

# Chapter Outline

- **14.1 The Dynamics of Chemical Equilibrium**
- 14.2 Writing Equilibrium Constant Expressions
- 14.3 Relationships between  $K_c$  and  $K_p$  Values
- 14.4 Manipulating Equilibrium Constant Expressions
- 14.5 Equilibrium Constants and Reaction Quotients
- 14.6 Heterogeneous Equilibria
- 14.7 Le Châtelier's Principle
- 14.8 Calculations Based on  $K$
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- 14.10 Changing  $K$  with Changing Temperature

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## The Dynamics of Chemical Equilibrium

Reactants  $\rightleftharpoons$  Products

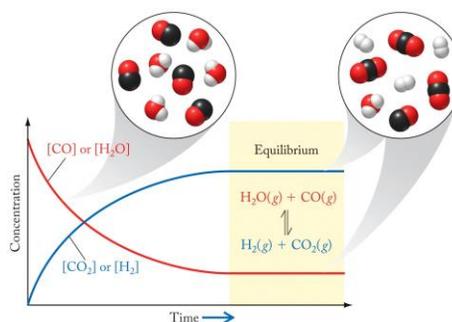
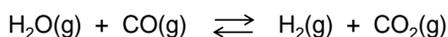
$\rightleftharpoons$  = symbol for equilibrium

Rate<sub>forward</sub> = Rate<sub>reverse</sub>

Equil. far to the right  
(product favored)  $\rightleftharpoons$

Equil. far to the left  
(reactant favored)  $\leftleftharpoons$

**Example:**

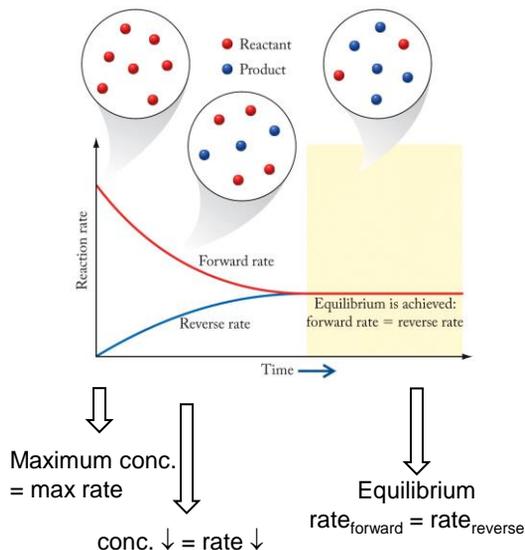


**Reversibility:**

If the rxn is interrupted by changing the T, conc. Reactants/products, then the rxn can be forced in the reverse direction

Le Chatelier's Principle

## Reaction Rate vs. Time



## Kinetics of a Reversible Reaction



From experiments it's known that the forward reaction rate is second order:

$$rate_{\text{forward}} = k_f [\text{NO}_2]^2$$

And the reverse rate is first order:

$$rate_{\text{reverse}} = k_r [\text{N}_2\text{O}_4]$$

At equilibrium that rates are equal:

$$k_f [\text{NO}_2]^2 = k_r [\text{N}_2\text{O}_4]$$



which can be rearranged to:

$$\frac{k_f}{k_r} = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} \quad \text{and finally}$$

$$K_{\text{eq}} = \frac{k_f}{k_r} \quad K_{\text{eq}} = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$$

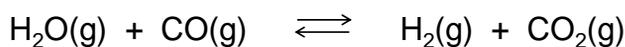
"Equilibrium constant"

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## Writing Equilibrium Constant Expressions



Consider 4 experiments with different starting concentrations in a sealed container which are then allowed to reach equilibrium:

**TABLE 14.1** Initial and Equilibrium Concentrations of the Reactants and Products in the Water–Gas Shift Reaction  $[\text{H}_2\text{O}(g) + \text{CO}(g) \rightleftharpoons \text{H}_2(g) + \text{CO}_2(g)]$  at 500 K

Experiment	INITIAL CONCENTRATION (M)				EQUILIBRIUM CONCENTRATION (M)			
	$[\text{H}_2\text{O}]$	$[\text{CO}]$	$[\text{H}_2]$	$[\text{CO}_2]$	$[\text{H}_2\text{O}]$	$[\text{CO}]$	$[\text{H}_2]$	$[\text{CO}_2]$
1	0.0200	0.0200	0	0	0.0034	0.0034	0.0166	0.0166
2	0	0	0.0200	0.0200	0.0034	0.0034	0.0166	0.0166
3	0.0100	0.0200	0.0300	0.0400	0.0046	0.0146	0.0354	0.0454
4	0.0200	0.0100	0.0200	0.0100	0.0118	0.0018	0.0282	0.0182

## The Law of Mass Action

Experiments 1 and 2	$\frac{[\text{H}_2][\text{CO}_2]}{[\text{H}_2\text{O}][\text{CO}]} = \frac{(0.0166)(0.0166)}{(0.0034)(0.0034)} = 24$
Experiment 3	$\frac{[\text{H}_2][\text{CO}_2]}{[\text{H}_2\text{O}][\text{CO}]} = \frac{(0.0354)(0.0454)}{(0.0046)(0.0146)} = 24$
Experiment 4	$\frac{[\text{H}_2][\text{CO}_2]}{[\text{H}_2\text{O}][\text{CO}]} = \frac{(0.0282)(0.0182)}{(0.0118)(0.0018)} = 24$

$$K = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = 24$$

## Generically for any reaction -



$$K_c = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b} \quad K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

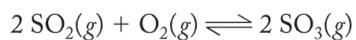
[X] = concentration in  
Molarity

$P_x$  = partial pressures  
(remember Dalton's Law)

Equilibrium constants are **unitless** (even though there could be different powers on each concentration)

**SAMPLE EXERCISE 14.1 Writing Equilibrium  
Constant Expressions****LO2**

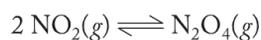
A key reaction in the formation of acid rain involves the reversible combination of  $\text{SO}_2$  and  $\text{O}_2$  in the atmosphere, producing  $\text{SO}_3$ :



Write the  $K_c$  and  $K_p$  expressions for this reaction.

