2-1 Recall that $\Delta G = \Delta H - T\Delta S$. Note that one must use deg Kelvin as both the centigrade and fahrenheit scales have arbitrary zero points.

For the reaction under consideration, $\Delta H = +22.4$ kcal/mol and DS = 33.3 kcal/deg mol. Thus, at 25

0C (298 deg K):$\Delta G = 22.4$ kcal/mol - (298 deg)*(0.0333 kcal/deg mol) = 12.5 Kcal/mol

and the reaction is thus endothermic and the equilibrium lies to the left.

The key here is that 1 e.u. = 1 cal/deg mol or 0.001 kcal/deg mol.

To determine the temperature at which the reaction is favorable, we take DG to be 0.0 at

that temperature and recast the equation to solve for T:$\Delta G = 0 = \Delta H - \Delta DS\Delta H = T\Delta ST =$

$\Delta H/\Delta S = (22.4$ Kcal/mol)/(0.0333Kcal/deg mol) = 673 deg Kelvin which is 400 deg

centigrade.

2-2 Recall that $\Delta G = \Delta H - T\Delta S$. Note that one must use deg Kelvin as both the centigrade and fahrenheit scales have arbitrary zero points.

$\Delta G = -15.5$ kcal/mol - (298 degK)(-0.0313 kcal/deg K mol) = -6.17 kcal/mol. Entropy

favors disorder and more pieces. Thus, a reaction that converts two molecules into

one is entropically unfavorable.

2-3 Answered in "Working with the Concepts" on page 57 of the textbook.

2-4 To find ΔG for the reverse of a given reaction, simply change the sign. Thus

ΔG is +6.17kcal/mol. The same is true for the components of ΔG, ΔH. To find

ΔG at 500 degC (773 degK):$\Delta G = +15.5$ kcal/mol - (773 degK)(+0.0313

kcal/deg K mol)

2-5 We are looking to solve the Arrhenius equation for k:

$$k = Ae^{-E_a/RT}$$

where $A = 10$; $R = 1.986$; $T = 500$ degC $= 773$ K; and $E_a = 58.4$ kcal/mole $= 58,400$ cal/mole (in solving these problems, do not fail to convert temperatures to Kelvin and energy to cal/mol.

$k = 3.03 \times 10^{-3}$

2-8 The formula for the conjugate base of an acid is derived by removing a proton. When the acid is neutral, the derived conjugate bases will have a negative charge. If the acid has a positive charge, the base will be neutral, and if the acid bears a negative charge, the base will have two negative charges.

$HSO_3^{\ominus}$ $ClO_3^{\ominus}$ $HS^{\ominus}$ $(CH_3)_2O$ $SO_4^{\ominus\ominus}$
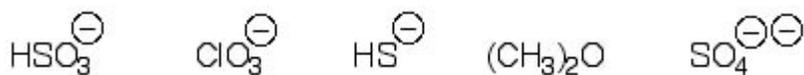
2-9 We derive the conjugate acid of a base by adding a proton. Don't forget to adjust the charge.

$(CH_3)_2NH$ $HS^{\ominus}$ $\overset{\oplus}{N}H_4$ $(CH_3)_2C=\overset{\oplus}{O}H$ CF_3CH_2OH
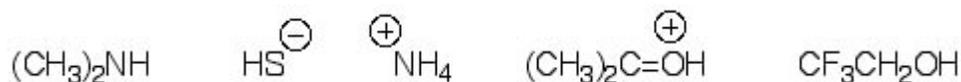
2-10 Because pK_a is the *negative* log of K_a, the lower the value of pK_a, the larger is K_a and the stronger is the acid.

