Alternative Activity 3.1 Solution

Suppose a gas mixture of 3 moles of CO and 2 moles of CO_2 is held at 800 °C and 1 atm. Determine whether graphite can form according to reaction (1), and if so, calculate the equilibrium ratio of CO to CO_2. Note that at 800 °C the free energies of formation of CO and CO_2 are -182.5, and -395.6 kJ mol^{-1}, respectively, and the free energy of formation of graphite is 0 kJ mol^{-1}.

$$2\,CO \rightleftarrows CO_2 + C_g \qquad (1)$$

Solution

The equilibrium expression for reaction (1) is given in equation (2). If we assume that the gases are ideal and take the activity of graphite to equal 1.0 (since graphite is a solid and it is the standard state for carbon), equation (3) results.

$$K_{1(1073\text{ K})} = \frac{a_C a_{CO_2}}{a_{CO}^2} \qquad (2)$$

$$K_{1(1073\text{ K})} = \frac{\left(\dfrac{y_{CO_2}P}{1\text{ atm}}\right)}{\left(\dfrac{y_{CO}P}{1\text{ atm}}\right)^2} = \frac{\left(\dfrac{n_{CO_2}}{n_{gas,total}}\right)}{P\left(\dfrac{n_{CO}}{n_{gas,total}}\right)^2}\text{atm} \qquad (3)$$

The value of the equilibrium constant can be calculated using equation (4) since we are given free energies of formation at 1073 K. That is, we can calculate the change in the standard Gibbs free energy at 1073 K from the free energies of formation using equation (5) and substitute the result into equation (4).

$$K_{1(1073K)} = \exp\left\{\frac{-\Delta G^0_{1(1073K)}}{R(1073K)}\right\} \qquad (4)$$

$$\Delta G^0_{1(1073K)} = \sum_{\substack{i=\text{ all}\\ \text{species}}} \nu_{i,1}\Delta G^0_{f(1073K),i} \qquad (5)$$

The resulting value of the equilibrium constant is 30.9, and substitution into equation (3) along with the pressure of 1 atm gives equation (6).

$$30.9 = \frac{n_{gas,total}n_{CO_2}}{n_{CO}^2} \qquad (6)$$

A mole table can be used to express each of the molar quantities appearing in equation (6) in terms of the extent of reaction (1). This leads to equation (7).

Species, i	Initial Number of Moles, n_i^0	Number of Moles after Reaction, $n_i = n_i^0 + \sum_{j=1}^{N_{\text{independent reactions}}} \nu_{i,j}\xi_j$
CO	3 mol	$3\text{ mol} - 2\xi_1$
CO_2	2 mol	$2\text{ mol} + \xi_1$
C	0	ξ_1
Total Moles	5 mol	5 mol

$$30.9 = \frac{\left(5\text{ mol} - \xi_1\right)\left(2\text{ mol} + \xi_1\right)}{\left(3\text{ mol} - 2\xi_1\right)^2} \quad (7)$$

Solving equation (7) gives values of 1.81 and 1.19 mol for the extent of reaction. There can't be two different equilibrium extents of reaction, so one of these probably corresponds to a situation that is not physically possible. Indeed, using the first value to calculate the final moles of CO leads to a negative number, so the second value is the desired answer. Using that value to additionally calculate the moles of CO_2 and then taking the ratio of CO to CO_2 leads to a value of 0.197 for their ratio.

Before quitting, it is worthwhile to point out that had the initial composition been different, we might have found both of the roots to equation (7) to correspond to physically impossible solutions. What this would have meant was that reaction (1) does not occur. In effect, by writing the equilibrium expression and inserting a value of 1 for the activity of the solid, we implicitly assumed that the solid carbon would form. The calculated results would not make physical sense because this implicit assumption would be incorrect.