**SAMPLE EXERCISE 14.2 Calculating the Value of  $K_c$** **LO3**

Table 14.2 contains data from four experiments on the dimerization of  $\text{NO}_2$ :



The experiments were run at  $100^\circ\text{C}$  in a rigid, closed container. Use the data from each experiment to calculate a value of the equilibrium constant  $K_c$  for the dimerization

**TABLE 14.2** Data for the Reaction  $2 \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$  at  $100^\circ\text{C}$

Experiment	INITIAL CONCENTRATION (M)		EQUILIBRIUM CONCENTRATION (M)	
	$[\text{NO}_2]$	$[\text{N}_2\text{O}_4]$	$[\text{NO}_2]$	$[\text{N}_2\text{O}_4]$
1	0.0200	0.0000	0.0172	0.00139
2	0.0300	0.0000	0.0244	0.00280
3	0.0400	0.0000	0.0310	0.00452
4	0.0000	0.0200	0.0310	0.00452

$$K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$$

$$\text{Experiment 1: } \frac{0.00139}{(0.0172)^2} = 4.70$$

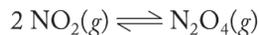
$$\text{Experiment 2: } \frac{0.00280}{(0.0244)^2} = 4.70$$

$$\text{Experiment 3: } \frac{0.00452}{(0.0310)^2} = 4.70$$

$$\text{Experiment 4: } \frac{0.00452}{(0.0310)^2} = 4.70$$

**SAMPLE EXERCISE 14.3** Calculating the Value of  $K_p$  **LO3**

A sealed chamber contains an equilibrium mixture of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  at  $300^\circ\text{C}$  and partial pressures  $P_{\text{NO}_2} = 0.101 \text{ atm}$  and  $P_{\text{N}_2\text{O}_4} = 0.074 \text{ atm}$ . What is the value of  $K_p$  for the following reaction under these conditions?



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## Relationships Between $K_c$ and $K_p$ Values

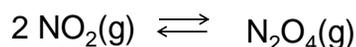
- As will be shown a little later in the chapter,  **$K_c$  does not necessarily equal  $K_p$**  when the number of moles of gaseous reactants isn't equal to the number of moles of gaseous products
- The mathematical relationship between  $K_c$  and  $K_p$  can be determined by starting with the **Ideal Gas Law**:

$$PV = nRT$$

$$P = \frac{n}{V}RT$$

$$P = MRT$$

Back to the example -





$$P_{\text{N}_2\text{O}_4} = \frac{n_{\text{N}_2\text{O}_4}}{V}RT = [\text{N}_2\text{O}_4]RT \quad P_{\text{NO}_2} = \frac{n_{\text{NO}_2}}{V}RT = [\text{NO}_2]RT$$

$$K_p = \frac{P_{\text{N}_2\text{O}_4}}{(P_{\text{NO}_2})^2} = \frac{[\text{N}_2\text{O}_4]RT}{([\text{NO}_2]RT)^2}$$

$$= \frac{[\text{N}_2\text{O}_4]RT}{[\text{NO}_2]^2(RT)^2} = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2(RT)} = K_c \frac{1}{RT}$$

$$K_p = K_c \frac{1}{RT} = K_c (RT)^{-1}$$



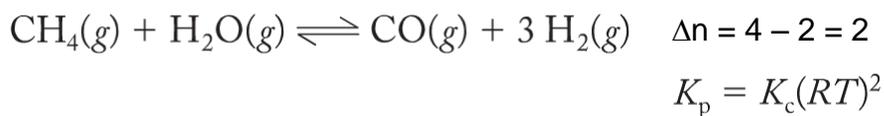
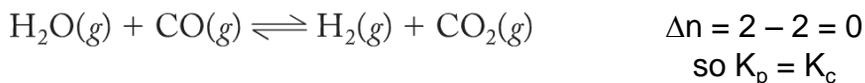
$\Delta n = \Sigma \text{ moles products} - \Sigma \text{ moles reactants}$

$$\Delta n = [c + d] - [a + b]$$

$$\begin{aligned} K_p &= \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} = \frac{([\text{C}]RT)^c ([\text{D}]RT)^d}{([\text{A}]RT)^a ([\text{B}]RT)^b} \\ &= \frac{[\text{C}]^c (RT)^c [\text{D}]^d (RT)^d}{[\text{A}]^a (RT)^a [\text{B}]^b (RT)^b} \\ &= \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \times \frac{(RT)^c (RT)^d}{(RT)^a (RT)^b} \\ &= \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \times \frac{(RT)^{c+d}}{(RT)^{a+b}} \\ &= \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \times (RT)^{[c+d]-[a+b]} \\ &= K_c (RT)^{\Delta n} \end{aligned}$$

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

Returning to the previous statement that  $K_c$  **does not necessarily equal**  $K_p$  when the number of moles of gaseous reactants isn't equal to the number of moles of gaseous products -



**SAMPLE EXERCISE 14.4** Calculating  $K_c$  from  $K_p$

**L04**

In Sample Exercise 14.3 we calculated the value of  $K_p$  (7.3) for the dimerization of  $\text{NO}_2$  to  $\text{N}_2\text{O}_4$  at  $300^\circ\text{C}$ . What is the value of  $K_c$  for this reaction at  $300^\circ\text{C}$ ?

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### Manipulating Equilibrium Constant Expressions

For this hypothetical reaction, let  $K_c = 100$



What is  $K_c$  for the reverse reaction?

