

# Chapter 14: Chemical Equilibrium

## Chemical Equilibrium

- What does it mean to describe a chemical reaction as being in a state of *dynamic equilibrium*?

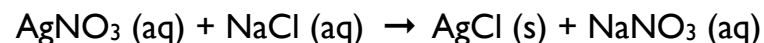
What are the *characteristics* and *requirements* of dynamic equilibrium?

- What does the equilibrium constant, K represent?
- How can we determine (*quantitatively*) the composition of a reaction mixture when it is at a state of dynamic equilibrium?
- How do specific changes made to a system at equilibrium affect the equilibrium position?

*qualitatively* understand changes

## Dynamic Chemical Equilibrium

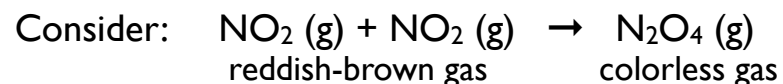
- To date, we have mostly focussed on describing chemical reactions as going to completion:



identify limiting reactant

calculate theoretical & percent yields

- For many chemical reactions, this discussion is not appropriate because they do not go to completion.
- For these reactions we want to talk about:  
when they reach dynamic equilibrium  
[reactants] & [products] present at equilibrium



- put  $\text{NO}_2 (\text{g})$  in a sealed container at  $25^\circ\text{C}$
- see decrease in intensity of brown color as  $\text{NO}_2$  is converted to  $\text{N}_2\text{O}_4$
- contents of container never go completely colorless  $\therefore$  the reaction does not go to completion
- at some point the intensity of brown color stops changing  $\therefore$  the  $[\text{NO}_2]$  is constant
- the system has reached a state of dynamic equilibrium



$\text{NO}_2$

$\text{N}_2\text{O}_4$

For a system at equilibrium:

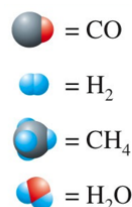
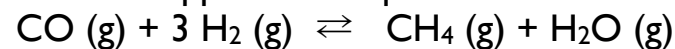
- both forward and reverse reactions are occurring simultaneously
- rate of forward reaction must equal rate of reverse reaction

OR

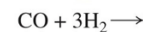
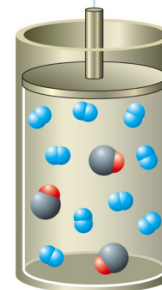
$$\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$$

- concentrations of reactants and products remain constant with time

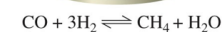
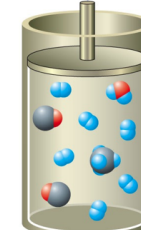
## Changes in Rate and Concentration as a System Approaches Equilibrium:



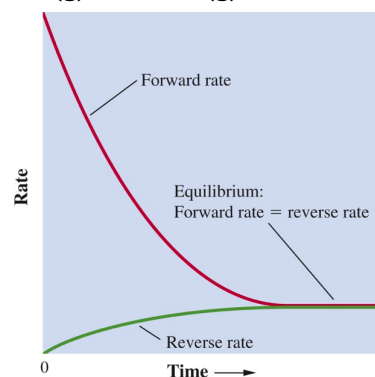
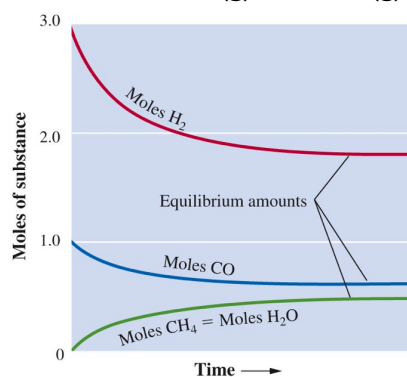
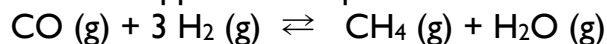
Initially, only the reaction  $\text{CO} + 3\text{H}_2 \rightarrow$  occurs, because the concentrations of  $\text{CH}_4$  and  $\text{H}_2\text{O}$  are zero.



