Reconciliation of the Limiting Reactant Approach to Stoichiometry and the Law of Mass Action Approach

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We desire to solve the following problem: given the balanced chemical reaction and the initial amounts of reactants, determine (a) which reactant limits the amount of products that can be formed, (b) how much of the other reactants are used up, and (c) how much of the product(s) are made. There are two approaches to this problem: (1) The limiting reactant approach. The principle of the limiting reactant is built upon the idea of atom conservation and the assumption that the reaction goes to completion, i.e. makes the maximum amount of product. (2) The Law of mass action approach. Here it is assumed that the final concentrations of reactants and products are constrained by the expression for the equilibrium constant. Thus it would seem that (a) the two approaches would agree only in the case where K is sufficiently large, and (b) that the mass action approach would have a greater range of validity.

To illustrate the foregoing, let us perform calculations for both approaches. We take the following problem from Zumdahl, section 6.7. For a synthesis of hydrogen fluoride from hydrogen and fluorine, 3.000 moles of H_2 and 6.000 moles of F_2 are mixed in a 3.000 liter flask. The equilibrium constant for the synthesis reaction at this temperature is 1.15×10^2.

We begin by treating this problem as a limiting reagent problem. The first step is to calculate the reactant ratios:

$$RR_{H_2} = 3\,\text{mol}/1 = 3\,\text{mol}$$

$$RR_{F_2} = 6\,\text{mol}/1 = 6\,\text{mol}$$

$$RR_{\min} = RR_{H_2} = 3\,\text{mol}$$

H_2 is the limiting reagent.

Concentration of product. Moles HF = $(RR_{min})2$ = 6 mol; [HF] = 6 mol/3.00 L = 2.00 M.

Moles of excess reactant (F_2) remaining = [6 mol – 3 mol] = 3 mol; Concentration = 3 mol/3.00 L = 1.00 M.

Amount of limiting reactant (H_2) remaining = 0 M.

Now let us compare this result with that calculated assuming that the problem is an equilibrium problem. We start from the following ICE table:

$H_2(g)$ +	$F_2(g)$ =	2 $HF_2(g)$
1.00	2.00	0
-x	-x	+2x
1.000-x	2.000-x	2x

Substituting the equilibrium concentrations into the equilibrium expression gives:

$$K = 1.15 \times 10^2 = \frac{[HF]^2}{[H_2][F_2]} = \frac{(2x)^2}{(1.000 - x)(2.000 - x)}$$

Rearranging this expression we obtain a second order polynomial:

$$(1.15 \times 10^2)x^2 - (3.45 \times 10^2)x + 2.30 \times 10^2 = 0$$

The relevant of the two roots is x = 0.968 nol/L

This leads to the equilibrium concentrations:

$[H_2]$ = 1.000 *M* - 0.968 *M* = 3.2 x 10^{-2} *M*

$[F_2]$ = 2.000 *M* – 0.968 *M* = 1.032 *M*

[HF] = 2(0.968 *M*) = 1.936 *M*

Let us make a summary table to better compare results from limiting reactant and equilibrium methods:

Molecular Specie	Results from Limiting Reagent Calculation	Results from Equilibrium Calculation
H_2	0 M	3.2 x 10-2 *M*
F_2	1.000 *M*	1.032 *M*
HF	2.000 *M*	1.936 *M*

We see that the limiting reagent result is only approximately correct. It is about 3% off for the reactants and 5% for the product. This makes sense from the standpoint of the equilibrium constant which is approximately 100. Thus the errors made by assuming that K is infinity, should be off by the reciprocal of 100 or about one percent.