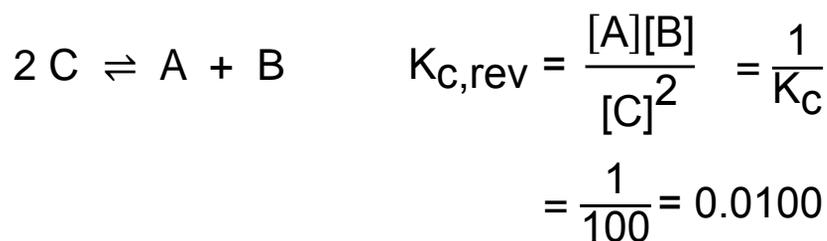


What is  $K_c$  for the rxn if the stoichiometric coefficients are mult/div by a number, e.g. divide by 2?



## *K for Reverse Reactions*

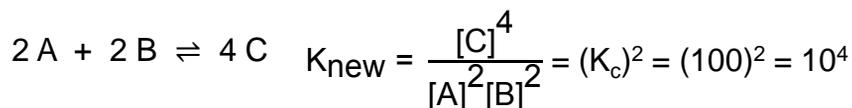
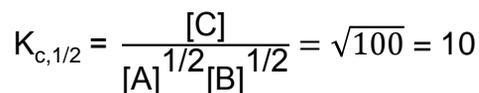
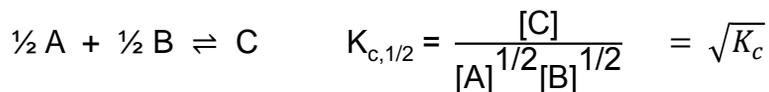
$$\textcircled{1} \quad K_{\text{reverse}} = 1/K_{\text{forward}}$$



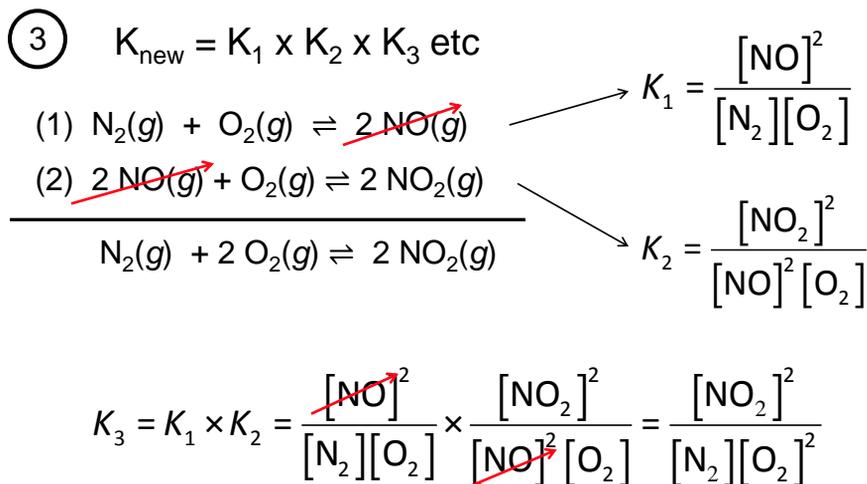
## *K for an Equation Multiplied/Divided by a Number*

$$\textcircled{2} \quad K_{\text{new}} = (K_c)^n \quad \text{where } n = 1, 2, 3 \text{ when multiplying}$$

and  $\frac{1}{2}, \frac{1}{3}, \frac{1}{4}$  etc when dividing



## Combining $K$ values



### SAMPLE EXERCISE 14.5 Calculating the $K$ Values of Related Chemical Reactions

L05

We learned in Chapter 13 that a key reaction in the formation of photochemical smog is the one between NO and atmospheric  $\text{O}_2$  that forms  $\text{NO}_2$ :

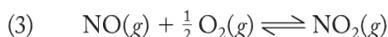


The  $K_p$  value of this reaction is  $2.4 \times 10^{12}$  at  $25^\circ\text{C}$ .

a. What is the  $K_p$  value of the decomposition of  $\text{NO}_2(g)$ ?

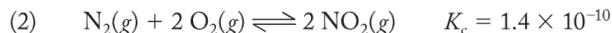
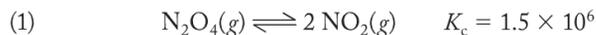


b. What is the  $K_p$  value of the reaction in which NO and  $\text{O}_2$  combine to form only one mole of  $\text{NO}_2$ ?

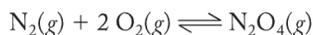


**SAMPLE EXERCISE 14.6 Calculating Overall  $K$  Values of Combined Reactions**
**L05**

At 1000 K, the  $K_c$  values of these reactions are as follows:



What is the  $K_c$  value at 1000 K of the reaction?



**COLLECT AND ORGANIZE** We are given two reactions and their  $K_c$  values. We need to combine the two reactions in such a way that  $\text{N}_2$  and  $\text{O}_2$  are on the reactant side of the overall equation and  $\text{N}_2\text{O}_4$  is on the product side and then calculate the  $K_c$  value of the overall reaction.

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## Equilibrium Constants and Reaction Quotients

### The Law of Mass Action:

$$K_{\text{eq}} = \frac{[\text{products}]^m}{[\text{reactants}]^n}$$

where  $m$  and  $n$  represent the stoichiometric coefficients.

Even if the **initial** concentrations of the reactants and products are different from experiment to experiment, once the system reestablishes equilibrium, the value of  $K_{\text{eq}}$  **remains the same**.