Later, as this reaction proceeds, the concentrations of  $\text{CH}_4$  and  $\text{H}_2\text{O}$  increase, and the reaction  $\text{CH}_4 + \text{H}_2\text{O} \rightarrow$  begins. The rate of the reaction  $\text{CH}_4 + \text{H}_2\text{O} \rightarrow$  steadily increases, whereas the rate of the reaction  $\text{CO} + 3\text{H}_2 \rightarrow$  decreases. Eventually, the two rates become equal.



## Changes in Rate and Concentration as a System Approaches Equilibrium:



Equilibrium is achieved at the point when:

- $[\text{H}_2]$ ,  $[\text{CO}]$ ,  $[\text{CH}_4]$ , and  $[\text{H}_2\text{O}]$  are constant with time
- rate of  $\text{CO} + 3 \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$  is the same as the rate of  $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3 \text{H}_2$

## Position of Chemical Equilibrium

- the *equilibrium position* refers to the relative amounts of reactants and products in the system at the point of equilibrium
- a reaction with an equilibrium position that favors the products :

$[\text{product}] > [\text{reactant}]$  at equilibrium  
equilibrium lies to the right

- a reaction with an equilibrium position that favors the reactants :

$[\text{reactant}] > [\text{product}]$   
equilibrium lies to the left

## The Equilibrium Constant, K

What is the quantitative relationship between [reactants] & [products] present in a system at equilibrium?

- established by Guldberg & Waage in 1864
- Law of Mass Action
- concentrations of reactants and products in a mixture at equilibrium always satisfy a specific, mathematic relationship

*Stay tuned!*

## Concentrations of Reactants & Products at Equilibrium

consider the reaction:  $2 \text{SO}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2 \text{SO}_3 (\text{g})$

- reaction run multiple times
- same temperature ( $T = 1000 \text{ K}$ )
- initial concentrations of reactants changed
- equilibrium concentrations of all species determined

exp't	$[\text{O}_2]_{\text{eq, M}}$	$[\text{SO}_2]_{\text{eq, M}}$	$[\text{SO}_3]_{\text{eq, M}}$	$K_C$
1	0.390	0.660	0.0840	
2	0.220	0.380	0.00360	
3	0.110	0.110	0.00750	
4	0.880	0.950	0.180	
5	1.98	1.44	0.410	

- there is no obvious trend in the concentration data until it is treated in this way:

$$K_C = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$$

exp't	$[\text{O}_2]_{\text{eq, M}}$	$[\text{SO}_2]_{\text{eq, M}}$	$[\text{SO}_3]_{\text{eq, M}}$	$K_C$
1	0.390	0.660	0.0840	0.0415
2	0.220	0.380	0.00360	0.0409
3	0.110	0.110	0.00750	0.0423
4	0.880	0.950	0.180	0.0408
5	1.98	1.44	0.410	0.0409

## The Law of Mass Action

- the concentrations of reactants and products in a mixture at equilibrium always satisfy a specific relationship
- for a reaction:  $a \text{A} + b \text{B} \rightleftharpoons c \text{C} + d \text{D}$

$$K_C = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$$

- this is called the equilibrium expression
- $K_C$  – the subscript “C” represents that this is the equilibrium constant in terms of molar concentrations

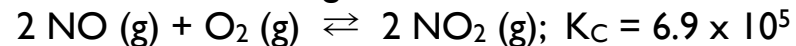
## The Equilibrium Constant

$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- ♦ typically unitless
- ♦ concentrations used are relative to a standard molar concentration of 1M
- ♦ dependent on specific reaction
- ♦ dependent on temperature
- ♦ dependent on equilibrium composition
- ♦ independent of initial concentrations

example:

Consider the following reaction at 500 K:



This reaction is allowed to reach equilibrium, and then analyzed and found to contain the following concentrations:

$$[\text{O}_2] = 1.0 \times 10^{-3} \text{ M} \quad [\text{NO}_2] = 5.0 \times 10^{-2} \text{ M}$$

Write the equilibrium expression for this reaction, and then determine the equilibrium concentration of NO (g).

