1. (30 minutes) Describe evidence to support FIVE (5 ONLY) of the following eight assertions. The more specific your evidence and explanation, the better.
   a) b-form DNA is a double helix with major and minor grooves.
   b) An organic compound can be chiral without possessing a stereogenic carbon.
   c) An enzyme can distinguish between enantiomeric hydrogens.
   d) NH₃ is pyramidal in its minimum-energy structure.
   e) Some cycloalkane rings with more than 5 carbon atoms are strained.
   f) The mathematical expressions used for van der Waals repulsion in molecular mechanics calculations are inadequate.
   g) Ladenburg’s prism structure is no better than Kekulé’s ring structure for discussing isomerism in disubstituted benzenes.
   h) Covalent bonds result from sharing electrons.
2. (7 min) If Legos had been available in the 1860s, someone would almost certainly have used them as molecular models.

   a) **Draw** a Crum-Brown style “Kekulé” structure (lines for bonds) of the molecule whose Lego model is shown on the right, and **name the functional group** it contains.

   b) **Name** the individual who might have used these models, **and explain the experimental basis** on which one might choose between his molecular structures and those of Crum-Brown using evidence that would have been available to 19th Century chemists.
3. The figure on the right shows pentane in a conformation that would result from replacing a \( \text{CH}_2 \) group in an **idealized** cyclohexane structure by two hydrogen atoms.

   a) (5 min) The two methyl groups might also be regarded as the axial methyls of a chair 1,3-dimethylcyclohexane in which two other hydrogen atoms of the structure shown are replaced by a chain of 3 \( \text{CH}_2 \) groups. **Or the figure draw additional bonds to** show the proper position and orientation of these 9 new carbon and hydrogen atoms and **complete the chair structure of 1,3-dimethylcyclohexane with the existing methyl groups in axial positions.**

   b) (5 min) For the pentane structure shown in the figure, Chem3D calculates a total strain energy of 242.5 kcal/mole. Chem 3D breaks this total strain energy down into 6 classes, one of which is bond stretching. Three of these values are near zero, one is 4.5 kcal/mole and one is 237.3 kcal/mole. Complete the first two lines of the table below with names of the strain energy classes and the corresponding energy values for the idealized structure above.

   c) (6 min) Chem3D finds the local energy minimum nearest in structure to the figure above whose total strain energy is only 6.0 kcal/mole. After this adjustment in structure **two** components of the strain energy are positive, but less than 0.3 kcal/mole, one is actually favorable (-0.7), the others are **1.3, 1.9, and 3.1 kcal/mole**. Make an educated guess as to which of these strain energy component is which, and **enter the 6 values in the appropriate column of third row of the table above.** [To be eligible for partial credit give a brief explanation of your energy assignments.]

<table>
<thead>
<tr>
<th>Type of energy</th>
<th>Bond Stretching</th>
</tr>
</thead>
<tbody>
<tr>
<td>idealized pentane</td>
<td>0 (kcal/mole)</td>
</tr>
<tr>
<td>minimized pentane</td>
<td></td>
</tr>
</tbody>
</table>

[To be eligible for partial credit give a brief explanation of your energy assignments.]
4. (12 min) Describe three completely different approaches for isolating a single enantiomer from a racemic sample. (The more specific your answer, the better. Real examples are best.)

5. (6 min) In what way are the electron density functions for one-electron atoms and the Boltzmann factor for equilibrium distribution of energy mathematically analogous? [write mathematical functions]

How is the role of nuclear charge in the density function case analogous to temperature in the equilibrium case?
6. The photo on the right shows chemists at the German University of Göttingen in 1863. The arrow points to Professor Friedrich Wöhler.

a) (7 min) Name one of the two important development in organic chemical theory about 30 years earlier that was due, at least in part, to Wöhler. Mention the implications of this contribution and the experiment on which it was based.

b) (7 min) On the right is a detail from the photo above showing the apparatus displayed on the lecture bench. Presumably what looks like a rank of organ pipes (arrow) is a set of Bunsen burners. Explain what this apparatus is used for in general, and specifically what the three white devices in the white box on the right are and what they do.
7. (6 min) Interpret one of the following two statements (CHOOSE ONE ONLY):
   “It is the change from an ordered arrangement to a disordered arrangement which is the source of the irreversibility.”
   or  “Entropy becomes increasingly important as temperature increases.”

8. (8 min) This plot shows the amount of energy radiated at different wavelengths by a surface heated to 1650 K. What feature of this curve was most difficult to understand, and how was it finally explained?

   IRRELEVANT FOR 2004

9. (5 min) Under what conditions should the lowest energy orbital of an isolated hydrogen atom be a hybrid orbital, rather than a 1s orbital. Explain.
10. (4 min) Explain the curious shape of this histogram showing the frequency of occurrence of different bond lengths between nitrogen atoms and aromatic carbon atoms.

![Histogram of N-C bond lengths](image)

11. (7 min) What is the magnitude of the average C-H bond energy in CH₄? __________ kcal/mole

How much do the four successive bond dissociation energies of bonds in CH₄ differ from this ABE? (circle correct value)

±0.5%   ±5%   ±15%   ±50%   by a factor of two

Identify five actual experiments which, taken together, allow one to determine the average C-H bond energy in CH₄.
12. Methylene (CH₂) appeared in a Disney comic book about 50 years ago. Donald Duck, who had just been struck on the head, had the idea of mixing CH₂ with NH₄⁺. The absence of the positive charge on nitrogen must be a typo.

a) (2 min) Why should NH₄ normally have a positive charge?

b) (5 min) If an extra electron were added to NH₄⁺ to give a neutral molecule, what orbital might it go into and what influence would presence of this additional electron have on the structure of the molecule? [For purposes of this question you may consider MOs to be composed of two or fewer AOs.]

c) (7 min) The name “methylene” for the radical CH₂ had been coined a little more than a century before the Donald Duck reference by a famous French chemist. The name came from Greek meaning “daughter of the spirit of wood.” Name the French chemist, explain the meaning of “daughter of the spirit of wood,” and write two or three sentences explaining what experiments ultimately led this chemist to abandon the radical theory of organic chemistry.
d) (7 min) Assume that CH$_2$ should have the structure expected for the CH$_3^+$ cation with one proton missing. **Discuss** the **factors** determining the **hybridization** of the carbon atom in :CH$_2$ and the nature of its **HOMO** and **LUMO**. **Draw** these orbitals.

I am not certain what the results of Donald Duck’s experiment was, but I can imagine two ways that :CH$_2$ might react with NH$_4^+$ to give the same ultimate product.

e) (7 min) One would be a **two-step** reaction in which the first step gives two small molecules which subsequently react with one another to give a single molecule. Propose such a two-step process and **explain both steps** in terms of HOMO/LUMO interactions.
f) (7 min) The other possibility for the Donald Duck reaction would be a **one-step process** in which two orbitals of \( \text{CH}_2 \) react simultaneously with two orbitals of \( \text{NH}_4^+ \) to generate the ultimate product directly. To explain this process, **draw two identical pictures of \( \text{CH}_2 \) adjacent to \( \text{NH}_4^+ \)** appropriately arranged for this one-step reaction to occur. On one of these pictures show the **HOMO of \( \text{CH}_2 \) interacting with the LUMO of \( \text{NH}_4^+ \)**. On the other show the **LUMO of \( \text{CH}_2 \) interacting with the HOMO of \( \text{NH}_4^+ \)**.