### Reaction Quotient (Q):

Has the same general form as  $K_{\text{eq}}$ , but the concentrations are not the equilibrium concentrations, but some starting, or initial, amount.

$$Q = \frac{[\text{products}]_o^m}{[\text{reactants}]_o^n}$$

where the subscript 'o' refers to initial

Just like  $K$ , there is a  $Q_c$  and a  $Q_p$



From Experiment 3 in Table 14.1, the initial concentrations of reactants and products are (note that I have added the 'o' sign):

$[\text{H}_2\text{O}]_o(\text{M})$	$[\text{CO}]_o(\text{M})$	$[\text{H}_2]_o(\text{M})$	$[\text{CO}_2]_o(\text{M})$
0.0100	0.0200	0.0300	0.0400

$$Q_c = \frac{[\text{H}_2][\text{CO}_2]}{[\text{H}_2\text{O}][\text{CO}]} = \frac{(0.0300)(0.0400)}{(0.0100)(0.0200)} = 6.00$$

From last slide

$[\text{H}_2\text{O}]_0 (M)$	$[\text{CO}]_0 (M)$	$[\text{H}_2]_0 (M)$	$[\text{CO}_2]_0 (M)$
0.0100	0.0200	0.0300	0.0400

$$Q_c = \frac{[\text{H}_2][\text{CO}_2]}{[\text{H}_2\text{O}][\text{CO}]} = \frac{(0.0300)(0.0400)}{(0.0100)(0.0200)} = 6.00$$

- Since  $Q_c$  is less than  $K_c = 24$ , that means that there are **more reactants and fewer products** than there are at equilibrium.
- So the reaction **will shift towards products** until  $Q_c = K_c$

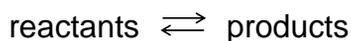
At equil.

$[\text{H}_2\text{O}] (M)$	$[\text{CO}] (M)$	$[\text{H}_2] (M)$	$[\text{CO}_2] (M)$
0.0046	0.0146	0.0354	0.0454

$$\frac{[\text{H}_2][\text{CO}_2]}{[\text{H}_2\text{O}][\text{CO}]} = \frac{(0.0354)(0.0454)}{(0.0046)(0.0146)} = 24$$

## Rate Laws and Equilibrium

What is the underlying cause of the shifting of the reaction towards equilibrium? Your book doesn't explicitly state that it's kinetics and rate laws.

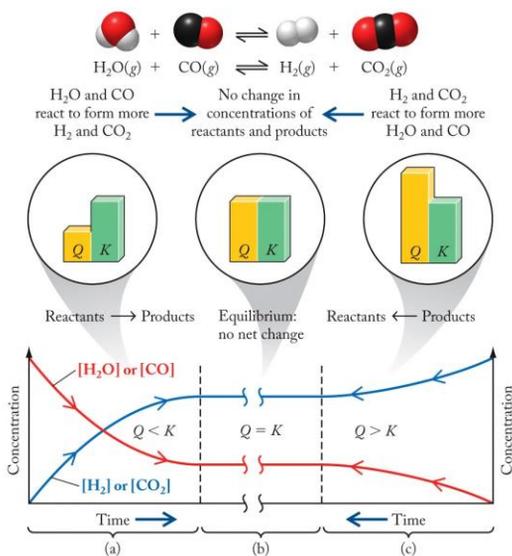


$$\text{rate}_f = \text{rate}_r$$

$$k_f [\text{reactants}]^m = k_r [\text{products}]^n$$

- In our reaction,  $Q_c = 6$  and  $K_c = 24$
- So the concentration of reactants is too high, and the concentration of products is too low
- Since there are more reactants present than at equil., the forward rate increases
- so the reaction shifts towards the right, generating more products until the system reestablishes equilibrium

# Summary

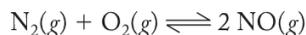


**TABLE 14.3 Comparison of  $Q$  and  $K$  Values**

Value of $Q$	What It Means
$Q < K$	Reaction as written proceeds in forward direction ( $\rightarrow$ )
$Q = K$	Reaction is at equilibrium ( $\rightleftharpoons$ )
$Q > K$	Reaction as written proceeds in reverse direction ( $\leftarrow$ )

## SAMPLE EXERCISE 14.7 Using $Q$ and $K$ Values to Predict the Direction of a Reaction LO6

At 2300 K the value of  $K$  of the following reaction is  $1.5 \times 10^{-3}$ :



At the instant when a reaction vessel at 2300 K contains  $0.50 \text{ M N}_2$ ,  $0.25 \text{ M O}_2$ , and  $0.0042 \text{ M NO}$ , is the reaction mixture at equilibrium? If not, in which direction will the reaction proceed to reach equilibrium?

$$Q = \frac{[\text{NO}]_0^2}{[\text{N}_2]_0[\text{O}_2]_0} \quad Q = \frac{(0.0042)^2}{(0.50)(0.25)} = 1.4 \times 10^{-4}$$

$$K = 1.5 \times 10^{-3}$$

Since  $K > Q$ , the reaction will shift to the right to produce more product, increasing  $Q$  until it equals  $K$

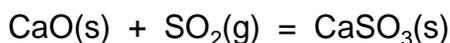
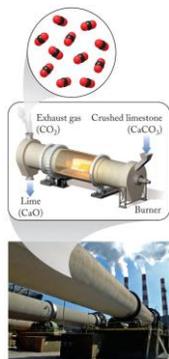
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## Heterogeneous Equilibria

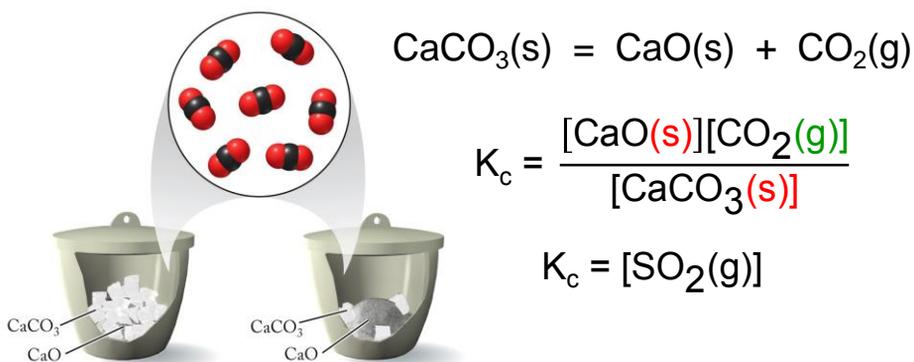
- **Homogeneous equilibria** - products and reactants are all in the same phase
- **Heterogeneous equilibria** - products and reactants are in different phases



$$K = \frac{[\text{CaO(s)}][\text{CO}_2(\text{g})]}{[\text{CaCO}_3(\text{s})]}$$

## Pure Solids and Liquids do not Appear in Equilibrium Constant Expressions

Do not appear in equil. const. expressions because there is so much mass per unit volume that the amount consumed is insignificant compared to aqueous or gas phase reactants and products.



