Chemical Equilibrium

Ideal Gases

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

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

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 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 $G = \sum_i n_i \mu_i$

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

where ε is an arbitrary small number that allows to let the reaction proceed just a bit.

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

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

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

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

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

and $Q = \frac{p_C^{\nu_C}\,p_C^{\nu_D}}{p_A^{\nu_A}\,p_B^{\nu_B}}$ is the reaction quotient

ΔG° is the standard change in free energy for taking pure reactants into pure products.

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

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

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

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

$\Delta G(\varepsilon) = 0$ No spontaneous changes $\Rightarrow$ Equilibrium

At Equilibrium $\Delta G(\varepsilon) = 0$ and this implies $\Delta G^o_{rxn} = -RT\ln Q_{eq}$

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 thus $\boxed{\Delta G^o_{rxn} = -RT\ln K_p \ , \ K_p = e^{-\Delta G^o/RT}}$

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.	$\frac{a-x}{a+b}$	$\frac{b-x}{a+b}$	$\frac{x}{a+b}$	$\frac{x}{a+b}$

ΔG°_{form} (kJ/mol)	0	-396.6	-228.6	-137.2

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

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

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

$x \approx 0.0044$ 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 $\Rightarrow$ $x = 0.0044$ 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.	$\frac{n-x}{n+x}$	$\frac{2x}{n+x}$	

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

$K_p = p\frac{4\alpha^2}{1-\alpha^2}$ where $\alpha = x/n$ 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:

	$2\,NO(g)$	+	$O_2(g)$	=	$2\,NO_2(g)$	$K_p = 2.3x10^{12}$ at 298 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 $x \approx 1 \Rightarrow 3 - x \approx 2$

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

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