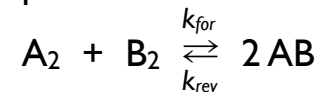
- ♦ What does the magnitude of  $K_C$  tell you about a chemical reaction and its equilibrium position?

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

- ♦ if  $K_C > 1 \dots$   
[products] > [reactants]  
equilibrium position *favors products*  
equilibrium position *lies to the right*
- ♦ if  $K_C < 1 \dots$   
[reactants] > [products]  
equilibrium position *favors reactants*  
equilibrium position *lies to the left*

## Relationship Between Kinetics and Equilibrium: K and k

- ♦ consider the equilibrium:



- ♦ when this system is at equilibrium:

$$\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$$

- ♦ the rate laws:

$$\text{Rate}_{\text{forward}} = k_{\text{for}}[\text{A}_2][\text{B}_2] \quad \text{Rate}_{\text{reverse}} = k_{\text{rev}}[\text{AB}]^2$$

$$k_{\text{for}}[\text{A}_2][\text{B}_2] = k_{\text{rev}}[\text{AB}]^2$$
$$\frac{k_{\text{for}}}{k_{\text{rev}}} = \frac{[\text{AB}]^2}{[\text{A}_2][\text{B}_2]} = K_C$$

## Relationship Between Kinetics and Equilibrium:

K and k

$$\frac{k_{\text{for}}}{k_{\text{rev}}} = \frac{[\text{AB}]^2}{[\text{A}_2][\text{B}_2]} = K_C$$

- ♦ if  $k_{\text{for}} > k_{\text{rev}}$   
 $K_C > 1$   
forward reaction is favored  
equilibrium position lies to the *right*
- ♦ if  $k_{\text{for}} < k_{\text{rev}}$   
 $K_C < 1$   
reverse reaction is favored  
equilibrium position lies to the *left*
- ♦ typically,  $k_{\text{for}} \neq k_{\text{rev}}$

## $K_C$ Values for Related Reactions

- ♦ How does  $K_C$  change if a chemical reaction is written in *reverse*?
- ♦ How does  $K_C$  change if the stoichiometric coefficients of a chemical reaction are changed (i.e. multiplied by  $n$ )?
- ♦ How do you determine  $K_C$  for a chemical reaction if you can write it as the sum of 2 or more chemical reactions?

## $K_C$ Values for Related Reactions

- ♦ How does  $K_C$  change if a chemical reaction is written in *reverse*?

consider:  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g}); K_C = 54$

and:  $2 \text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g}); K_{C1} = ???$

$$K_C = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = 54$$

and

$$K_{C1} = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = (K_C)^{-1} = 0.018$$

- ♦ If you write a chemical equation in reverse, the new equilibrium constant is equal to the reciprocal of the original equilibrium constant.

## $K_C$ Values for Related Reactions

- ♦ How does  $K_C$  change if the stoichiometric coefficients of a chemical reaction are changed (i.e. multiplied by  $n$ )?

consider:  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g}); K_C = 54$

and:  $2 \text{H}_2(\text{g}) + 2 \text{I}_2(\text{g}) \rightleftharpoons 4 \text{HI}(\text{g}); K_{C2} = ???$

$$K_C = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = 54$$

and

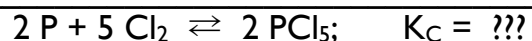
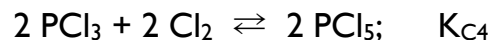
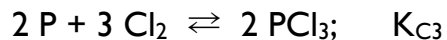
$$K_{C2} = \frac{[\text{HI}]^4}{[\text{H}_2]^2[\text{I}_2]^2} = (K_C)^2 = 2900$$

- ♦ If the stoichiometric coefficients of a chemical reaction are multiplied by some factor,  $n$ , the equilibrium constant for the reaction must be raised to the  $n^{\text{th}}$  power.

### K<sub>C</sub> Values for Related Reactions

- How do you determine K<sub>C</sub> for a chemical reaction if you can write it as the sum of 2 or more chemical reactions?