### SAMPLE EXERCISE 14.8 Writing Equilibrium Constant Expressions for Heterogeneous Equilibria L02

Write  $K_c$  expressions for these reactions:

- $\text{CaO}(\text{s}) + \text{SO}_2(\text{g}) \rightleftharpoons \text{CaSO}_3(\text{s})$
- $\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq})$

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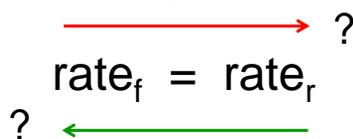
## Le Chatelier's Principle

If a system at equilibrium is perturbed (or stressed), the position of the equilibrium shifts in the direction that relieves the stress.

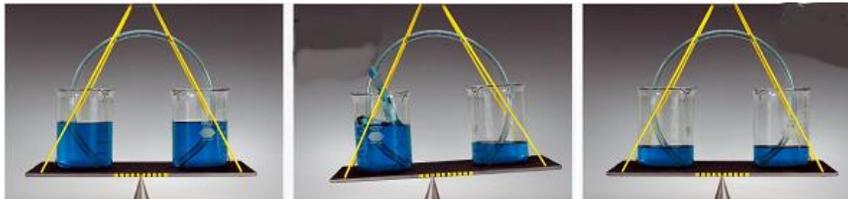


Henri Louis Le Chatelier

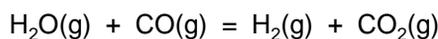
1. Effects of Adding or Removing Reactants or Products
2. Effects of Changes in Pressure and Volume
3. Effect of Temperature Changes



# 1. Effects of Adding or Removing Reactants or Products



**Industrial prep of  $H_2(g)$ :**



$$rate_f = rate_r \quad K = \frac{[H_2][CO_2]}{[H_2O][CO]}$$

**“Scrubbing”  $CO_2(g)$**   
Shifts 1<sup>st</sup> rxn towards  
products



$$Q = \frac{[H_2]_o[CO_2]_o}{[H_2O]_o[CO]_o}$$

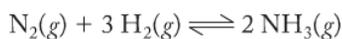
Now  $Q < K$

$rate_f > rate_r$

Until equilibrium re-established

## SAMPLE EXERCISE 14.9 Adding or Removing Reactants or Products to Stress an Equilibrium LO7

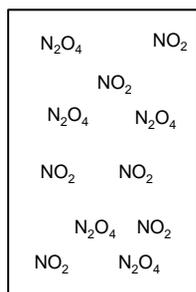
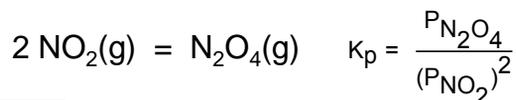
Suggest three ways the production of ammonia via the reaction



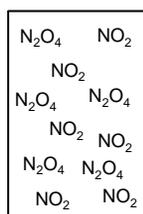
could be increased without changing the reaction temperature.

## 2. Effects of Changes in Pressure and Volume

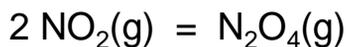
- A rxn with gas-phase reactants or products may be perturbed by changing the partial pressures of the gases
- A simple way to do this is to change the volume while keeping the temperature constant



Halve the  
volume  
⇒



At const T and n,  
according to **Boyle's Law** halving the  
volume will double the  
pressure.



$$K_p = \frac{P_{\text{N}_2\text{O}_4}}{(P_{\text{NO}_2})^2} = \frac{Y}{X^2}$$

- For clarity, **substitute X and Y** for the partial pressures
- After halving the volume and doubling the pressure, **calculate Q<sub>p</sub>** to determine which direction the equilibrium will shift

$$Q_p = \frac{2Y}{(2X)^2} = \frac{2Y}{4(X)^2} = \frac{Y}{2X^2} = \frac{1}{2} K_p$$

- **Q < K<sub>p</sub>**, so the amount of products needs to increase in order to re-attain equilibrium
- So the rxn shifts towards products

- Notice that there is a **total of 2 moles** of gas on the reactant side and **1 mole total** of gas on the product side
- Since there are **fewer moles on the product side**, shifting the rxn to the right **decreases the total number of moles** in the reaction chamber
- When the total number of moles decreases, so does the pressure, and then equilibrium is re-established
- Conversely, if the **volume of the reaction chamber increases**, then the rxn would **shift towards reactants** in order to increase the total pressure

**SAMPLE EXERCISE 14.10 Assessing the Effect of Compression on Gas-Phase Equilibria L07**

In which of the following reactions would isothermal compression of a reaction mixture at equilibrium promote the formation of more product(s)?

