

# Equilibrium

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Chem 36  
Spring 2002

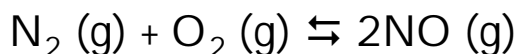
## The Equilibrium Condition

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- **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

## K and *Equilibrium Position*

**Case 1:** K very small ( $K \ll 1$ )



$$K = \frac{(\text{P}_{\text{NO}})^2}{(\text{P}_{\text{N}_2})(\text{P}_{\text{O}_2})} = 1. \times 10^{-30} \quad \text{at } 25 \text{ }^\circ\text{C}$$

At equilibrium, do reactants or products predominate?

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## Calculate it!

Suppose we know that:

$$\text{P}_{\text{N}_2} = \text{P}_{\text{O}_2} = 1.0 \text{ atm} \quad (\text{at equilibrium})$$

**Calculate  $\text{P}_{\text{NO}}$**

Solve equilibrium constant expression for  $\text{P}_{\text{NO}}$ :

$$(\text{P}_{\text{NO}})^2 = K \text{P}_{\text{N}_2}\text{P}_{\text{O}_2} = (1. \times 10^{-30})(1.0)(1.0)$$

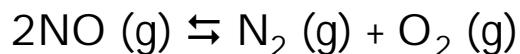
$$(\text{P}_{\text{NO}})^2 = 1. \times 10^{-30}$$

$$\text{P}_{\text{NO}} = (1. \times 10^{-30})^{1/2} = \underline{1. \times 10^{-15} \text{ atm}}$$

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## Reverse it!

**Case 2:**  $K$  very large ( $K \gg 1$ )



$$K = \frac{(P_{\text{N}_2})(P_{\text{O}_2})}{(P_{\text{NO}})^2} = 1. \times 10^{30} \text{ at } 25 \text{ }^\circ\text{C}$$

At equilibrium, *products* predominate

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## A Third Case

**Case 3:**  $K \approx 1$



$$K = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} = 11. \text{ At } 100 \text{ }^\circ\text{C}$$

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

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## Calculate!

Suppose we know that:

$$P_{\text{N}_2\text{O}_4} = 1.0 \text{ atm (at equilibrium)}$$

**Calculate  $P_{\text{NO}_2}$**

Solve equilibrium constant expression for  $P_{\text{NO}_2}$ :

$$(P_{\text{NO}_2})^2 = K P_{\text{N}_2\text{O}_4} = (11.)(1.0)$$

$$(P_{\text{NO}_2})^2 = 11.$$

$$P_{\text{NO}_2} = (11.)^{1/2} = \underline{\underline{3.3 \text{ atm}}}$$

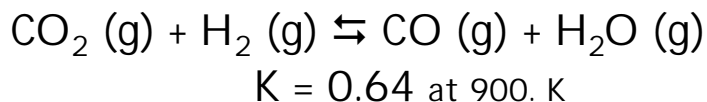
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## Are we there yet?

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

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## Example



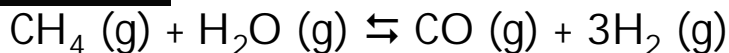
• If we have **1 atm of each gas**, in which direction will reaction proceed spontaneously?

$$Q = \frac{P_{\text{CO}} P_{\text{H}_2\text{O}}}{P_{\text{CO}_2} P_{\text{H}_2}} = \frac{(1)(1)}{(1)(1)} = 1 > 0.64 = K$$

**Q > K: Reverse Rxn is Spontaneous**

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## Example: Calculating K



At equilibrium (at 600 K):

P, atm:      1.40      2.30                      1.60      7.1 x 10<sup>-3</sup>

Into the equilibrium constant expression:

$$K = \frac{(P_{\text{CO}})(P_{\text{H}_2})^3}{(P_{\text{CH}_4})(P_{\text{H}_2\text{O}})} = \frac{(1.60)(7.1 \times 10^{-3})^3}{(1.40)(2.30)}$$

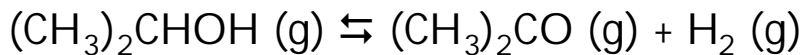
Not always quite so easy!

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

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## Calculating Equilibrium Activities

Example:



$$K = 0.444 \text{ (at 452 K)}$$

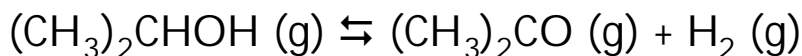
Calculate: equilibrium pressures if we start out with 1.000-g isopropanol in a 2.00-L vessel, at 452 K

Convert to pressure:

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

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## The *ICE* Method



<i>I</i> nitial:	0.3086 atm	-	-
<i>C</i> hange:	<u>      -<b>x</b>      </u>	<u>      +<b>x</b>      </u>	<u>      +<b>x</b>      </u>
<i>E</i> quilibrium:	<b>0.3086 - x</b>	<b>x</b>	<b>x</b>

Plug values into equilibrium constant expression:

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

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## Solving for x

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

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

*It's a quadratic!*

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

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

**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

## Relating x to pressures

- Substitute x back into equilibrium pressure expressions:

$$P_{\text{acetone}} = P_{\text{H}_2} = x = \underline{\underline{0.210 \text{ atm}}}$$

$$P_{\text{isopropanol}} = 0.3086 - x = \underline{\underline{0.099 \text{ atm}}}$$

➤ What is the %-dissociation of isopropanol?