- consider combining the following equations:



$$K_C = K_{C3} \cdot K_{C4}; \quad K_C = \frac{[\text{PCl}_5]^2}{[\text{Cl}_2]^5[\text{P}]^2} = \frac{[\text{PCl}_3]^2}{[\text{Cl}_2]^3[\text{P}]^2} \cdot \frac{[\text{PCl}_5]^2}{[\text{Cl}_2]^2[\text{PCl}_3]^2}$$

- If a chemical reaction can be expressed as the sum of 2 or more chemical equations, the equilibrium constant for the overall reaction is the product of the equilibrium constants for the component reactions.

### Summary of K's for Related Equations:

Chemical Equation	Equilibrium Constant
$a \text{A} + b \text{B} \rightleftharpoons c \text{C} + d \text{D}$	$K_C$
$c \text{C} + d \text{D} \rightleftharpoons a \text{A} + b \text{B}$	$K_{C1} = (K_C)^{-1}$
$(n \cdot a) \text{A} + (n \cdot b) \text{B} \rightleftharpoons (n \cdot c) \text{C} + (n \cdot d) \text{D}$	$K_{C2} = (K_C)^n$
sum of 2 reactions with $K_{C3}$ & $K_{C4}$	$K_C = (K_{C3})(K_{C4})$

### Equilibrium Constant, K<sub>P</sub>

- for gas phase reaction mixtures, we can consider the *partial pressures* of reactants and products present at equilibrium

- consider:  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$

$$K_P = \frac{(P_{\text{HI}})^2}{(P_{\text{H}_2})(P_{\text{I}_2})}$$

- relationship between K<sub>C</sub> and K<sub>P</sub> for a reaction at a given temperature is:

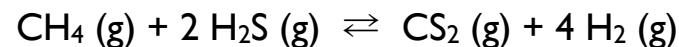
$$K_P = K_C(RT)^{\Delta n}$$

$\Delta n = \text{mol gas phase product} - \text{mol gas phase reactant}$

$$K_P = K_C \text{ when } \Delta n = 0$$

example:

CH<sub>4</sub> reacts with H<sub>2</sub>S to form H<sub>2</sub> and CS<sub>2</sub>:



Determine the value of K<sub>P</sub> for this reaction at 1000 K if the following equilibrium pressures were measured:

$$P_{\text{CH}_4} = 0.20 \text{ atm}$$

$$P_{\text{H}_2\text{S}} = 0.25 \text{ atm}$$

$$P_{\text{CS}_2} = 0.52 \text{ atm}$$

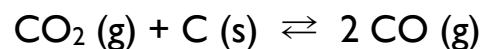
$$P_{\text{H}_2} = 0.10 \text{ atm}$$

Determine the value of K<sub>C</sub> for this reaction at 1000 K.

## Heterogeneous Equilibria

- heterogeneous equilibria – reactants and products are present in more than one phase

examples:

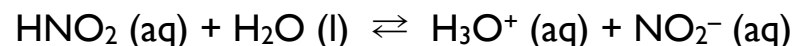


- concentrations of pure liquids and pure solids are constant and do not change
- bottom line – *solids and liquids are not included in the equilibrium expression*

## Heterogeneous Equilibria

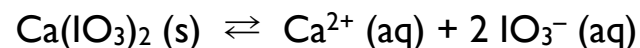
two very important examples for upcoming chapters

- heterogeneous equilibria involving weak acids and/or weak bases:



$$K_C = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]}$$

- heterogeneous equilibria involving the solubility of ionic compounds:



$$K_C = [\text{Ca}^{2+}][\text{IO}_3^-]^2$$

## Predicting the Direction of Change:

Q vs K

- How do you decide if a system is at equilibrium?