- a.  $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}(g)$
- b.  $2 \text{NO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}_2(g)$
- c.  $\text{N}_2\text{O}_4(g) \rightleftharpoons 2 \text{NO}_2(g)$
- d.  $\text{H}_2\text{O}(\ell) + \text{CO}_2(g) \rightleftharpoons \text{H}_2\text{CO}_3(aq)$
- e.  $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$

Reaction	Moles of Gaseous Reactants	Moles of Gaseous Products
a	2	2
b	3	2
c	1	2
d	1	0
e	0	1

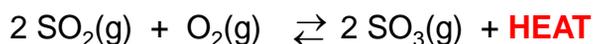
### 3. Effect of Temperature Changes

The only perturbation that changes the value of the equilibrium constant  $K$ . More in Section 14.10

- **Changes in Temperature** - Exothermic Reactions



Reaction gives off heat so THINK OF AS A PRODUCT



#### Change

#### Shifts the Equilibrium

Increase temperature (add product)

left

Decrease temperature (remove product)

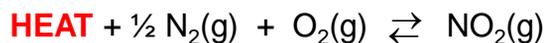
right

### 3. Effect of Temperature Changes

- **Changes in Temperature** - Endothermic Reactions



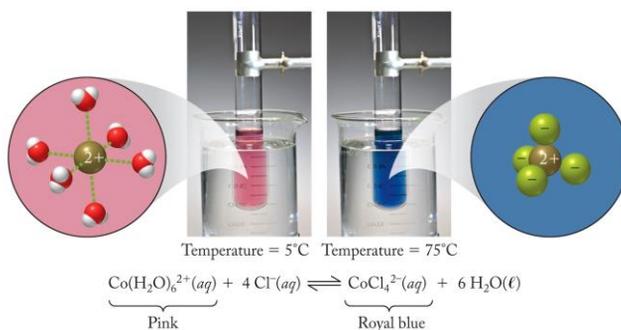
Reaction absorbs heat so THINK OF AS A REACTANT



<u>Change</u>	<u>Shifts the Equilibrium</u>
Increase temperature (add "reactant")	right
Decrease temperature ("remove reactant")	left

**SAMPLE EXERCISE 14.11** Predicting How Temperature Changes Impact Chemical Equilibria L07

The color of an aqueous acidic solution of cobalt(II) chloride depends on the temperature (Figure 14.9). In aqueous HCl, the solution is pink at 0°C, magenta at 25°C, and dark blue at 75°C. Is the reaction producing the pink-to-blue color change exothermic or endothermic?



## Summary - Changes in Concentration

**TABLE 14.4** Responses of an Exothermic Reaction [ $2 \text{A(g)} \rightleftharpoons \text{B(g)}$ ] at Equilibrium to Different Kinds of Stress

Kind of Stress	How Stress Is Relieved	Direction of Shift
Add A	Consume A	To the right
Remove A	Produce A	To the left
Add B	Consume B	To the left
Remove B	Produce B	To the right

## Summary - Changes in Pressure and Volume

**TABLE 14.4** Responses of an Exothermic Reaction [ $2 \text{A(g)} \rightleftharpoons \text{B(g)}$ ] at Equilibrium to Different Kinds of Stress

Kind of Stress	How Stress Is Relieved	Direction of Shift
Increase pressure by compressing the reaction mixture	Consume A to relieve pressure increase	To the right
Decrease pressure by expanding volume	Produce A to maintain equilibrium pressure	To the left

## Summary - Changes in Temperature

- **Exothermic Reactions**

Reaction gives off heat so THINK OF AS A PRODUCT

<u>Change</u>	<u>Shifts the Equilibrium</u>
Increase temperature (add product)	left
Decrease temperature (remove product)	right

- **Endothermic Reactions**

Reaction absorbs heat so THINK OF AS A REACTANT

<u>Change</u>	<u>Shifts the Equilibrium</u>
Increase temperature (add reactant)	right
Decrease temperature (remove reactant)	left

## Chapter Outline

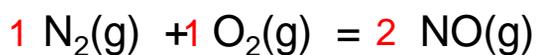
- 14.1 The Dynamics of Chemical Equilibrium
- 14.2 Writing Equilibrium Constant Expressions
- 14.3 Relationships between  $K_c$  and  $K_p$  Values
- 14.4 Manipulating Equilibrium Constant Expressions
- 14.5 Equilibrium Constants and Reaction Quotients
- 14.6 Heterogeneous Equilibria
- 14.7 Le Châtelier's Principle
- **14.8 Calculations Based on  $K$**
- 14.9 Equilibrium and Thermodynamics
- 14.10 Changing  $K$  with Changing Temperature

## Calculations Based on $K$

1. We want to determine whether a reaction mixture has reached equilibrium (Sample Exercise 14.7)
2. We know the value of  $K$  and the starting concentrations or partial pressures of reactant and/or products, and we want to calculate their equilibrium concentrations or pressures

$$K = \frac{[\text{products}]^m}{[\text{reactants}]^n}$$

## The "RICE" Table



Reaction	$\text{N}_2(\text{g})$	+	$\text{O}_2(\text{g})$	$\rightleftharpoons$	$2 \text{ NO}(\text{g})$
	$P_{\text{N}_2} \text{ (atm)}$		$P_{\text{O}_2} \text{ (atm)}$		$P_{\text{NO}} \text{ (atm)}$
<b>Initial</b>	0.79		0.21		0
<b>Change</b>	$-x$		$-x$		$+2x$
<b>Equilibrium</b>	$0.79 - x$		$0.21 - x$		$2x$

## Algebra

$$ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Reaction	$\text{N}_2(\text{g})$	+	$\text{O}_2(\text{g})$	$\rightleftharpoons$	$2 \text{NO}(\text{g})$
	$P_{\text{N}_2} \text{ (atm)}$		$P_{\text{O}_2} \text{ (atm)}$		$P_{\text{NO}} \text{ (atm)}$
<b>Initial</b>	0.79		0.21		0
<b>Change</b>	$-x$		$-x$		$+2x$
<b>Equilibrium</b>	$0.79 - x$		$0.21 - x$		$2x$

$$K_p = \frac{(P_{\text{NO}})^2}{(P_{\text{N}_2})(P_{\text{O}_2})} = \frac{(2x)^2}{(0.79 - x)(0.21 - x)}$$

$$= \frac{(2x)^2}{(0.79 - x)(0.21 - x)} = \frac{4x^2}{0.1659 - 1.00x + x^2} = 1.00 \times 10^{-5}$$

