CHEM 100  
Chemistry I  
Problem Set VIII  
Answers

1) We are given the equation:

\[ \text{CH}_3\text{CN(g)} + 2\text{H}_2(g) \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2(g) \]

and are asked to use bond energies to estimate the \( \Delta H \) for the reaction. Remember that we can approximate \( \Delta H_{\text{rxn}} \) by \( \Sigma(\text{bonds broken}) - \Sigma(\text{bonds made}) \). We are breaking a CN triple bond (887 kJ/mol) and 2 H-H bonds (432 kJ/mol each); we are making 2 C-H bonds (411 kJ/mol each), a C-N bond (305 kJ/mol) and 2 N-H bonds (386 kJ/mol each). Here we go:

\[ \Delta H = [887 + 2(432)] - [2(411) + 305 + 2(386)] = -148 \text{ kJ/mol}. \]

2) We have a gas, so we should use the ideal gas law. Given a mass and a volume, we can get a density:

\[ \rho = \frac{0.1500 \text{ g}}{0.01698 L} = 8.834 \text{ g/L} \]

which we can use directly in \( PM_m = \rho RT \) to yield

\[ M_m = \frac{(8.834 \text{ g/L})(0.08206 \text{ L \cdot atm / K \cdot mol})(297.15 \text{ K})}{755 \text{ mmHg / atm}} = 216.836 \text{ g/mol}. \]

We are now left with the problem of finding a sensible formula. Antimony has an atomic mass of 121.75 g/mol and fluorine has an atomic mass of 18.9984 g/mol. We are therefore left with SbF\(_5\) as the only good fit for the \( M_m \). That said, we can get the Lewis formula as:

\[ \text{Sb} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \]

(although anything that looks like this will do.)

3) What we are doing here is using the approximation that \( \Delta H_{\text{rxn}} = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds made}) \). We realize that in making acetaldehyde, we are doing the reverse of:

\[ \text{CH}_3\text{CHO} \rightarrow 2\text{C} + 4\text{H} + \text{O} \], all in the gas phase

We need the heat of formation of acetaldehyde, which we find to be: -166 kJ/mol. In making these atoms, we are using the following heats: 2(carbon atoms) + 4(hydrogen atoms) + 1(oxygen atom) which equals: \( 2(715) + 4(218) + 249.2 \text{ kJ} = 2551.2 \text{ kJ} \) to yield an overall reaction heat of: 2551.2 -(-166) = 2717.2 kJ (Remember products - reactants?!)

(All the previous data are out of Appendix C) Bonds made are: 4 C-H, 1 C-C, and 1 C=O. (These data are out of Table 9.5). Since we are after C=O, we can’t (or shouldn’t) look
that one up, but the others give rise to the following values: \(4(411) + 346 + (C=O) = 1644 + 346 + (C=O) = 1990 + (C=O) \text{ kJ}\).

Those are all our data; here we go: \(2717.2 \text{ kJ} = 1990 + (C=O)\) which leads to \(727.2 \text{ kJ} = B.E.(C=O)\). This value compares well to the one in the book.

(An alternate treatment looks at the bonds broken as: \(1/2\) O-O and 2 H-H, and yields, using the heat of formation of acetaldehyde again, a value for the BE(C=O) of 713 kJ, which compares less well with the value given in the book, but is certainly adequate. Either treatment seems fine to me.)

(A third treatment looks at the combustion reaction:
\[
\text{CH}_3\text{CHO} + \frac{5}{2} \text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}
\]
In this treatment, we use the heats of formation to get a heat of reaction, then we use bond energies to get the answer. Doing so, we find that we are breaking: 4 C-H bonds, 1 C-C bond, 2.5 O\(_2\) bonds and 1 C=O bond; we are making 4 C=O bonds (CO\(_2\) has two of them each) and 4 H-O bonds, for a net of 4 C-H bonds + 1 C-C bond broken, and 3 C=O bonds + 4 O-H bonds made. Here is that calculation:

\[
\Delta H = 2(-393.5 \text{ kJ}) + 2(-285.8 \text{ kJ}) - 0 - (-166) = -1192.6 \text{ kJ}.
\]
This heat has to equal the bonds broken minus the bonds made, or:

\[
-1192.6 \text{ kJ} = 4(411) + (346) + 2.5(494)-[3(C=O) + 4(459)] \text{ which leads to:}
\]

\[
-1192.6 = 1644 + 346 + 1235– 3(C=O) – 1836 \rightarrow -1192.6 = 1389 - 3(C=O) \text{ which leads us to: -2581.6 = -3(C=O). Doing the division gives us a bond energy for C=O equal to 860.5 kJ, which is in not great agreement with the textbook either.) [Relative errors: 8.99%; 10.76%; 7.70%]}

Looks like the heat of combustion method gives the closest relative answer. Live and learn!

4) Taking the hint given, (and the correction on the problem set assignment sheet!) we discover that: \(\text{BE(A-B)} = \frac{1}{2} [\text{BE(A-A)} + \text{BE(B-B)}] + 98.6 \text{ kJ}(X_A - X_B)^2\) Collecting all our energies and values we have: \(\text{BE(S-S)} = 226 \text{ kJ}; \text{BE(F}_2\) = 155 kJ; \(\text{BE(S-F)} = 284 \text{ kJ}; X_F = 4.0. \) Let fluorine be atom 'A', and sulfur be atom 'B'. Then we get: \(284 = \frac{1}{2} [155 + 226 ]+ 98.6(4.0-X_S)^2\). We can solve this for \(X_s = 4.0 - \sqrt{\frac{935}{98.6}} = 3.0\), which isn't the most superb agreement with the value in Figure 9.15, but is fine for an approximation.
5) We are asked to rationalize why the bond energy in CHBr$_3$ is 33 kJ/mol lower than that in CH$_4$. A good answer is that the electronegativity of bromine makes the tribromomethyl (CBr$_3$) group itself more electronegative. Since the bond energy is the enthalpy change when a bond is broken homolytically (one electron to each partner), pulling on those electrons harder via a greater electronegativity would mean less electron density of bond the hydrogen to the carbon, and therefore a weaker bond.