OR

- If a system is *not* at equilibrium, does it proceed in the *forward* or *reverse* direction to reach equilibrium?
- use “arbitrary initial concentrations” to calculate the reaction quotient,  $Q_C$

for the reaction:  $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$

$$Q_C = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$$

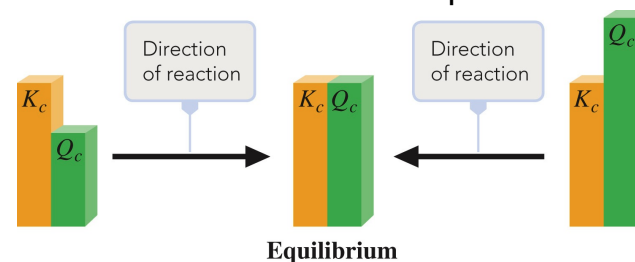
## Predicting the Direction of Change: Q vs K

- compare Q and K

if  $Q = K$ : the system is at equilibrium

if  $Q < K$ : the system is *not* at equilibrium  
the reaction proceeds in the forward direction to reach equilibrium

if  $Q > K$ : the system is *not* at equilibrium  
the reaction proceeds in the reverse direction to reach equilibrium



example:

Consider the following reaction:



A 5.0 L vessel contains 0.060 mol NO, 1.0 mol O<sub>2</sub>, and 0.80 mol NO<sub>2</sub>.

Is this system at equilibrium?

If the system is not at equilibrium, does the reaction proceed in the *forward* or *reverse* direction to reach equilibrium?

### Process for Solving Equilibrium Problems: Using an Equilibrium (or ICE) Table

- ♦ start with balanced chemical equation
- ♦ 3 rows for each gas or sol'n phase species:
  - initial* concentration or pressure
  - change* ( $\Delta$ ) in concentration or pressure as system moves to equilibrium
  - equilibrium* concentration or pressure

### Process for Solving Equilibrium Problems: Using an Equilibrium (or ICE) Table

consider the reaction:  $2 \text{A} (\text{g}) + \text{B} (\text{g}) \rightleftharpoons 3 \text{C} (\text{g})$

	2 A (g)	+	B (g)	$\rightleftharpoons$	3 C (g)
initial [ ]	1.00 M		2.00 M		0
$\Delta$ [ ]	- 2x		- x		+ 3x
equil [ ]	(1.00 - 2x) M		(2.00 - x) M		3x M

notes:

- ♦ reactants A and B are consumed, so their  $\Delta$  [ ] is -
- ♦ product C is formed, so its  $\Delta$  [ ] is +
- ♦ equil [ ]'s are the sum of the initial [ ] row and the  $\Delta$  [ ] row
- ♦ if we start with true initial data - *before any reaction has occurred*, initial [product] = 0

### Process for Solving Equilibrium Problems: Using an Equilibrium (or ICE) Table

consider the reaction:  $2 \text{A} (\text{g}) + \text{B} (\text{g}) \rightleftharpoons 3 \text{C} (\text{g})$

	2 A (g)	+	B (g)	$\rightleftharpoons$	3 C (g)
initial [ ]	1.00 M		2.00 M		0
$\Delta$ [ ]	- 2x		- x		+ 3x
equil [ ]	(1.00 - 2x) M		(2.00 - x) M		3x M

- ♦ what we *don't know*:

How much A and B will be *consumed* (and how much C *will form*) to get the system to equilibrium?

OR - we don't know how [A], [B], and [C] will change as system approaches equilibrium

$\therefore$  define our unknown "x"



Process for Solving Equilibrium Problems:  
Using an Equilibrium (or ICE) Table

consider the reaction:  $2 A (g) + B (g) \rightleftharpoons 3 C (g)$

	2 A (g)	+	B (g)	$\rightleftharpoons$	3 C (g)
initial [ ]	1.00 M		2.00 M		0
$\Delta$ [ ]	- 2x		- x		+ 3x
equil [ ]	(1.00 - 2x) M		(2.00 - x) M		3x M

- what we do know:

stoichiometry of how A and B combine to form C

for every 1 mol B consumed, 2 mol A consumed & 3 mol C form

OR – if x mol B are consumed, 2·x mol A will be consumed and 3·x mol C will form

Process for Solving Equilibrium Problems:  
Using an Equilibrium (or ICE) Table

consider the reaction:  $2 A (g) + B (g) \rightleftharpoons 3 C (g)$

	2 A (g)	+	B (g)	$\rightleftharpoons$	3 C (g)
initial [ ]	1.00 M		2.00 M		0
$\Delta$ [ ]	- 2x		- x		+ 3x
equil [ ]	(1.00 - 2x) M		(2.00 - x) M		3x M

