \).

9. The energy of a rigid rotor as a function of the rotational quantum number \( J \) is given by the following equation, where \( I \) is the moment of inertia.

\[
\varepsilon_J = \frac{\hbar^2}{2I} J(J+1)
\]

In addition, the degeneracy of each \( s, p, d, \) etc. quantum state is given by the following equation.

\[
g_J = (2J + 1)
\]

From statistical mechanics, the rotational partition function for rotation in one dimension is given by the following expression.

\[
g_{rot} = \sum_J g_J e^{\frac{-\varepsilon_J}{k_B T}}
\]

a. Use these collective relationships to prove that the internal energy from the total rotational degrees of freedom based on statistical mechanics is equal to \( 2Nk_B T \) at room temperature.

\[
\begin{align*}
\text{For one degree of freedom:} \\
E_{rot} &= Nk_B T \left( \frac{d u_{rot}}{d J} \right) \\
\frac{d u_{rot}}{d J} &= \int_0^\infty (2J+1) e^{-\frac{\varepsilon_J}{k_B T}} dJ \\
&= \frac{\hbar^2}{2I k_B T} J(J+1) \\
u &= J(J+1), \quad dJ = du \\
g_{rot} &= \int_0^\infty e^{-\frac{x^2}{2\sigma^2}} dx = \sqrt{2\pi \sigma^2}
\end{align*}
\]

b. What is the corresponding value for the rotational contribution to the heat capacity at constant volume?

\[E_{rot} = 2Nk_B T\]

(Hint #1: The rotational constant for \( \text{H}_2^+ \) is 29 cm\(^{-1}\) compared to \( k_B T = 208 \text{ cm}^{-1} \) at room temperature.

Hint #2: consider the substitution \( u = \sqrt{J(J+1)} \) when evaluating the integral.)

\[
C_V = \left( \frac{\partial E_{rot}}{\partial T} \right)_V = \left[ \frac{\partial}{\partial T} \left( 2Nk_B T \right) \right]_V = 2Nk_B
\]