Equilibrium

Chem 36

Spring 2002

The Equilibrium Condition

- **Recall:** a system is at *equilibrium* when $\Delta G = 0$
  - No *net* driving force for process in *either direction*
- **Equilibrium is a *dynamic* condition**
  - Reaction has not *stopped*
  - No *net change* in the amounts of products or reactants

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K and *Equilibrium Position*

Case 1: K *very* small (K << 1)

$$N_2\,(g) + O_2\,(g) \leftrightarrows 2NO\,(g)$$

$$K = \frac{(P_{NO})^2}{(P_{N2})(P_{O2})} = 1.\ X\ 10^{-30} \quad \text{at } 25\ ^oC$$

At equilibrium, do reactants or products predominate?

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Calculate it!

Suppose we know that:

$$P_{N2} = P_{O2} = 1.0\ atm \quad \text{(at equilibrium)}$$

Calculate P_{NO}

Solve equilibrium constant expression for P_{NO}:

$$\mathbf{(P_{NO})^2 = K\ P_{N2}P_{O2}} = (1.\ x\ 10^{-30})(1.0)(1.0)$$

$$\mathbf{(P_{NO})^2 = 1.\ x\ 10^{-30}}$$

$$P_{NO} = (1.\ X\ 10^{-30})^{½} = \mathbf{1.\ x\ 10^{-15}\ atm}$$

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Reverse it!

Case 2: K *very* large (K >> 1)

$$2NO\ (g) \leftrightarrows N_2\ (g) + O_2\ (g)$$

$$K = \frac{(P_{N2})(P_{O2})}{(P_{NO})^2} = 1.\ X\ 10^{30} \quad \text{at } 25\ ^oC$$

At equilibrium, *products* predominate

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A Third Case

Case 3: K ≈ 1

$$N_2O_4\ (g) \leftrightarrows 2NO_2\ (g)$$

$$K = \frac{(P_{NO2})^2}{P_{N2O4}} = 11. \quad \text{At } 100\ ^oC$$

Here, we expect to have *similar* amounts of products and reactants

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Calculate!

Suppose we know that:

P_{N2O4} = 1.0 atm (at equilibrium)

Calculate P_{NO2}

Solve equilibrium constant expression for P_{NO2}:

$(P_{NO2})^2 = K\ P_{N2O4}$ = (11.)(1.0)

$(P_{NO2})^2$ = *11.*

$P_{NO2} = (11.)^{½}$ = ***3.3 atm***

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Are we there yet?

- How do we know whether a system is at equilibrium?
  - **Evaluate DG** (*lotsa work!*): $\Delta G = \Delta G^o + RTLnQ$
  - **Calculate Q** and compare with K
    1. If **Q < K**: ΔG is *negative* (rxn proceeds forward)
    2. If **Q > K:** ΔG is **positive** (rxn proceeds in reverse)
    3. If **Q = K:** $\Delta G = 0$ (system is AT equilibrium)

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Example

$CO_2\ (g) + H_2\ (g) \leftrightarrows CO\ (g) + H_2O\ (g)$

$K = 0.64$ at 900. K

- If we have ***1 atm of each gas***, in which direction will reaction proceed spontaneously?

$$Q = \frac{P_{CO}\,P_{H2O}}{P_{CO2}\,P_{H2}} = \frac{(1)(1)}{(1)(1)} = 1 > 0.64 = K$$

Q > K: *Reverse Rxn is Spontaneous*

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Example: Calculating K

$CH_4\ (g) + H_2O\ (g) \leftrightarrows CO\ (g) + 3H_2\ (g)$

At equilibrium (at 600 K):

P, atm:	1.40	2.30	1.60	7.1×10^{-3}

Into the equilibrium constant expression:

$$K = \frac{(P_{CO})(P_{H2})^3}{(P_{CH4})(P_{H2O})} = \frac{(1.60)(7.1 \times 10^{-3})^3}{(1.40)(2.30)}$$

Not always quite so easy!

$K = 1.8 \times 10^{-7}$

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Calculating Equilibrium Activities

Example:

$(CH_3)_2CHOH\ (g) \leftrightarrows (CH_3)_2CO\ (g) + H_2\ (g)$

$K = 0.444$ (at 452 K)

Calculate: equilibrium pressures if we start out with 1.000-g isopropanol in a 2.00-L vessel, at 452 K

Convert to *pressure:*

$P_{iso} = nRT/V = \mathbf{0.3086\ atm}$

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The *ICE* Method

$(CH_3)_2CHOH\ (g) \leftrightarrows (CH_3)_2CO\ (g) + H_2\ (g)$

Initial:	0.3086 atm	-	-
Change:	**-x**	**+x**	**+x**
Equilibrium:	***0.3086 - x***	***x***	***x***