- what we do know:

$$K_C = \frac{[C]^3}{[A]^2[B]}$$

OR

$$K_C = \frac{(3x)^3}{(1.00 - 2x)^2(2.00 - x)}$$

Equilibrium Calculations

- determine the equilibrium composition of a reaction:  
determine the concentration (or pressure) of each species present in the system when equilibrium is established

example:  $SO_2 (g) + NO_2 (g) \rightleftharpoons SO_3 (g) + NO (g)$

$$K_C = 3.75$$

1.24 mol  $SO_2 (g)$  and 0.750 mol  $NO_2 (g)$  are combined in a 2.50 L flask, and the reaction is allowed to reach equilibrium.

Determine the concentration of each species present at equilibrium.

example:  $SO_2 (g) + NO_2 (g) \rightleftharpoons SO_3 (g) + NO (g)$ ;  $K_C = 3.75$

1.24 mol  $SO_2 (g)$  and 0.750 mol  $NO_2 (g)$  are combined in a 2.50 L flask, and the reaction is allowed to reach equilibrium.

Determine the concentration of each species present at equilibrium.

	$SO_2 (g)$	+	$NO_2 (g)$	$\rightleftharpoons$	$NO (g)$	+	$SO_3 (g)$
initial [ ]	0.496 M		0.300 M		0 M		0 M
$\Delta$ [ ]	- x		- x		+ x		+x
equil [ ]	(.496 - x) M		(.300 - x) M		x M		x M

$$K_C = \frac{[NO][SO_3]}{[SO_2][NO_2]}$$

$$3.75 = \frac{(x)(x)}{(.496 - x)(.300 - x)} = \frac{x^2}{.149 - .796x + x^2}$$

## Quadratic Equations and the Quadratic Formula

♦ quadratic equation:  $ax^2 + bx + c = 0$

♦ quadratic formula:

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

♦ you will get 2 *mathematically* correct answers for  $x$   
only one is the right answer for our problem  
the other is the “extraneous root”

back to our example ... the solution!

	SO <sub>2</sub> (g)	+ NO <sub>2</sub> (g)	$\rightleftharpoons$	NO (g)	+ SO <sub>3</sub> (g)
initial [ ]	0.496 M	0.300 M		0 M	0 M
$\Delta$ [ ]	-x	-x		+x	+x
equil [ ]	(.496 - x) M	(.300 - x) M		x M	x M

$$3.75 = \frac{(x)(x)}{(.496 - x)(.300 - x)} = \frac{x^2}{.149 - .796x + x^2}$$

♦ using the quadratic formula:  $x = 0.847$  (*extraneous*) or 0.240  
♦ so at equilibrium:

$$[\text{SO}_2] = 0.496 - x = 0.256 \text{ M} \quad \checkmark \text{ Check your answer?}$$

$$[\text{NO}_2] = 0.300 - x = 0.060 \text{ M}$$

$$[\text{SO}_3] = [\text{NO}] = x = 0.240 \text{ M}$$

## Equilibrium Calculations

♦ determine the equilibrium composition of a reaction using pressure data and  $K_P$

example:  $\text{CO (g)} + \text{H}_2\text{O (g)} \rightleftharpoons \text{CO}_2 \text{ (g)} + \text{H}_2 \text{ (g)}$ ;  $K_P = 4.24$

A vessel is filled with 12.0 atm CO (g) and 12.0 atm H<sub>2</sub>O (g) at 800 K, and the reaction progresses until equilibrium is established.

Determine the pressure (in atm) of each species present in the reaction mixture at equilibrium.