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

$$= (x/0.3086) \times 100$$

$$= (0.20963/0.3086) \times 100 = \underline{\underline{67.9\%}}$$

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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:

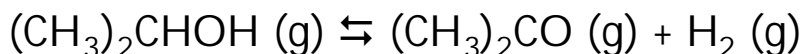
- Amount of a product or reactant
- Volume
- Pressure

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## Changing Amounts of Reactant or Product

Back to our example reaction:



➤ 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:

$$P_{\text{acetone}} = P_{\text{H}_2} = \underline{\underline{0.210 \text{ atm}}}$$

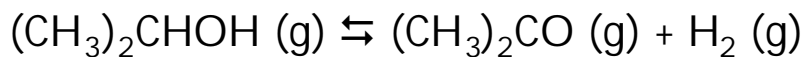
$$P_{\text{isopropanol}} = \underline{\underline{0.099 \text{ atm}}}$$

➤ What will the equilibrium pressures become if we add  $\text{H}_2$  so that:

$$P_{\text{H}_2} = 0.300 \text{ atm?}$$

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## ***ICE* Again**



← **Shift**

<b><i>I</i></b> initial:	0.0990 atm	0.210	0.300
<b><i>C</i></b> hange:	<u>+X</u>	<u>-X</u>	<u>-X</u>
<b><i>E</i></b> quilibrium:	$0.0990 + x$	$0.210 - x$	$0.300 - x$

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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:

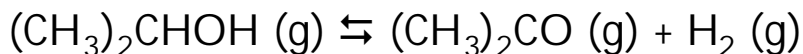
$$\mathbf{x = 0.0204}$$

Substituting into *ICE* equilibrium expressions, gives:

$P_{\text{isopropanol}}$	$= 0.0990 + x$	$= \mathbf{0.119 atm}$	$= P_{\text{isopropanol}}$
$P_{\text{acetone}}$	$= 0.210 - x$	$= \mathbf{0.190 atm}$	$= P_{\text{acetone}}$
$P_{\text{H}_2}$	$= 0.300 - x$	$= \mathbf{0.280 atm}$	$= P_{\text{H}_2}$

## Changing Volume

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



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?**

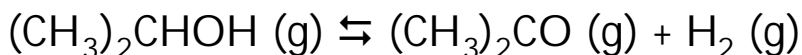
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## Equilibrium Check!

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

$$Q = 0.988 > 0.444 = K$$

**Too much product**, so reaction shifts:



← Shift

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## Volume Change: I n 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  $Dn_{\text{gas}} = 0$ ? 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  $P_{\text{total}}$  must *increase*:

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

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

- 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:  $P_{\text{total}} = P_{\text{reactants}} + P_{\text{products}}$

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

**BUT:  $P_{\text{total}}$  (before) =  $P_{\text{total}}$  (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)

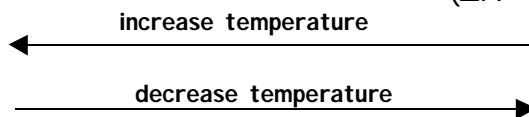
Reactant (for endothermic process)

Example:



( $\Delta H = -92.4 \text{ kJ}$ )

Quantify  
using van't  
Hoff  
equation!

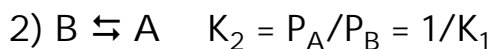


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## Manipulating K's and Equilibria

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

Reverse Reaction:

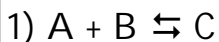


✓ Reverse Reaction  
= **INVERSE of K**

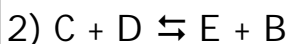
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## Adding Equilibria

Let's add these two reactions:



$$K_1 = \frac{P_C}{P_A P_B}$$



$$K_2 = \frac{P_E P_B}{P_C P_D}$$

✓ Add Rxns =  
Multiply K's

✓ Subtract Rxns  
= Divide K's



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

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## K<sub>p</sub> versus K<sub>c</sub>

➤ What if gas amounts are expressed as **concentrations (mol/L)**?

- K<sub>p</sub> = thermodynamic K (atm)
- K<sub>c</sub> = *concentration* -based equilib constant

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

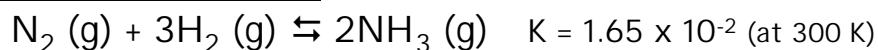
It can be shown that:

$$K_p = K_c (RT)^{\Delta n}$$

Change in #mol gas

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## Example using $K_c$



➤ Calculate the equilibrium concentrations of the gases if we start with:

$$[\text{N}_2] = 0.500 \text{ mol/L} \quad n_{\text{N}_2} = 2.0 \text{ L} (0.500 \text{ mol/L}) = 1.00 \text{ mol}$$

$$[\text{H}_2] = 1.500 \text{ mol/L} \quad n_{\text{H}_2} = 2.0 \text{ L} (1.500 \text{ mol/L}) = 3.00 \text{ mol}$$

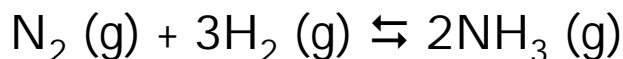
$$\text{Total Volume} = 2.0 \text{ L}$$

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!



**Initial mol**    1.00 mol    3.00 mol    0 mol

**Change**        -x            -3x            +2x

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**Equilib mol**    1.00 - x    3.00 - 3x    2x

<b>Equilib conc.</b>	$\frac{1.00 - x}{2.0}$	$\frac{3.00 - 3x}{2.0}$	$\frac{2x}{2.0}$
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## Solving for x

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2] [\text{H}_2]^3} = 10.0$$

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:  $x = \cancel{1.63}$  and  $\mathbf{0.6143}$

Substituting:

Too big!

$$[\text{NH}_3] = 2x/2.0 = 2(0.6143)/2.0 = \mathbf{0.61 \text{ mol/L}}$$

$$[\text{H}_2] = \frac{3.00 - 3(0.6143)}{2.0} = \mathbf{0.58 \text{ mol/L}}$$

$$[\text{N}_2] = \frac{1.00 - 0.6143}{2.0} = \mathbf{0.19 \text{ mol/L}}$$

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