Plug values into equilibrium constant expression:

$$K = (P_{acet})(P_{H2})/(P_{isopro})$$

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Solving for x

$$K = \frac{(x)(x)}{0.3086 - x} = 0.444$$

It's a quadratic!

$$x^2 = 0.13702 - 0.444x$$

$$x^2 + 0.444x - 0.13702 = 0$$

$$x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a}$$

a **b** **c**

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Solving for x (continued)

- Substituting into the quadratic equation:

$$x = \frac{-0.444 \pm [(0.444)^2 - 4(1)(-0.13702)]^{1/2}}{2(1)}$$

- Rearranging and solving:

$$x = \frac{-0.444 \pm 0.863259}{2} = 0.20963$$

Negative root has no physical meaning

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Relating x to pressures

- Substitute x back into equilibrium pressure expressions:

$P_{acetone} = P_{H2} = x =$ ***0.210 atm***

$P_{isopropanol} = 0.3086 - x =$ ***0.099 atm***

➢ What is the *%-dissociation* of isopropanol?

%-dissoc = $(P_{reacted}/P_{initial}) \times 100$

$= (x/0.3086) \times 100$

$= (0.20963/0.3086) \times 100 =$ ***67.9%***

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Disturbing Equilibrium

What happens when we *disturb* a system at equilibrium?

Le Chatelier's Principle:

Reaction will proceed so as to *counteract* the effects of the disturbance

Let's look at the effects of changing:

- Amount of a product or reactant
- Volume
- Pressure

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Changing Amounts of Reactant or Product

Back to our example reaction:

$(CH_3)_2CHOH\ (g) \leftrightarrows (CH_3)_2CO\ (g) + H_2\ (g)$

- *Remove* a product: rxn shifts to the **right**
- **Add** a reactant: rxn shifts to the **right**

- *Remove* a reactant : rxn shifts to the **left**
- **Add** a product : rxn shifts to the **left**

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Now, Quantitatively

- We start at our established point of equilibrium:

$P_{acetone} = P_{H2} =$ ***0.210 atm***

$P_{isopropanol} =$ ***0.099 atm***

- What will the equilibrium pressures become IF we add H_2 so that:
  $P_{H2} = 0.300$ atm?

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ICE Again

$(CH_3)_2CHOH\ (g) \leftrightarrows (CH_3)_2CO\ (g) + H_2\ (g)$

← ***Shift***

Initial:	0.0990 atm	0.210	0.300
Change:	**+x**	**-x**	**-x**
Equilibrium:	*0.0990 + x*	*0.210 - x*	*0.300 - x*

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Solve for x

$$K = \frac{(0.210 - x)(0.300 - x)}{0.0990 + x} = 0.444$$

From the quadratic formula, we get:

x = 0.0204

Substituting into *ICE* equilibrium expressions, gives:

$P_{isopropanol}$	= 0.0990 + x	= ***0.119 atm = $P_{isopropanol}$***
$P_{acetone}$	= 0.210 - x	= ***0.190 atm = $P_{acetone}$***
P_{H2}	= 0.300 - x	= ***0.280 atm = P_{H2}***

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Changing Volume

- Let's see what happens if we *halve* the volume of our reaction vessel:

$(CH_3)_2CHOH\ (g) \leftrightarrows (CH_3)_2CO\ (g) + H_2\ (g)$

At equilibrium:

0.119 atm 0.210 atm 0.280 atm

Halving the volume will **double** the pressures:

0.238 atm *0.420 atm* *0.560 atm*

What happened to Q?

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Equilibrium Check!

$$Q = \frac{(0.420)(0.560)}{0.238} = 0.988$$

$Q = 0.988 > 0.444 = K$

Too much product, so reaction shifts:

$(CH_3)_2CHOH\ (g) \leftrightarrows (CH_3)_2CO\ (g) + H_2\ (g)$

← ***Shift***

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Volume Change: In General

- Changing the *volume* will change the partial pressures of all gases
  - ✓ If the ***number of moles of gas*** products or reactants is not the same, then the change in pressure will be different for the products and reactants (and $Q \neq K$)
  - ✓ Equilibrium shifts to *decrease* the overall pressure and the reaction shifts to the side with the fewest number of moles of gas (until Q = K).
  - ✓ What ***if*** Δn_{gas} ***= 0? No Shift!*** (Q = K).

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Effect of Adding an Inert Gas

- Suppose we add some *Argon* to a system at equilibrium . . . Will that change the position of equilibrium?
- The Simple Answer: *No!*
  - ✓ The partial pressures of the reactants and products are not affected (Q = K)
- The Real Answer: *It Depends!*
  - ✓ Constant Volume or Constant Pressure?

