Chemical Equilibrium in Ideal Gas Mixtures

Question: What is the composition of a reacting mixture of ideal gases?

\[ \frac{1}{2}N_2(g,T,p) + \frac{3}{2}H_2(g,T,p) = NH_3(g,T,p) \]

What are \( p_{N_2}, p_{H_2}, \) and \( p_{NH_3} \) at equilibrium?

Let's look at a more general case

\[ \nu_A A(g, T, p) + \nu_B B(g, T, p) = \nu_C C(g, T, p) + \nu_D D(g, T, p) \]

The \( \nu_i \)'s are the stoichiometric coefficients.

Let's take a mixture of \( A, B, C, \) and \( D \) with partial pressures

\[ p_{A\square} X_A p, \quad p_{B\square} X_A p, \quad p_{C\square} X_C p, \] and \( p_{D\square} X_D p \)

Is this mixture in equilibrium?

We can answer by finding \( \Delta G \) if we allow the reaction to proceed further.

We know \( \mu_i(T, p) \) for an ideal gas in a mixture and we know that \( G = \sum n_i \mu_i \)

\[ \Rightarrow \Delta G = [\nu_C \mu_C(g,T,p) + \nu_D \mu_D(g,T,p)] - [\nu_A \mu_A(g,T,p) + \nu_B \mu_B(g,T,p)] \]

But \( \mu_i(g,T,p) = \mu_i^0(T) + RT \ln p_i \quad \left[ \frac{p_i}{1\text{ bar}} \text{ implied} \right] \)
where $\mu_i^c(T)$ is the chemical potential of species “i” at 1 bar and in a pure (not mixed) state.

\[
\Delta G = [v_C \mu_C^o(T) + v_D \mu_D^o(T)] - [v_A \mu_A^o(T) + v_B \mu_B^o(T)] + RT \ln \left( \frac{p_C^{v_C}}{p_A^{v_A}} \frac{p_D^{v_D}}{p_B^{v_B}} \right)
\]

\[
\Rightarrow \Delta G = \Delta G^o + RT \ln Q
\]

where

\[
\Delta G^o = [v_C \mu_C^o(T) + v_D \mu_D^o(T)] - [v_A \mu_A^o(T) + v_B \mu_B^o(T)]
\]

and

\[
Q = \frac{p_C^{v_C}}{p_A^{v_A}} \frac{p_D^{v_D}}{p_B^{v_B}}
\]

$\Delta G^o$ is the change in free energy associated with transforming pure reactants into pure products.

\[
\Delta G^o = \Delta G^o_{rxn} = \Delta H^o_{rxn} - T \Delta S^o_{rxn}
\]

or

$\Delta G^o = \Delta G^o_{form\ (products)} - \Delta G^o_{form\ (reactants)}$

If $\Delta G < 0$ then the reaction will proceed spontaneously to form more products

If $\Delta G > 0$ then the backward reaction is spontaneous

$\Delta G = 0$ No spontaneous changes $\Rightarrow$ Equilibrium

Define $Q_{eq} = K_{p}$ the equilibrium constant

\[
K_p = \left( \frac{p_C^{v_C}}{p_A^{v_A}} \right)_{eq} = p^{\Delta v} \left( \frac{X_C^{v_C}}{X_A^{v_A}} \right)_{eq} = p^{\Delta v} K_X
\]
and

\[ K_p e^{-\Delta G^0/RT} \]

Note from this that \( K_p(T) \) is not a function of total pressure \( p \).

It is \( K_X = p^{-\Delta \nu} K_p \) which is \( K_X(p,T) \).

Recall that all \( p_i \) values are divided by 1 bar, so \( K_p \) and \( K_X \) are both unitless.

Example: \( H_2(g) + CO_2(g) = H_2O(g) + CO(g) \)

\( T = 298 \text{ K} \)
\( p = 1 \text{ bar} \)

<table>
<thead>
<tr>
<th></th>
<th>( H_2(g) )</th>
<th>( CO_2(g) )</th>
<th>( H_2O(g) )</th>
<th>( CO(g) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>b</td>
<td>0</td>
<td>0</td>
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<tr>
<td>#</td>
<td>a-x</td>
<td>b-x</td>
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<td>of</td>
<td>moles</td>
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<td>moles</td>
<td>at Eq.</td>
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<td></td>
<td>Total # moles at Eq. = (a - x) + (b - x) + 2x = a + b</td>
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</tbody>
</table>

\[ \Delta G_{form}^o (\text{kJ/mol}) \]

\[ 0 \quad -394.4 \quad -228.6 \quad -137.2 \]

\[ \Delta G_{rxn}^o = 28.6 \text{ kJ/mol} \] \( \Rightarrow \) \[ \frac{27,600 \text{ kJ/mol}}{8.314 \text{ J/K-mol}} \left( \frac{298 \text{ K}}{1} \right) = e^{-11.54} = 9.7 \times 10^{-6} \]
\[ K_p = \frac{p_{H_2O}p_{CO}}{p_{H_2}p_{CO_2}} = \frac{X_{H_2O}X_{CO}}{X_{H_2}X_{CO_2}} = \frac{x^2}{(a-x)(b-x)} \]

