More on chemical equilibrium

In general the chemical potential of species A will depend on the number of molecules of all species present. However things simplify tremendously if we have a gaseous reaction and all species can be treated as ideal gases at these temperatures and pressures. For a single ideal gas we have

$$S(T, P) = S(T_0, P_0) + C_P \ln \frac{T}{T_0} - nR \ln \frac{P}{P_0}.$$

The Gibbs free energy is defined for an ideal gas as $G = E - TS + PV = E(T) - TS + nRT$. Hence for one mole at constant temperature T_0,

$$g(P, T_0) - g(P_0, T_0) = -T_0 \big(S(T_0, P) - S(T_0, P_0) \big) = RT_0 \ln \frac{P}{P_0}.$$

Recall that in a mixture, the relevant pressure is the partial pressure of the species in question.

So for a reaction in which ν_A moles of A , ν_B moles of B, etc, react to form ν_X moles of X , ν_Y moles of Y etc

$$\nu_A A + \nu_B B \rightleftharpoons \nu_X X + \nu_Y Y$$
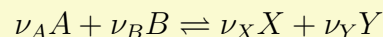
we define the Gibbs free energy of reaction as

$$g_r = \nu_X g_X + \nu_Y g_Y - \nu_A g_A - \nu_B g_B$$

and this will be zero at equilibrium. (Recall μ and g are the same for ideal gases.)

If we know this quantity g_r at some reference temperature and pressure, the same for all reactants and products, usually 25°C and 1 atm, call it g_r^0, then at other partial pressures but the same temperature it will be

$$g_r(P_X, P_A, T_0) = g_r^0 + RT_0 \left(\nu_X \ln \frac{P_X}{P_0} + \nu_Y \ln \frac{P_Y}{P_0} - \nu_A \ln \frac{P_A}{P_0} - \nu_B \ln \frac{P_B}{P_0} \right) = RT_0 \ln \left[\left(\frac{P_X}{P_0}\right)^{\nu_X} \left(\frac{P_Y}{P_0}\right)^{\nu_Y} \left(\frac{P_0}{P_A}\right)^{\nu_A} \left(\frac{P_0}{P_B}\right)^{\nu_B} \right]$$

Hence, since at equilibrium $g_r = 0$,

$$\left(\frac{P_X}{P_0}\right)^{\nu_X} \left(\frac{P_Y}{P_0}\right)^{\nu_Y} \left(\frac{P_0}{P_A}\right)^{\nu_A} \left(\frac{P_0}{P_B}\right)^{\nu_B} = \exp\left(-\frac{g_r^0}{RT_0}\right).$$

If at standard pressure and temperature $g_r^0 < 0$, the reaction will tend to increase the amount of the products (X, Y) and decrease the amount of the reactants (A, B); if on the other hand $g_r^0 > 0$ the reaction will proceed in the other direction.

The general forms of these equations for N reactants and N' products can be written

$$g_r = \sum_{i=1}^{N'} \nu_{X_i} g_{X_i} - \sum_{j=1}^{N} \nu_{A_j} g_{A_j}$$

and, at equilibrium,

$$\prod_{i=1}^{N'} \left(\frac{P_{X_i}}{P_0}\right)^{\nu_{X_i}} \prod_{1=1}^{N} \left(\frac{P_0}{P_{A_j}}\right)^{\nu_{A_j}} = \exp\left(-\frac{g_r^0}{RT_0}\right).$$

As given, g_r will depend on whether the reaction is written, e.g., $O_2 + 2H_2 \rightleftharpoons 2H_2O$ or $\frac{1}{2}O_2 + H_2 \rightleftharpoons H_2O$, being twice as large in the first case as in the second. You should be able to convince yourself that the partial pressures at equilibrium do not depend on this. For a reaction with a single product like this one, though, it is usual to talk about the standard Gibbs free energy of formation as referring to a single mole of product, i.e. the second case.