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Added Inert Gas: *Constant Volume*

- If *volume* is unchanged upon addition of gas, then P_{total} must *increase*:

Before: $P_{total} = P_{reactants} + P_{products}$

After: $P_{total} = P_{reactants} + P_{products} + P_{gas}$

- Partial Pressures of reactants and products are unchanged:

No Shift

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Added Inert Gas: *Constant Pressure*

- If *pressure* is unchanged upon addition of gas, then ***volume*** must increase.

Before: $P_{total} = P_{reactants} + P_{products}$

After: $P_{total} = P_{reactants} + P_{products} + P_{gas}$

BUT: P_{total} (before) = P_{total} (after)

- Partial pressures of reactants and products must *decrease* in order to keep total pressure constant

Reaction Can Shift

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Effect of Temperature

- Treat *heat* as a:
  - Product (for exothermic process)
  - Reactant (for endothermic process)

Example:

$$N_2\,(g) + 3H_2\,(g) \leftrightarrows 2NH_3\,(g) + \text{heat}$$

($\Delta H = -92.4$ kJ)

Quantify using van't Hoff equation!

increase temperature ←

decrease temperature →

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Manipulating K's and Equilibria

- What happens to K when we add/subtract/reverse equilibria?

Reverse Reaction:

1) $A \leftrightarrows B \quad K_1 = P_B/P_A$

2) $B \leftrightarrows A \quad K_2 = P_A/P_B = 1/K_1$

✓Reverse Reaction = **INVERSE of K**

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Adding Equilibria

Let's add these two reactions:

✓Add Rxns = Multiply K's

✓Subtract Rxns = *Divide K's*

1) $A + B \leftrightarrows C$ $\quad K_1 = \dfrac{P_C}{P_A P_B}$

2) $C + D \leftrightarrows E + B$ $\quad K_2 = \dfrac{P_E P_B}{P_C P_D}$

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3) $A + \cancel{B} + \cancel{C} + D \leftrightarrows \cancel{C} + E + \cancel{B}$

A + D ⇆ E

$K_3 = K_1 K_2 = \dfrac{\cancel{P_C} P_E \cancel{P_B}}{P_A \cancel{P_B} \cancel{P_C} P_D} = \dfrac{P_E}{P_A P_D}$

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K_p versus K_c

- What if gas amounts are expressed as **concentrations (mol/L)?**
  - K_p = thermodynamic K (atm)
  - K_c = *concentration* -based equilib constant

Ideal Gas Law: **P = (n/V)RT**

It can be shown that:

Change in # mol *gas*

$$K_p = K_c (RT)^{Dn}$$

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Example using K_c

$N_2\ (g) + 3H_2\ (g) \leftrightarrows 2NH_3\ (g)$ $K = 1.65 \times 10^{-2}$ (at 300 K)

➢Calculate the *equilibrium concentrations* of the gases if we start with:

$[N_2] = 0.500$ mol/L $n_{N2} = 2.0$ L (0.500 mol/L) = 1.00 mol

$[H_2] = 1.500$ mol/L $n_{H2} = 2.0$ L (1.500 mol/L) = 3.00 mol

Total Volume = 2.0 L

Converting K to K_c:

$$K_c = K_p/(RT)^{\Delta n} = \frac{1.65 \times 10^{-2}}{[(0.08206)(300)]^{-2}} = 10.0 = K_c$$

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ICE Time!

$$N_2\ (g) + 3H_2\ (g) \leftrightarrows 2NH_3\ (g)$$

Initial mol	1.00 mol	3.00 mol	0 mol
Change	-x	-3x	+2x
Equilib mol	1.00 - x	3.00 - 3x	2x
***Equilib* conc.**	$\frac{1.00 - x}{2.0}$	$\frac{3.00 - 3x}{2.0}$	$\frac{2x}{2.0}$

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Solving for x

$$K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3} = 10.0$$

Substituting and collecting terms:

$$\frac{x^2}{(1.00 - x)^4} = 16.875$$

Reduces to the following quadratic:

$$4.108\,x^2 - 9.216x + 4.108 = 0$$

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Finally, the Answers

From the quadratic: **x = ~~1.63~~ and 0.6143**

Too big!

Substituting:

$[NH_3] = 2x/2.0 = 2(0.6143)/2.0 =$ ***0.61 mol/L***

$[H_2] = \frac{3.00 - 3(0.6143)}{2.0} =$ ***0.58 mol/L***

$[N_2] = \frac{1.00 - 0.6143}{2.0} =$ ***0.19 mol/L***

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