$$1.659 \times 10^{-6} - (1.00 \times 10^{-5})x + (1.00 \times 10^{-5})x^2 = 4x^2$$

$$\underbrace{3.99999}_{a} x^2 + \underbrace{(1.00 \times 10^{-5})}_{b} x - \underbrace{1.659 \times 10^{-6}}_{c} = 0$$

$$P_{\text{O}_2} = 0.21 - x$$

$$= 0.21 - (6.428 \times 10^{-4}) = 0.21 \text{ atm}$$

$$P_{\text{N}_2} = 0.79 - x$$

$$= 0.79 - (6.428 \times 10^{-4}) = 0.79 \text{ atm}$$

$$P_{\text{NO}} = 2x$$

$$= 2(6.428 \times 10^{-4}) = 1.2855 \times 10^{-3} = 0.0013 \text{ atm}$$

### *Approximations to Simplify the Math*

$$K_p = \frac{(P_{\text{NO}})^2}{(P_{\text{N}_2})(P_{\text{O}_2})} = \frac{(2x)^2}{(0.79 - x)(0.21 - x)} \quad K_p = 1.00 \times 10^{-5}$$

$$x = 6.428 \times 10^{-4}$$

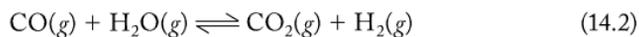
*The algebra also simplifies when the concentrations of reactants are the same.*

Reaction	$\text{N}_2(g)$	+	$\text{O}_2(g)$	$\rightleftharpoons$	$2 \text{NO}(g)$
	$[\text{N}_2] (M)$		$[\text{O}_2] (M)$		$[\text{NO}] (M)$
<b>Initial</b>	0.100		0.100		0
<b>Change</b>	$-x$		$-x$		$+2x$
<b>Equilibrium</b>	0.100		0.100		$2x$

**SAMPLE EXERCISE 14.12 Calculating an Equilibrium Partial Pressure I**

**LO8**

Much of the  $\text{H}_2$  used in the Haber–Bosch process is produced by the water–gas shift reaction:

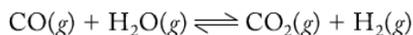


If a reaction vessel at  $400^\circ\text{C}$  is filled with an equimolar mixture of CO and steam such that  $P_{\text{CO}} = P_{\text{H}_2\text{O}} = 2.00 \text{ atm}$ , what is the partial pressure of  $\text{H}_2$  at equilibrium? The equilibrium constant  $K_p = 10$  at  $400^\circ\text{C}$ .

SAMPLE EXERCISE 14.13 **Calculating an Equilibrium Partial Pressure II**

L08

Suppose that in a reaction vessel running the water–gas shift reaction,



at 400°C the initial partial pressures are  $P_{\text{CO}} = 2.00$  atm,  $P_{\text{H}_2\text{O}} = 2.00$  atm,  $P_{\text{H}_2} = 0.15$  atm, and  $P_{\text{CO}_2} = 0.00$  atm. What is the partial pressure of  $\text{H}_2$  at equilibrium, given  $K_p = 10$  at 400°C?

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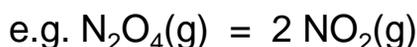
- 14.1 The Dynamics of Chemical Equilibrium
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## Equilibrium and Thermodynamics

It won't be derived here, but there is a relationship between  $\Delta G$  and the reaction quotient  $Q$  -

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

This equation incorporates  $Q$  and therefore also predicts in which direction an equilibrium will shift

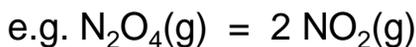


**Case 1:** Under standard conditions of 1.0 atm,  $\Delta G^{\circ} = + 4.8 \text{ kJ}$

$$\begin{aligned} \Delta G_{\text{rxn}}^{\circ} &= \sum n_{\text{products}} \Delta G_{\text{f,products}}^{\circ} - \sum n_{\text{reactants}} \Delta G_{\text{f,reactants}}^{\circ} \\ &= 2 \text{ mol} (51.3 \text{ kJ/mol}) - 1 \text{ mol} (97.8 \text{ kJ/mol}) = +4.8 \text{ kJ} \end{aligned}$$

So the reaction **under standard conditions** is non-spontaneous, but...

**Case 2:** What if at 298K there is only 1 atm of  $\text{N}_2\text{O}_4(\text{g})$  and virtually no  $\text{NO}_2(\text{g})$  ?



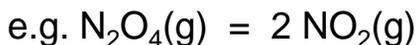
$$Q_p = \frac{P_{\text{NO}_2(\text{g})}^2}{P_{\text{N}_2\text{O}_4(\text{g})}} = \frac{\approx 0}{1} \approx 0$$

$Q_p < K$  and the reaction shifts towards products

$$\Delta G = \Delta G^{\circ} + \underbrace{RT \ln Q}_{-\infty}$$

So  $\Delta G \lllll 0$  and the reaction is spontaneous

**Case 3:** What if at 298K there is only 1 atm of  $\text{NO}_2(\text{g})$  and virtually no  $\text{N}_2\text{O}_4(\text{g})$  ?