2-11 This is a "classical" question posed at this point in almost all textbooks. But for many students, the answer is not at all obvious *until* they have seen it. And many fail to follow the hint and actually draw the two structures that result from placing a proton on each of the two oxygen atoms.
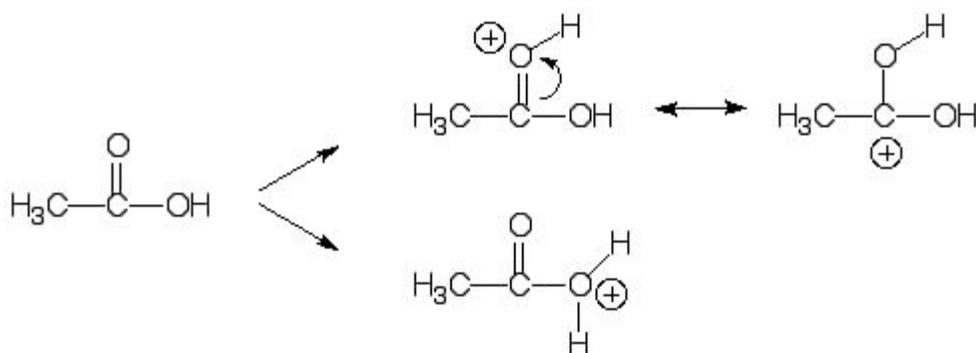
When we place the proton on the oxygen atom with two bonds to carbon, we can derive another resonance structure by moving one of the bonds to the oxygen. In essence, the pair of electrons that was shared between carbon and oxygen now belongs to oxygen. This adds an electron to the count for oxygen but decreases that for carbon. The oxygen becomes neutral and the carbon becomes positively charged.

2-12 Answered in "Working with the Concepts" on page 63 of the textbook.

**2-13** Answer in the back of the book is adequate.

2-14 We use curved arrows to show all bond making and breaking operations. Thus, we must redrawthe structure of ethyl iodide to explicity include the bond between carbon and iodine that is broken inthe second reaction.
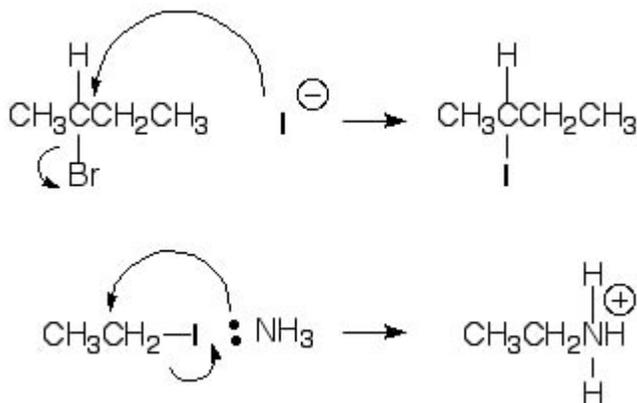
2-15 Answer in the back of the book is adequate. (The arrows represent the flow of electrons away from nitrogen to form the new C–N bond present in the products but not in the starting materials and the flow of electrons from the bond between C and I to the I. We know the flow is away from nitrogen as it starts out neutral and becomes positively charged. Likewise, we know that the flow of electrons must be to iodine as it becomes negatively charged in the products.

2-16 In drawing all of the isomers of a compound, it is best to take a systematic approach. Otherwise, you are likely to miss some and duplicates. For any hydrocarbon, there is only one way to put allof the atoms in a straight chain, so this is the easiest isomer with which

to start. Next, we remove one carbon from the chain and then add it back. If it is added to either end, then the straight chain will be recreated so we will not have a new isomer. The removed carbon must be added to one of the interior carbons of the chain. One of the reasons that an exercise such as this one is very useful is because it helps you learn to recognize which carbons in a structure are identical and which are different. Having removed one carbon from hexane, we now have pentane to which we must add a methyl group. There are three carbon atoms that are *not* at the ends---two are the same, the ones next to the ends and the other is different as it is in the middle and attached to two methylene groups. Thus, there are two unique positions on pentane where we can add the methyl group and create isomers.
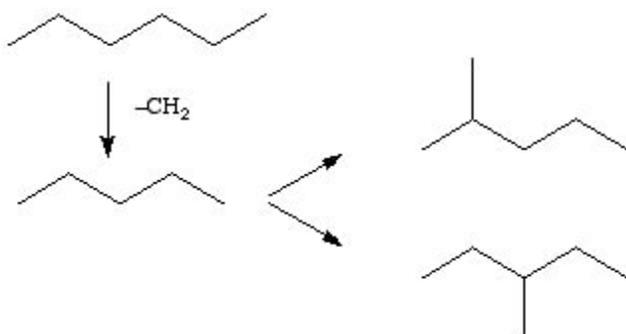

