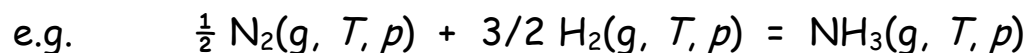


## Chemical Equilibrium

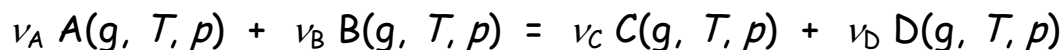
### Ideal Gases

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



What are  $p_{\text{N}_2}$ ,  $p_{\text{H}_2}$ , and  $p_{\text{NH}_3}$  at equilibrium?

Let's look at a more general case



The  $\nu_i$ 's are the stoichiometric coefficients.

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

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

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  $G = \sum_i n_i \mu_i$

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

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

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

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

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

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

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

and  $Q = \frac{p_C^{v_C} p_D^{v_D}}{p_A^{v_A} p_B^{v_B}}$  is the reaction quotient

$\Delta G^\circ$  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  $\Delta G_{rxn}^{\circ} = -RT \ln Q_{eq}$

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

$$K_p = \left( \frac{p_C^{v_C} p_D^{v_D}}{p_A^{v_A} p_B^{v_B}} \right)_{eq} = p^{\Delta v} \left( \frac{X_C^{v_C} X_D^{v_D}}{X_A^{v_A} X_B^{v_B}} \right)_{eq} = p^{\Delta v} K_X$$

and thus  $\Delta G_{rxn}^{\circ} = -RT \ln K_p$ ,  $K_p = e^{-\Delta G^{\circ}/RT}$

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

It is  $K_X = p^{-\Delta v} K_p$  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:  $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) = \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$   $T = 298 \text{ K}$   
 $p = 1 \text{ bar}$

	$\text{H}_2(\text{g})$	$\text{CO}_2(\text{g})$	$\text{H}_2\text{O}(\text{g})$	$\text{CO}(\text{g})$
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.	$\frac{a-x}{a+b}$	$\frac{b-x}{a+b}$	$\frac{x}{a+b}$	$\frac{x}{a+b}$

$$\Delta G_{\text{form}}^{\circ} \text{ (kJ/mol)} \quad 0 \quad -396.6 \quad -228.6 \quad -137.2$$

$$\therefore \Delta G_{\text{rxn}}^{\circ} = 28.6 \text{ kJ/mol} \Rightarrow K_p = e^{-\frac{28,600 \text{ kJ/mol}}{(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K})}} = e^{-11.54} = 9.7 \times 10^{-6}$$

$$\text{and} \quad K_p = \frac{P_{\text{H}_2\text{O}} P_{\text{CO}}}{P_{\text{H}_2} P_{\text{CO}_2}} = \frac{X_{\text{H}_2\text{O}} X_{\text{CO}}}{X_{\text{H}_2} X_{\text{CO}_2}} = \frac{x^2}{(a-x)(b-x)}$$

Let's take  $a = 1 \text{ mol}$  and  $b = 2 \text{ mol}$

$$\text{We need to solve} \quad \frac{x^2}{(1-x)(2-x)} = 9.7 \times 10^{-6}$$

A) Using approximation method:

$K \ll 1$ , so we expect  $x \ll 1$  also.

$$\text{Assume} \quad 1-x \approx 1, \quad 2-x \approx 2 \Rightarrow \frac{x^2}{(1-x)(2-x)} \approx \frac{x^2}{2} = 9.7 \times 10^{-6}$$

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

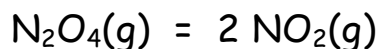
B) Exactly:  $\frac{x^2}{x^2 - 3x + 2} = K_p = 9.7 \times 10^{-6}$

$$x^2(1 - 9.7 \times 10^{-6}) + 3x(9.7 \times 10^{-6}) - 2(9.7 \times 10^{-6}) = 0$$

$$x = \frac{-3(9.7 \times 10^{-6}) \pm \sqrt{9(9.7 \times 10^{-6})^2 + 4(1 - 9.7 \times 10^{-6})2(9.7 \times 10^{-6})}}{2(1 - 9.7 \times 10^{-6})}$$

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

Initial mol #	n	0	
# at Eq.	n-x	2x	Total # moles at Eq. = n - x + 2x = n + x
X <sub>i</sub> 's at Eq.	$\frac{n-x}{n+x}$	$\frac{2x}{n+x}$	

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

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

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

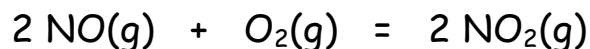
∴ If  $p$  increases,  $\alpha$  decreases

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.

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Another example:

$$K_p = 2.3 \times 10^{12} \text{ at } 298 \text{ K}$$

Initial mol #	2	1	0	
# at Eq.	2-2x	1-x	2x	Total # moles at Eq. = 2 - 2x + 1 - x + 2x = 3 - x
X <sub>i</sub> 's at Eq.	$\frac{2(1-x)}{3-x}$	$\frac{1-x}{3-x}$	$\frac{2x}{3-x}$	

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

$$K_p \gg 1 \text{ so we expect } x \approx 1 \Rightarrow 3-x \approx 2$$

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

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