20.110J / 2.772J / 5.601J
Thermodynamics of Biomolecular Systems
Instructors: Linda G. Griffith, Kimberly Hamad-Schifferli, Moungi G. Bawendi, Robert W. Field

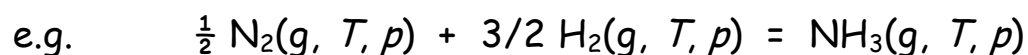20.110/5.60 Fall 2005   Lecture #10   page   1

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

$\quad$ ν_A A(g, T, p) + ν_B B(g, T, p) = ν_C C(g, T, p) + ν_D D(g, T, p)
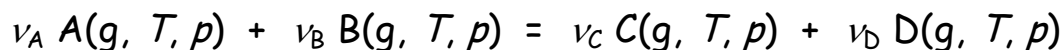
$\quad$ The ν_i's are the stoichiometric coefficients.

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

$\quad$ $p_A = X_A p$, $p_B = X_A p$, $p_C = X_C p$, 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 $G = \sum_i n_i \mu_i$

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

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20.110/5.60 Fall 2005   Lecture #10   page   2

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

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

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

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

$\Rightarrow \quad \Delta G = \Delta G^o + RT\ln Q$

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

and $\quad Q = \dfrac{p_C^{v_C} p_C^{v_D}}{p_A^{v_A} p_B^{v_B}}$ 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 $\quad \Delta G^o = \Delta G_{form}^o(\text{products}) - \Delta G_{form}^o(\text{reactants})$

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

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

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

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20.110/5.60 Fall 2005   Lecture #10   page   3

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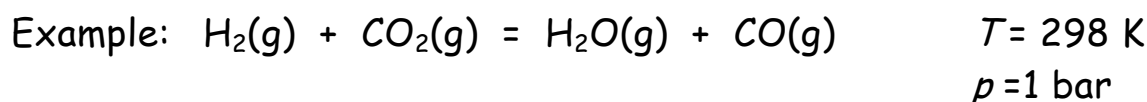
Define $Q_{eq} = K_p$ the equilibrium constant

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

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>.

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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 at Eq. | $\dfrac{a-x}{a+b}$ | $\dfrac{b-x}{a+b}$ | $\dfrac{x}{a+b}$ | $\dfrac{x}{a+b}$ |

20.110J / 2.772J / 5.601J
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20.110/5.60 Fall 2005   Lecture #10   page   4

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

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

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

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

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

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

   K ≪ 1, so we expect x ≪ 1 also.

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

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

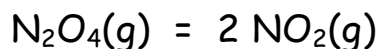B)   <u>Exactly</u>: $\quad \dfrac{x^2}{x^2 - 3x + 2} = K_p = 9.7 \times 10^{-6}$

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

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

   The "-" sign gives a nonphysical result (negative x value)
   Take the "+" sign only $\Rightarrow \quad x = 0.0044 \text{ mol}$ (same)

20.110J / 2.772J / 5.601J
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20.110/5.60 Fall 2005   Lecture #10   page   5

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

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

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

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

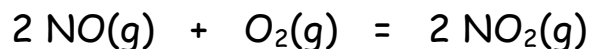$\therefore$ If p increases, α decreases

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.

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20.110/5.60 Fall 2005   Lecture #10   page   6

Another example:

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

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

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 $x \approx 1 \Rightarrow 3 - x \approx 2$

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

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