5.60 Thermodynamics & Kinetics
Spring 2008

<u>Chemical Equilibrium</u>

<u>Ideal Gases</u>

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

e.g. $\frac{1}{2}$ $N_2(g, T, p)$ + 3/2 $H_2(g, T, p)$ = $NH_3(g, T, p)$
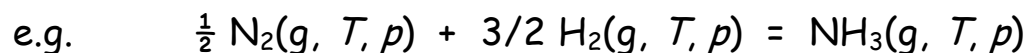
What are p_{N_2}, p_{H_2}, and p_{NH_3} at equilibrium?

Let's look at a more general case

$$v_A \, A(g, T, p) \; + \; v_B \, B(g, T, p) \; = \; v_C \, C(g, T, p) \; + \; v_D \, D(g, T, p)$$
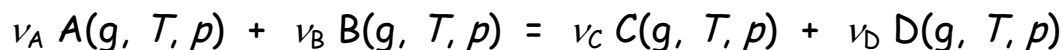
The v_i's are the stoichiometric coefficients.

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 $G = \sum_i n_i \mu_i$

$\Rightarrow$ $\Delta G(\varepsilon) = \varepsilon \left\{ \left[v_C \mu_C (g, T, p) + v_D \mu_D (g, T, p) \right] - \left[v_A \mu_A (g, T, p) + v_B \mu_B (g, T, p) \right] \right\}$

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

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

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

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

$\Rightarrow$ $\Delta G = \Delta G^o + RT\ln Q$ (taking ε=1)

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

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

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

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

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

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

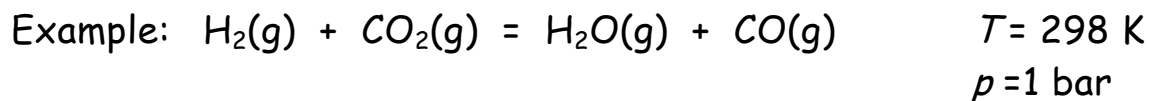Define $Q_{eq} = K_p$ the equilibrium constant

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

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

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

It is $K_X = p^{-\Delta v} K_p$ 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 <u>unitless</u>.

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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 | $\dfrac{a-x}{a+b}$ | $\dfrac{b-x}{a+b}$ | $\dfrac{x}{a+b}$ | $\dfrac{x}{a+b}$ |

at Eq.

ΔG_{form}^{o} (kJ/mol)   0   -396.6   -228.6   -137.2

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

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

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

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

A)   Using <u>approximation method</u>:
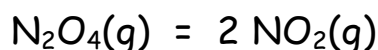
   K << 1, so we expect x << 1 also.

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

      $x \approx 0.0044$ mol (indeed $\ll 1$)

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

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

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

      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. $\dfrac{n-x}{n+x}$ $\dfrac{2x}{n+x}$

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

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

$$\left(1-\alpha^2\right)\frac{K_p}{4p} = \alpha^2 \quad \alpha^2\left(1+\frac{K_p}{4p}\right) = \frac{K_p}{4p} \quad \alpha^2 = \frac{\dfrac{K_p}{4p}}{\left(1+\dfrac{K_p}{4p}\right)} = \frac{1}{\left(1+\dfrac{4p}{K_p}\right)} \quad \alpha = \left(1+\frac{4p}{K_p}\right)^{-1/2}$$
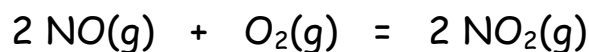
∴   If p increases, α decreases

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:

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

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

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. $\dfrac{2(1-x)}{3-x}$ $\dfrac{1-x}{3-x}$ $\dfrac{2x}{3-x}$ = 3 - x

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

$K_p \gg 1$ so we expect $x \approx 1 \implies 3 - x \approx 2$

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

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