A First Course on Kinetics and Reaction Engineering Example 1.1

Problem Purpose

This problem illustrates how to write a balanced chemical reaction and how to use the stoichiometric coefficients in that reaction to determine the limiting reactant in a reaction given the starting composition. It also points out some important facts about stoichiometric coefficients.

Problem Statement

Write a balanced reaction equation for the oxidation of carbon monoxide by molecular oxygen. If a system initially contained equal volumes of air and carbon monoxide, which of the reactants would be limiting, assuming the gases to behave ideally?

Problem Solution

We are told that the reactants are CO and O_2 . If we assume that these are the only reactants, then we can start to write the reaction as follows, using *x* to represent the as-yet-unknown stoichiometric coefficient of molecular oxygen.

 $CO + x O_2 \rightarrow$

You should know that when these two molecules react, the only product is carbon dioxide. This can be added to the reaction equation, using y as the stoichiometric coefficient for CO₂, as follows.

 $CO + x O_2 \rightarrow y CO_2$

Now we can balance the equation. Noting that there is only one C atom on the left hand side of the equation we can see that the value of y must equal 1 so that carbon is balanced. Setting y equal to 1 means that there are two oxygen atoms on the right hand side of the equation. On the left hand side of the equation there is one oxygen atom in the CO, so the only way for the equation to balance is if x is equal to one-half. Thus, equation (1) is a balanced equation for the oxidation of carbon monoxide by molecular oxygen. Some people prefer for all of the stoichiometric coefficients to be integers. It can be seen that if each side of equation (1) is multiplied by two the resulting reaction equation (2) will have stoichiometric coefficients that are all integers.

$$\mathrm{CO} + \frac{1}{2} \mathrm{O}_2 \to \mathrm{CO}_2 \tag{1}$$

$$2 \operatorname{CO} + \operatorname{O}_2 \to 2 \operatorname{CO}_2 \tag{2}$$

Before moving on to the second part of the question, you should recognize that both equations are valid balanced reactions. In fact, equation (1) is the form of the reaction that is used in defining the standard heat of combustion of CO. Generally, it is acceptable for stoichiometric coefficients to be non-integer. Notice also that the ratio of the stoichiometric coefficients of any two reagents will be the same, no matter which way the reaction is written. That is, in both forms of the reaction, the ratio of the stoichiometric coefficient of CO_2 to that of CO is equal to negative one (equations (3)), the ratio of the

stoichiometric coefficient of CO_2 to that of O_2 is negative two (equations (4)) and the ratio of the stoichiometric coefficient of CO to that of O_2 is positive two (equations (5)).

$$\left(\frac{v_{CO_2}}{v_{CO}}\right)_{\text{eq.1}} = \frac{1}{-1} = -1 = \frac{2}{-2} = \left(\frac{v_{CO_2}}{v_{CO}}\right)_{\text{eq.2}}$$
(3)

$$\left(\frac{v_{CO_2}}{v_{O_2}}\right)_{\text{eq.1}} = \frac{1}{-\frac{1}{2}} = -2 = \frac{2}{-1} = \left(\frac{v_{CO_2}}{v_{O_2}}\right)_{\text{eq.2}}$$
(4)

$$\left(\frac{v_{CO}}{v_{O_2}}\right)_{\text{eq. 1}} = \frac{-1}{-\frac{1}{2}} = 2 = \frac{-2}{-1} = \left(\frac{v_{CO}}{v_{O_2}}\right)_{\text{eq. 2}}$$
(5)

Turning to the second part of the question, recall that if the initial moles of each reactant is divided by the absolute value of that reactant's stoichiometric coefficient, the reactant which yields the smallest result is the limiting reactant. Having written the reaction above, we know the stoichiometric coefficients, so we next need to find the initial moles of each reactant.

We are told that there are equal volumes of air and CO, and for an ideal gas, the mole fraction is equal to the volume fraction. Therefore the initial moles of CO and the initial moles of air are equal. We can choose a basis of 100 moles of CO and 100 moles of air. Since air contains ~21% O₂, that means we initially have 100 moles of CO and 21 moles of O₂. Dividing each of these amounts by the absolute value of the corresponding stoichiometric coefficient shows that the result is smaller for O₂, and therefore O₂ is the limiting reactant.

$$\frac{n_{CO}^0}{|v_{CO}|} = \frac{100}{|-1|} = \frac{100}{1} = 100 > 42 = \frac{21}{\frac{1}{2}} = \frac{21}{|-\frac{1}{2}|} = \frac{n_{O_2}^0}{|v_{O_2}|}$$
(6)

In determining that O_2 is the limiting reactant, I used the stoichiometric coefficients for reaction (1). It shouldn't matter how the reaction is written, though, as long as it is balanced. I'll leave it to you, as an exercise, to repeat the analysis using the stoichiometric coefficients from reaction (2); if you do it properly, you will again come to the conclusion that O_2 is the limiting reactant.