

Chemistry 125 Third Examination  
November 12, 1999

Name \_\_\_\_\_

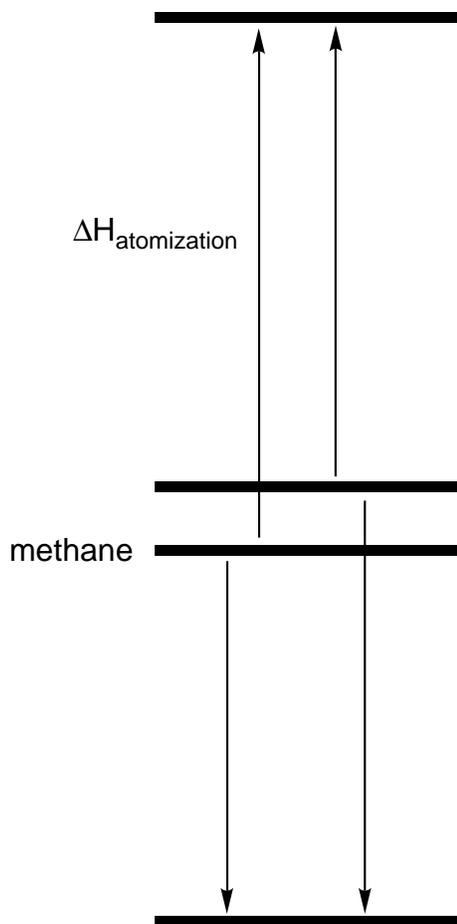
1. (2 minutes) Draw a constitutional formula for "3-isopropyl-5,5-dimethyloctane" and give its systematic (IUPAC) name.

2. (2 min) Give numerical values (kcal/mole) for the following quantities:

average bond energy (ABE) of C-H \_\_\_\_\_ ABE of C-C \_\_\_\_\_

energy difference between *gauche* and *anti* butane \_\_\_\_\_ ABE of O-O \_\_\_\_\_

3. (3 min) To estimate the heat of atomization of methane one must measure a number of experimental quantities indicated by arrows in the following diagram (not to scale). Label the unlabelled **substances** (horizontal lines) and the unlabelled **arrows**. Indicate which value was determined by Professor **Chupka**, who described his experiment in class.



4. (11 min) The table below shows minimum strain energies calculated by *Chem3D* for four substances: cyclohexane, cyclopentane, cyclobutane, and twist-boat (flexible) cyclohexane. (The columns are not in the same order as these names)

	A	B	C	D
Stretch	0.8	0.3	0.4	0.3
Bend	<b><u>16.4</u></b>	<b><u>2.3</u></b>	<b><u>0.7</u></b>	<b><u>0.4</u></b>
Stretch-Bend	-1.0	-0.1	0.1	0.1
Torsion	<b><u>10.8</u></b>	<b><u>6.2</u></b>	<b><u>5.6</u></b>	<b><u>2.2</u></b>
Non-1,4 VDW	-0.2	-0.5	-0.9	-1.1
1,4 VDW	2.4	3.2	5.9	4.7
TOTAL	29.2	11.4	11.9	6.6

a) Two of the rows in the table, Stretch-Bend and Non-1,4 VDW show some negative values. Explain **what each** of these rows represents **and** for **one** of the rows say **how** values can be negative.

b) Identify A,B,C, and D with specific compounds and comment on the underlined values.

A \_\_\_\_\_

B \_\_\_\_\_

C \_\_\_\_\_

D \_\_\_\_\_

5. (3 min) Use the energies you chose for the two conformations of cyclohexane in Question 4b to estimate their equilibrium ratio at room temperature.
6. (5 min) In order to use experiments to show that the positions in benzene are equivalent and then to identify which isomer was which among disubstituted hexagonal benzenes Koerner had to make two fundamental assumptions.
- a) What were Koerner's **two assumptions**?
- b) Draw a **diagram** that summarizes the logic of Koerner's demonstration of which isomer of disubstituted benzene is which. No words are necessary
7. (4 min) Explain briefly:
- a) The trouble Lavoisier encountered in applying his theory to the "acid of sea salt" (*muriatic acid*).
- b) The trouble Carl Wilhelm Scheele (1742-1786) encountered from his methods of purifying and characterizing organic acids.

**8. (8 min) Baeyer's Strain Theory**

- a) **What year** did Baeyer propose his strain theory, and what experimental **evidence** suggested it?
- b) What experimental **evidence** did Baeyer use to dismiss Sachse's criticism of his cyclohexane structure?
- c) What experimental **evidence** ultimately vindicated Sachse and how many **years** after his proposal did it come?
9. (5 min) Explain how Kekulé's formulae for the isomers of **propanol** and Paternó's for the isomers of **dibromoethane** suffered from analogous **experimental** difficulties.

- 10.** (7 min) The dominant theories of organic chemistry in the decade before 1850 have been called "dualistic" and "unitary". Explain the meaning of these names and how our use of the terms "Methyl Chloride" and "Chloromethane" for  $\text{CH}_3\text{Cl}$  reflects the difference between the theories.