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	CO (g)	+ H <sub>2</sub> O (g)	$\rightleftharpoons$	CO <sub>2</sub> (g)	+ H <sub>2</sub> (g)
initial P	12.0 atm	12.0 atm		0 atm	0 atm
$\Delta P$	-x	-x		+x	+x
equil P	(12.0-x) atm	(12.0-x) atm		x atm	x atm

$$K_P = \frac{(P_{\text{CO}_2})(P_{\text{H}_2})}{(P_{\text{CO}})(P_{\text{H}_2\text{O}})}$$

and

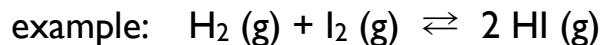
$$4.24 = \frac{x^2}{(12.0 - x)^2}$$

♦ solution:  $x = 8.07$

at equilibrium:  $P_{\text{CO}} = P_{\text{H}_2\text{O}} = 3.93 \text{ atm}$ ;  $P_{\text{CO}_2} = P_{\text{H}_2} = 8.07 \text{ atm}$

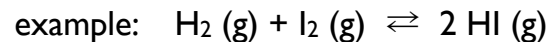
### Equilibrium Calculations

- determine the value of the equilibrium constant ( $K_C$  or  $K_P$ ) given initial concentrations or pressures, and one equilibrium concentration or pressure



0.750 M  $\text{H}_2$  and 0.990 M  $\text{I}_2$  are combined and allowed to react. When equilibrium is established, the concentration of  $\text{I}_2$  is found to be 0.330 M.

Determine  $K_C$  for this reaction.



0.750 M  $\text{H}_2$  and 0.990 M  $\text{I}_2$  are combined and allowed to react. When equilibrium is established, the concentration of  $\text{I}_2$  is found to be 0.330 M.

Determine  $K_C$  for this reaction.

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	$\rightleftharpoons$	$2 \text{HI}(\text{g})$
initial [ ]	0.750 M		0.990 M		0 M
$\Delta$ [ ]	-x		-x		+ 2x
equil [ ]	(0.750 - x) M		(0.990 - x) M		2x M

- strategy:

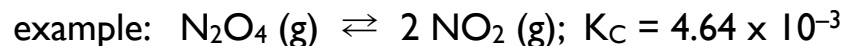
use given equilibrium [ $\text{I}_2$ ] and defined (*in table*) equilibrium [ $\text{I}_2$ ] to solve for x

use x to determine equilibrium [ $\text{H}_2$ ] and [ $\text{HI}$ ]

plug those concentrations in to solve for  $K_C$

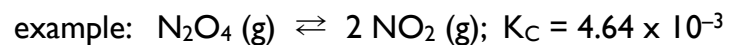
### Equilibrium Calculations

- determine the equilibrium composition of a reaction given arbitrary initial data



At some point after the initiation of the reaction, the mixture is found to contain 0.0200 M  $\text{N}_2\text{O}_4$  and 0.0300 M  $\text{NO}_2$ .

Determine the concentration of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  present in this system at equilibrium.



At some point after the initiation of the reaction, the mixture is found to contain .0200 M  $\text{N}_2\text{O}_4$  & .0300 M  $\text{NO}_2$ .

Determine the concentration of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  present in this system at equilibrium.

	$\text{N}_2\text{O}_4(\text{g})$	$\rightleftharpoons$	$2 \text{NO}_2(\text{g})$
initial [ ]	0.0200 M		0.0300 M
$\Delta$ [ ]			
equil [ ]			

- strategy:

calculate  $Q_C$  and compare to value of  $K_C$  to determine the direction of reaction to reach equilibrium

based on direction of reaction, complete table (*think carefully about how to define  $\Delta$  [ ] row*)

solve for x; determine [ $\text{N}_2\text{O}_4$ ] and [ $\text{NO}_2$ ]

## Le Chatelier's Principle

- ◆ When a *stress* is applied to a system at equilibrium, the equilibrium position will shift in the direction that relieves the applied stress.
- ◆ *stresses* include:
  - changes in concentration or pressure of reactants or products by the addition or removal
  - changes in pressure as a result of changes in volume of container
  - changes in temperature (*value of K will change*)
  - addition of a catalyst

## Effect of Changes in Concentration on Equilibrium Position

- ◆ If the concentration or pressure of a substance is increased by the addition of more reactant or product ...
    - the equilibrium position will shift in the direction that consumes the added substance
- OR
- the equilibrium position will shift *away from the increased concentration*

## Effect of Changes in Concentration on Equilibrium Position

- ◆ If the concentration or pressure of a substance is decreased by the removal of reactant or product ...

the equilibrium position will shift in the direction that replenishes the removed substance