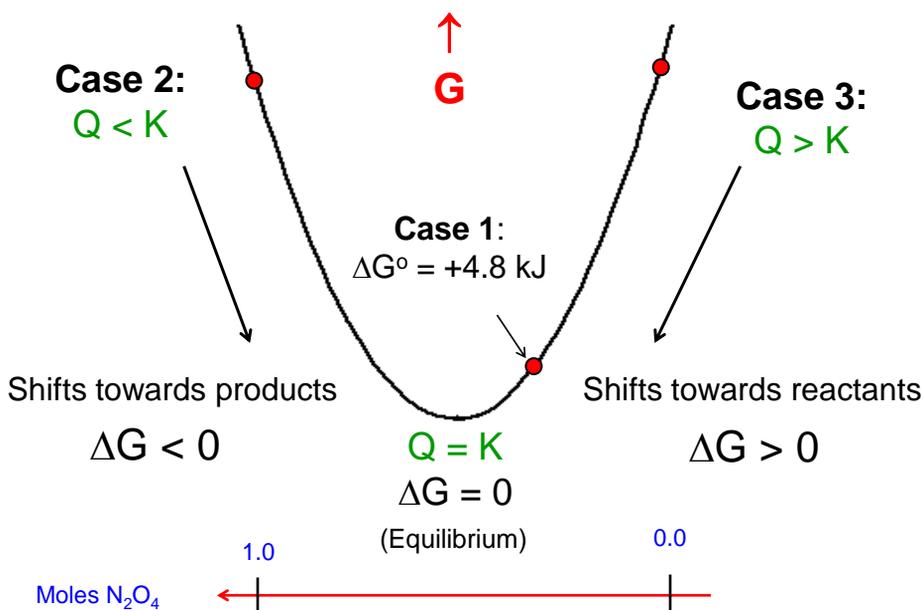
$$Q_p = \frac{P_{\text{NO}_2(\text{g})}^2}{P_{\text{N}_2\text{O}_4(\text{g})}} = \frac{1}{\approx 0} \approx \infty$$

$Q_p > K$  and the reaction shifts towards reactants

$$\Delta G = \underbrace{\Delta G^0}_{\infty} + \underbrace{RT \ln Q}_{\infty}$$

So  $\Delta G \gg \gg \gg 0$  so the reverse rxn is nonspontaneous

The point is that reactions shift in a direction that minimizes the available free energy of a system



## The Relationship Between $\Delta G$ and $K$

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

And since  $Q = K$   
at equilibrium

$$\Delta G = \Delta G^{\circ} + RT \ln K$$

And since  $\Delta G = 0$   
at equilibrium

$$0 = \Delta G^{\circ} + RT \ln K$$

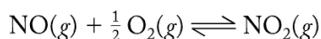
$$\Delta G^{\circ} = -RT \ln K \quad \Longrightarrow \quad \frac{\Delta G^{\circ}}{-RT} = \ln K$$

$$\Longrightarrow \quad K = e^{-\Delta G^{\circ}/RT}$$

### SAMPLE EXERCISE 14.14 Relating $K$ and $\Delta G^{\circ}_{\text{rxn}}$

L09

Use  $\Delta G_f^{\circ}$  values from Table A4.3 to calculate  $\Delta G^{\circ}_{\text{rxn}}$  and the value of  $K$  for the formation of  $\text{NO}_2$  from  $\text{NO}$  and  $\text{O}_2$  at 298 K:



$$\begin{aligned} \Delta G^{\circ}_{\text{rxn}} &= [\Delta G_f^{\circ}(\text{NO}_2)] - [\Delta G_f^{\circ}(\text{NO}) + \frac{1}{2} \Delta G_f^{\circ}(\text{O}_2)] \\ &= [1 \text{ mol } (51.3 \text{ kJ/mol})] - [1 \text{ mol } (86.6 \text{ kJ/mol}) + \frac{1}{2} \text{ mol } (0.0 \text{ kJ/mol})] \\ &= -35.3 \text{ kJ} \end{aligned}$$

$$-\frac{\Delta G^{\circ}_{\text{rxn}}}{RT} = -\frac{\left(\frac{-35,300 \text{ J}}{\text{mol}}\right)}{\left(\frac{8.314 \text{ J}}{\text{mol} \cdot \text{K}}\right)(298 \text{ K})}$$

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- 14.1 The Dynamics of Chemical Equilibrium
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- **14.10 Changing  $K$  with Changing Temperature**

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## Temperature, $K$ and $\Delta G^\circ$

Derivation of the relationship between  $\Delta K$ ,  $\Delta H$ , and  $T$  starting with -

$$\ln K = -\frac{\Delta G^\circ}{RT} \quad \text{and} \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\ln K = -\frac{(\Delta H^\circ - T\Delta S^\circ)}{RT}$$

$$\ln K = -\frac{\Delta H^\circ}{RT} - \left(-\frac{T\Delta S^\circ}{RT}\right)$$

$$\boxed{\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}}$$

## Linearization: $\ln K$ vs. $1/T$

### Simultaneous Measurement of $\Delta H^\circ_{\text{rxn}}$ and $\Delta S^\circ_{\text{rxn}}$

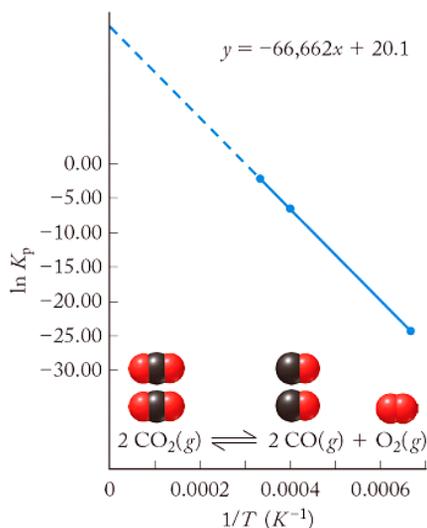
$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

$$\ln K = \underbrace{-\frac{\Delta H^\circ}{R}}_m \frac{1}{T} + \underbrace{\frac{\Delta S^\circ}{R}}_b$$

$$y = m x + b$$

$$m = -\frac{\Delta H^\circ}{R}$$

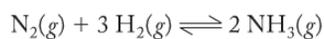
$$b = \frac{\Delta S^\circ}{R}$$



#### SAMPLE EXERCISE 14.15 Calculating an Equilibrium Constant Value at a Specific Temperature

LO10

Use data from Appendix 4 to calculate the equilibrium constant  $K_p$  for the exothermic reaction



at 298 K and at 773 K, a typical temperature used in the Haber–Bosch process for synthesizing ammonia.