Let’s take \( a = 1 \text{ mol} \) and \( b = 2 \text{ mol} \)
We need to solve \( \frac{x^2}{(1-x)(2-x)} = 9.7 \times 10^{-6} \)

A) Using approximation method:

\[ K \ll 1, \text{ so we expect } x \ll 1 \text{ also.} \]

Assume \( 1-x \approx 1, \ 2-x \approx 2 \Rightarrow \frac{x^2}{(1-x)(2-x)} \approx \frac{x^2}{2} = 9.7 \times 10^{-6} \]
\[ x \approx 0.0044 \text{ mol (indeed } \ll 1) \]

B) Exactly:
\[ \frac{x^2}{x^2 - 3x + 2} = K_p = 9.7 \times 10^{-6} \]
\[ x^2(1-9.7 \times 10^{-6}) + 3x(9.7 \times 10^{-6}) - 2(9.7 \times 10^{-6}) = 0 \]
\[ x = \frac{-3(9.7 \times 10^{-6}) \pm \sqrt{9(9.7 \times 10^{-6})^2 + 4(1-9.7 \times 10^{-6})2(9.7 \times 10^{-6})}}{2(9.7 \times 10^{-6})} \]

The "-" sign gives a nonphysical result (negative \( x \) value)
Take the "+" sign only \( \Rightarrow x = 0.0044 \text{ mol (same)} \)
**Effect of total pressure: example**

\[ \text{N}_2\text{O}_4(\text{g}) = 2 \text{NO}_2(\text{g}) \]

Initial mol # \( n \) \( 0 \)

\# at Eq. \( n-x \) \( 2x \) Total # moles at Eq. = \( n - x + 2x = n + x \)

\( X_i \)'s at Eq. \( \frac{n-x}{n+x} \) \( \frac{2x}{n+x} \)

\[ K_p = \frac{p_{\text{NO}_2}^2}{p_{\text{N}_2\text{O}_4}} = \frac{p^2X_{\text{NO}_2}^2}{pX_{\text{N}_2\text{O}_4}} = p \left( \frac{2x}{n+x} \right)^2 = p \frac{4x^2}{n^2-x^2} \]

\[ K_p = p \frac{4\alpha^2}{1-\alpha^2} \text{ where } \alpha = x/n \text{ is the fraction reacted} \]

\[ (1-\alpha^2)K_p = \alpha^2 \quad \alpha^2 \left( 1 + \frac{K_p}{4p} \right) = \frac{K_p}{4p} \quad \alpha^2 = \frac{K_p}{4p} \left( 1 + \frac{K_p}{4p} \right) = \frac{1}{1 + \frac{4p}{K_p}} \quad \alpha = \left( 1 + \frac{4p}{K_p} \right)^{-\frac{1}{2}} \]

\[ \therefore \text{ If } p \text{ increases, } \alpha \text{ decreases} \]

**Le Chatelier's Principle, for pressure:**

An increase in pressure shifts the equilibrium so as to decrease the total # of moles, reducing the volume.

In the example above, increasing \( p \) shifts the equilibrium toward the reactants.

**Another example:**
\[2 \text{NO}(g) + \text{O}_2(g) = 2 \text{NO}_2(g)\]

\[K_p = 2.3 \times 10^{12}\] at 298 K

Initial mol #
\[
\begin{array}{ccc}
2 & 1 & 0
\end{array}
\]

# at Eq.
\[
\begin{array}{ccc}
2-2x & 1-x & 2x
\end{array}
\]

Total # moles at Eq.
\[
= 2 - 2x + 1 - x + 2x
\]

\[= 3 - x\]

\[K_p = \frac{p_{\text{NO}_2}^2}{p_{\text{NO}}p_{\text{O}_2}} = \frac{p^2X_{\text{NO}_2}^2}{p^2X_{\text{NO}}X_{\text{O}_2}} = \frac{X_{\text{NO}_2}^2}{X_{\text{NO}}X_{\text{O}_2}} = \frac{1}{(1-x)^3}\]

\(K_p > 1\) so we expect \(x \approx 1 \Rightarrow 3 - x \approx 2\)

\[K_p = \frac{1}{p^3} \cdot \frac{2}{(1-x)^3}\quad \text{or} \quad (1-x)^3 = \frac{2}{pK_p} \quad x \approx 1 - \left(\frac{2}{pK_p}\right)^{\frac{1}{3}}\]

In this case, if \(p\uparrow\) then \(x\uparrow\) as expected from Le Chatelier's principle.