OR

the equilibrium position will shift *toward the decreased concentration*

## Effect of Changing Pressure on Equilibrium Position

There are 3 ways to change the pressure of a chemical reaction system:

- I. add or remove a gas phase reactant or product
  - recall that  $P_{\text{reactant}}$  or  $P_{\text{product}}$  are related (through  $PV=nRT$ ) to molar concentration
  - ◆ *the result of adding or removing gas phase reactant or product can be predicted according to the guidelines stated above for effect of changing concentration.*

## Effect of Changing Pressure on Equilibrium Position

### 2. add an inert gas

the addition of an inert gas to a system changes the total pressure of the system, but not the partial pressures (i.e. *changing concentrations*) of gas phase reactants or products

- ♦ *the result is no change in equilibrium position*

## Effect of Changing Pressure on Equilibrium Position

### 3. change the volume of the container

recall that  $P$  and  $V$  are inversely proportional to one another

If the equilibrium is disturbed by changing the volume of the container, Le Chatelier's Principle predicts:

- ♦ *An increase in pressure resulting from reduced container volume will bring about net reaction in the direction that decreases the number of moles of gas phase species (i.e. the volume of the chemical system will decrease).*
- ♦ *A decrease in pressure resulting from increased container volume will bring about net reaction in the direction that increases the number of moles of gas phase species (i.e. the volume of the chemical system will increase).*

## Effect of Changing Temperature on Equilibrium Position & $K$

- ♦ The temperature dependence of the equilibrium position *and the value of the equilibrium constant* is dependent on the sign of  $\Delta H$  of the reaction.

1. The equilibrium constant for an *exothermic reaction* will decrease as temperature increases;

equilibrium position will shift to the left as temperature increases

2. The equilibrium constant for an *endothermic reaction* will increase as temperature increases;

equilibrium position will shift to the right as temperature increases

## Effect of a Catalyst on the Equilibrium Position

- ♦ The addition of a catalyst does not effect the equilibrium position of a reaction – only the *rate* at which the system reaches equilibrium.

Consider the equilibria presented below, and apply Le Chatelier's principle to predict the effect of each change on the indicated quantity. Circle *I*, *D*, or *N* to indicate an increase, decrease, or no change in the quantity. Assume that each change is made independently to the system at equilibrium.

reaction	change	quantity	prediction
a. $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{HCl}(\text{g})$	add $\text{H}_2$	$P_{\text{Cl}_2}$	I D N
b. $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{HCl}(\text{g})$	add HCl	$K_p$	I D N
c. $\text{H}_2(\text{g}) + \text{Br}_2(\text{l}) \rightleftharpoons 2 \text{HBr}(\text{g})$	remove $\text{H}_2$	mass of $\text{Br}_2$	I D N
d. $\text{H}_2(\text{g}) + \text{Br}_2(\text{l}) \rightleftharpoons 2 \text{HBr}(\text{g})$	add $\text{Br}_2(\text{l})$	$P_{\text{HBr}}$	I D N
e. $\text{HCOOH}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HCOO}^-(\text{aq})$	reduce pH	$[\text{HCOO}^-]$	I D N
f. $\text{HCOOH}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HCOO}^-(\text{aq})$	add $\text{OH}^-(\text{aq})$	$[\text{HCOO}^-]$	I D N
g. $\text{HCOOH}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HCOO}^-(\text{aq})$	add HCOOH	$K_c$	I D N
h. $\text{PbBr}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2 \text{Br}^-(\text{aq})$	add $\text{PbBr}_2(\text{s})$	$[\text{Br}^-]$	I D N
i. $\text{PbBr}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2 \text{Br}^-(\text{aq})$	add $\text{Pb}(\text{NO}_3)_2(\text{aq})$	$[\text{Br}^-]$	I D N
j. $\text{PbBr}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2 \text{Br}^-(\text{aq})$	increase T	$[\text{Br}^-]$	I D N
k. $\text{PbBr}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2 \text{Br}^-(\text{aq})$	decrease T	$K_c$	I D N

\*note\* reaction in *h*, *i*, *j* and *k* is endothermic