3-1 This exercise is worked out on page 98 as "Working with Concepts".

3-2 There are two ways to approach this exercise. We can use Table 3-2 on page 99 to look up the value of the C—C bonds in ethane and in 2,2-dimethylpropane: 90 for the former and 87 kcal/mole for the later. The weaker bond will break faster and thus that in 2,2-dimethylpropane will be "first". (By the way, you should not use this terminology---both bonds will be breaking at the same time. However, the weaker bond will be breaking at a greater rate.)

Another way to approach this exercise is qualitative rather than quantitative. We know that the more stable the radicals are upon homolytic cleavage of a bond, the weaker is the bond. Breaking the C—C bond in ethane produces to methyl radicals whereas breaking a C—C bond in 2,2-dimethylpropane produces one methyl radical and one tertiary butyl radical. Both reactions have a methyl radical as a common product but one produces another methyl radical whereas the other produces a tertiary butyl radical. As the latter is more stable, then the bond in 2,2-dimethylpropane is weaker and will break at a greater rate.

Both methods are useful approaches to solving the exercise. The first provides a quantitative difference but requires that the information in Table 3.2 be available. The second method you can carry in your head by knowing only that the more substituted is more stable but gives only a qualitative difference.

3-3 This exercise is worked out on page 109 as "Working with Concepts".

3-4 In the first propagation step, a chlorine atom (generated in the initiation step) abstracts a hydrogen atom from carbon, forming HCl and a carbon radical:

$$CH_2Cl_2 + {}^{\bullet}Cl \longrightarrow {}^{\bullet}CHCl_2 + HCl$$

In the second, step, the carbon radical generated in the first propagation step reacts with molecular chlorine, forming the chlorinated product (in this case, trichloromethane) and a chlorine atom:

$${}^{\bullet}CHCl_2 + Cl_2 \longrightarrow CHCl_3 + {}^{\bullet}Cl$$

3-5 By referring to Table 3-5 on page 111, we find that the abstraction of hydrogen from methane by a chlorine atom is endothermic by 2 kcal/mole whereas the same reaction with a bromine atom is endothermic by 18 kcal/mole. For similar reactions, that which is more endothermic will have the higher activation energy and therefore be slower. The difference here of 16 kcal/mole is very large. Note that this is a "thought experiment" question as there is no way to actually determine that only chlorine atoms are abstracting hydrogen atoms. The first of the two propagation steps does not determine the carbon containing product---that happens in the second step. In the competition between bromine and chlorine atoms for hydrogen abstraction, the halogen acid produced would reveal which halogen was at work but IF a bromine atom did abstract a hydrogen atom to form HBr, this acid would react with chlorine atoms to form HCl because the bond in the latter is stronger (check Table 3-1 on page 98.)

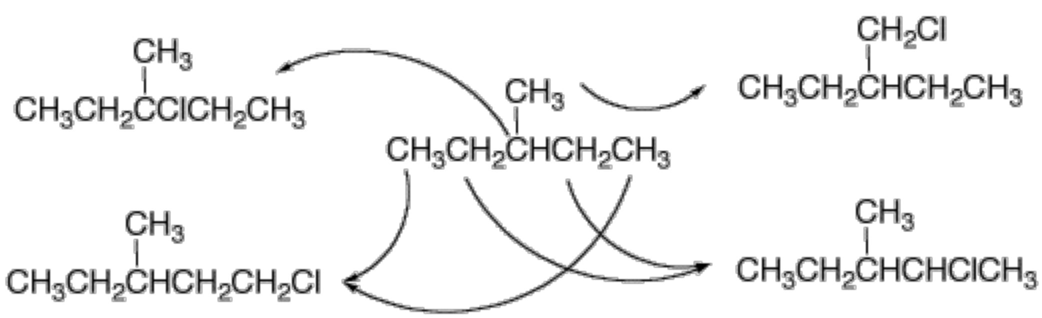
3-6 An important part of this question is asking you to identify how many *different* types of hydrogen atoms are present in butane. There are two different types, the six present on the two methyl groups and the four on the two methylene groups. Thus, there are two products. Removal of one of the six methyl group hydrogen atoms will produce 1-chlorobutane whereas removal of one on the four methylene hydrogen atoms with yield 2-chlorobutane.

The ratio of these to products is determine by a combination of the number of hydrogens that produce each (6 versus 4) and the relative rate of abstraction of each kind. We learned from the worked example with propane at the bottom of page 113 and the top of 114 that abstraction of hydrogen from a methylene group is four times faster that from a methyl group. Thus:

$$\frac{\text{1- chlorobutane}}{\text{2-chlorobutane}} = \frac{6 \text{ x } 1}{4 \text{ x } 4} = \frac{6}{16} = \frac{3}{8} \quad \text{or} \quad 27{:}73$$

3-7 This exercise is worked out on page 115 as "Working with Concepts".

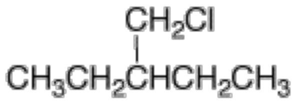
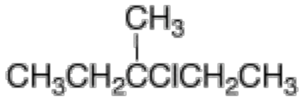
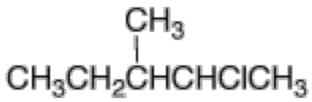
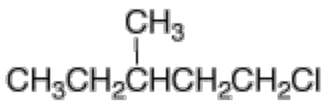
3-8 As in exercises 3-7 and 3-8, we start by identify how many different types of hydrogen atoms are present and how many of each there are. For 3-methylpentane, there are two different types of methyl groups (you can see this by what they are attached to---two methyl groups are attached to methylene groups and one is attached to a methine group). In addition, there are two identical methylene groups and on methine group. Each of these different types of hydrogens produces a different chlorination product.



We can find the relative reactivities at the top of page 116:

methyl	1
methylene	4
methine	5

and then for the relative ratios, we multiply the number of hydrogens that can produce each product times the realtive rate:

	# of H's	Rel reactivity	Rel ratio
	3	1	3
	1	5	5
	4	4	16
	6	1	6

By now you should have noticed (and your instructor should have emphasized) that the two components of the ratio of products, the relative number of hydrogens and the relative reactivity are always working against each other in these simple hydrocarbon examples. And, indeed, it is most often the case that there are more methyl hydrogen atoms than there are methylene hydrogen atoms and methine hydrogen atoms are the least prevalent.

3-9 The key to solving this problem is to not get hung up on the term "reasonable" before you even begin. Of the four compounds given, two have only one kind of hydrogen and thus can form one and only one monochlorination product.

You already know the result for chlorination of propane and 43:57 does not seem reasonable. For methylcycohexane, there are five different carbons, each giving its own monochlorination product. And just considering that three of them are methylene groups and would exhibit similar reactivity, a complex mixture will certainly result.

3-10 The answer provided in the textbook is wrong because it makes the assumption that none of the bond energies change except those involved in the hypothetical rearrangement. This is clearly not the case as there are six primary (methyl) C—H bonds in butane whereas there are nine in 2-methyl propane.

Here we consider breaking all bonds present so that each isomer becomes the same number of carbon and hydrogen atoms, representing a common energy position. By comparing the total of the bond dissociation energies, we can obtain the difference in energy between the two compounds.

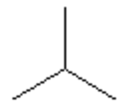
6 CH_2–H 101

4 CH—H 98.5

2 H_3C—CH_2 89

1 H_2C—CH_2 88

Total bond eneries = 1266 kcal/mole



9 CH_2–H 101

1 C—H 96.5

3 H_3C—CH 88

Total bond energies = 1269.5 kcal/mole

Thus, the difference is 3.5 kcal/mole.