Chemical Equilibrium in Ideal Gas Mixtures

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

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

What are $p_{N_2}, p_{H_2}, \text{and } p_{NH_3}$ 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 ν_i's are the stoichiometric coefficients.

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

$$p_A = X_A p,\ \ p_B = X_A p,\ \ p_C = X_C p, \text{ and } \ p_D = X_D p$$

Is this mixture in equilibrium?

We can answer by finding ΔG 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 $G=\sum_i n_i\mu_i$

$$\Rightarrow \qquad \Delta G=\left[\nu_C\mu_C(\text{g},T,p)+\nu_D\mu_D(\text{g},T,p)\right]-\left[\nu_A\mu_A(\text{g},T,p)+\nu_B\mu_B(\text{g},T,p)\right]$$

But $\mu_i(\text{g},T,p)=\mu_i^{\text{o}}(T)+RT\ln p_i \qquad \left[\frac{p_i}{1\text{ bar}}\text{ implied}\right]$

where $\mu_i^{\mathrm{o}}(T)$ is the chemical potential of species "i" at 1 bar and in a pure (not mixed) state.

$$\therefore \qquad \Delta G = \left[\nu_C \mu_C^{\mathrm{o}}(T) + \nu_D \mu_D^{\mathrm{o}}(T)\right] - \left[\nu_A \mu_A^{\mathrm{o}}(T) + \nu_B \mu_B^{\mathrm{o}}(T)\right] + RT \ln\left(\frac{p_C^{\nu_C} p_D^{\nu_D}}{p_A^{\nu_A} p_B^{\nu_B}}\right)$$

$$\Rightarrow \qquad \Delta G = \Delta G^\circ + RT \ln Q$$

where $\Delta G^\circ = \left[\nu_C \mu_C^{\mathrm{o}}(T) + \nu_D \mu_D^{\mathrm{o}}(T)\right] - \left[\nu_A \mu_A^{\mathrm{o}}(T) + \nu_B \mu_B^{\mathrm{o}}(T)\right]$

and $Q = \dfrac{p_C^{\nu_C} p_C^{\nu_D}}{p_A^{\nu_A} p_B^{\nu_B}}$

ΔG° is the change in free energy associated with transforming pure reactants into pure products.

$$\Delta G^{\mathrm{o}} = \Delta G_{rxn}^{\mathrm{o}} = \Delta H_{rxn}^{\mathrm{o}} - T\Delta S_{rxn}^{\mathrm{o}}$$

or $\Delta G^{\mathrm{o}} = \Delta G_{\text{form}}^{\mathrm{o}}(\text{products}) - \Delta G_{\text{form}}^{\mathrm{o}}(\text{reactants})$

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

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

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

Define $Q_{eq} = K_p$ the equilibrium constant

$$K_p = \left(\frac{p_C^{\nu_C} p_C^{\nu_D}}{p_A^{\nu_A} p_B^{\nu_B}}\right)_{eq} = p^{\Delta\nu}\left(\frac{X_C^{\nu_C} X_C^{\nu_D}}{X_A^{\nu_A} X_B^{\nu_B}}\right)_{eq} = p^{\Delta\nu} K_X$$

and

$$K_p = e^{-\Delta G^o / RT}$$

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 <u>unitless</u>.

Example: $H_2(g) + CO_2(g) = H_2O(g) + CO(g)$ $T = 298$ K, $p = 1$ bar

	$H_2(g)$	$CO_2(g)$	$H_2O(g)$	$CO(g)$
Initial # of moles	a	b	0	0
# moles at Eq.	a-x	b-x	x	x