We proceed by removing two carbons from the straight chain of six and now we must add these back but we can not add either of them to the ends. There are only two carbons that are not at the ends sowe can add the two carbons back in only two ways: both on the same carbon and one on each.
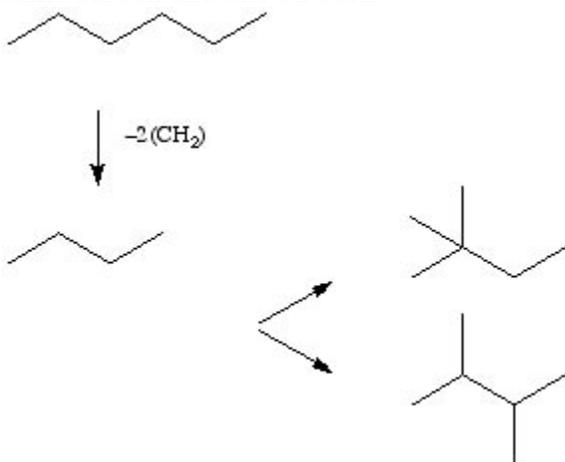
What happens if we now remove three carbons from the straight chain of six? We would have three carbons that we would need to add to the single carbon (the one not at the ends) of the remaining three. As this carbon can have a maximum of four carbons and already is attached to two, we can not create a new structure. We are done and have found all 5 of the isomers of hexane.

A higher homolog has one more carbon atom (plus the necessary two hydrogen atoms) and a lower homolog has one fewer. The lesson to be learned from this exercise is the skill to recognize unique carbon atoms in a structure.

2-17 A hydrocarbon name that starts with "iso" indicates that the compound has a straight chain of carbons except that at one end, there is a methyl group on the second carbon from the end. Thus isohexane is:

$$CH_3CHCH_2CH_2CH_3$$
with a CH_3 group attached above the second carbon.
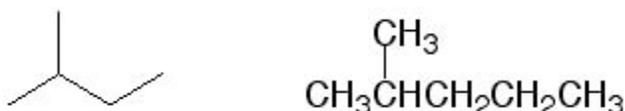
Notice that the longest chain has only five atoms adn thus IUPAC nomenclature would call this2-methylpentane.

The prefix "neo" refers to a hydrocarbon that has a straight chain of carbons except that *two* methyl groups are attached to the second carbon from one end. Thus, neopentane is:

$$CH_3CCH_2CH_3$$
with CH_3 groups attached above and below the second carbon.
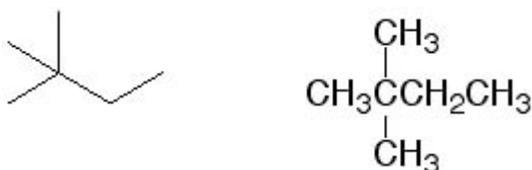
2-18 Primary carbons are attached to only one other carbon atom so we will always find a primary carbon atom at the end of a line. Secondary carbon atoms are attached to two other carbon atoms so they are at the junction of two lines. Correspondingly, tertiary carbon atoms are at the junction of three lines.

2-19 Best to do this exercise using ONLY bond-line notation

2-20 Remember that structures like that provided in the book for this exercise can be drawn in many different ways and still represent the same structure. What is important is the *connectivity* of the atoms to each other.

2-21 Do not be too concerned if your answer does not match that in the back of the textbook. There are always multiple ways to draw structures.

2-22 Answered in "Working with the Concepts" on page 85 of the textbook.

2-23 Answer in the back of the book is adequate.