Total # moles at Eq. = (a – x) + (b – x) + 2x = a + b

Mole fraction at Eq.	$\frac{a-x}{a+b}$	$\frac{b-x}{a+b}$	$\frac{x}{a+b}$	$\frac{x}{a+b}$
$\Delta G^o_{\text{form}}(\text{kJ/mol})$	0	-394.4	-228.6	-137.2

$$\therefore \quad \Delta G^o_{\text{rxn}} = 28.6 \text{ kJ/mol} \quad \Rightarrow \quad K_p = e^{-\frac{28{,}600 \text{ kJ/mol}}{(8.314 \text{ J/K-mol})(298 \text{ K})}} = e^{-11.54} = 9.7x10^{-6}$$

$$K_p = \frac{p_{H_2O}p_{CO}}{p_{H_2}p_{CO_2}} = \frac{X_{H_2O}X_{CO}}{X_{H_2}X_{CO_2}} = \frac{x^2}{(a-x)(b-x)}$$

Let's take a = 1 mol and b = 2 mol

We need to solve $$\frac{x^2}{(1-x)(2-x)} = 9.7x10^{-6}$$

A) Using <u>approximation method</u>:

K << 1, so we expect x << 1 also.

Assume $1-x \approx 1,\ \ 2-x \approx 2 \quad \Rightarrow \quad \frac{x^2}{(1-x)(2-x)} \approx \frac{x^2}{2} = 9.7x10^{-6}$

$x \approx 0.0044 \text{ mol (indeed} << 1)$

B) <u>Exactly</u>: $$\frac{x^2}{x^2-3x+2} = K_p = 9.7x10^{-6}$$

$$x^2\left(1-9.7x10^{-6}\right) + 3x\left(9.7x10^{-6}\right) - 2\left(9.7x10^{-6}\right) = 0$$

$$x = \frac{-3\left(9.7x10^{-6}\right)}{2\left(9.7x10^{-6}\right)} \pm \frac{\sqrt{9\left(9.7x10^{-6}\right)^2 + 4\left(1-9.7x10^{-6}\right)2\left(9.7x10^{-6}\right)}}{2\left(1-9.7x10^{-6}\right)}$$

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

$$N_2O_4(g) \; = \; 2\,NO_2(g)$$

Initial mol #	n	0	
# at Eq.	n-x	2x	Total # moles at Eq. = n – x + 2x = n + x
X_i's at Eq.	$\frac{n-x}{n+x}$	$\frac{2x}{n+x}$	

$$K_p = \frac{p_{NO_2}^2}{p_{N_2O_4}} = \frac{p^2 X_{NO_2}^2}{p X_{N_2O_4}} = p\frac{\left(\frac{2x}{n+x}\right)^2}{\left(\frac{n-x}{n+x}\right)} = p\frac{4x^2}{n^2-x^2}$$

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

$$\left(1-\alpha^2\right)\frac{K_p}{4p} = \alpha^2 \qquad \alpha^2\left(1+\frac{K_p}{4p}\right) = \frac{K_p}{4p} \qquad \alpha^2 = \frac{\frac{K_p}{4p}}{\left(1+\frac{K_p}{4p}\right)} = \frac{1}{\left(1+\frac{4p}{K_p}\right)} \qquad \alpha = \left(1+\frac{4p}{K_p}\right)^{-1/2}$$

$\therefore$ If p increases, α 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:

$$2\ NO(g) + O_2(g) = 2\ NO_2(g)$$

$$K_p = 2.3x10^{12} \text{ at } 298 \text{ K}$$

Initial mol #	2	1	0	
# at Eq.	2-2x	1-x	2x	Total # moles at Eq. = 2 – 2x + 1 – x + 2x
X_i's at Eq.	$\frac{2(1-x)}{3-x}$	$\frac{1-x}{3-x}$	$\frac{2x}{3-x}$	= 3 - x

$$K_p = \frac{p_{NO_2}^2}{p_{NO}^2 p_{O_2}} = \frac{p^2 X_{NO_2}^2}{p^2 X_{NO}^2 p X_{O_2}} = \frac{1}{p}\frac{X_{NO_2}^2}{X_{NO}^2 X_{O_2}} = \frac{1}{p}\frac{x^2(3-x)}{(1-x)^3}$$

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

$$K_p \approx \frac{1}{p}\frac{2}{(1-x)^3} \quad \text{or} \quad (1-x)^3 \approx \frac{2}{pK_p} \qquad x \approx 1-\left(\frac{2}{pK_p}\right)^{1/3}$$

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