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Chapter 12

Gaseous Chemical Equilibrium

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Outline



1. N_2O_4 - NO_2 equilibrium system
2. The equilibrium constant expression
3. Determination of K
4. Applications of the equilibrium constant
5. Effect of changes in conditions on an equilibrium system

Review of Liquid-Vapor Equilibrium



- In Chapter 9 we examined the equilibrium that is established between a liquid and a vapor, such as that for water
 - $\text{H}_2\text{O (l)} \rightleftharpoons \text{H}_2\text{O (g)}$
 - The state of the system can be described by stating the vapor pressure of water at the given temperature
 - The process is reversible
 - The forward and reverse processes take place at the same rate

Chemical Equilibria



- For a gaseous chemical equilibrium, more than one gas is present:
 - $aA (g) + bB (g) \rightleftharpoons cC (g) + dD (g)$
 - To describe the state of this system, the partial pressures of all gases must be known
 - Using the Ideal Gas Law:

$$P_i = \frac{n_i RT}{V}$$

- in a closed system, with fixed volume and temperature, the partial pressure of each species is proportional to the number of moles of that species

Working with Chemical Equilibria



1. Writing the expression for the equilibrium constant
2. Calculating the equilibrium constant from experimental data
3. Using the equilibrium constant to predict the extent to which a reaction will take place
4. Using the equilibrium constant to predict the effect that disturbing a system in equilibrium will have

12.1 The N_2O_4 - NO_2 Equilibrium



- N_2O_4 is colorless
- NO_2 is brown
- When N_2O_4 is sealed into a closed, evacuated container at 100°C , a reddish-brown color develops due to the decomposition to NO_2
 - $\text{N}_2\text{O}_4 (\text{g}) \rightleftharpoons 2\text{NO}_2 (\text{g})$
- As NO_2 builds up, it can react to form N_2O_4
 - The reverse reaction takes place
- An equilibrium is established where the rate of decomposition of N_2O_4 equals that of reaction of NO_2

Establishment of Equilibrium



- The rate of decomposition of N_2O_4 starts out fast but slows down as the pressure of N_2O_4 drops
- The rate of reaction of NO_2 starts out slow but speeds up as the pressure of NO_2 builds up
- Once the rates of reaction are equal, equilibrium is established
 - No further pressure change of either gas unless the temperature or the volume of the container is changed
 - The concentrations (pressures) of the gases are independent of the direction from which equilibrium is approached

Figure 12.1

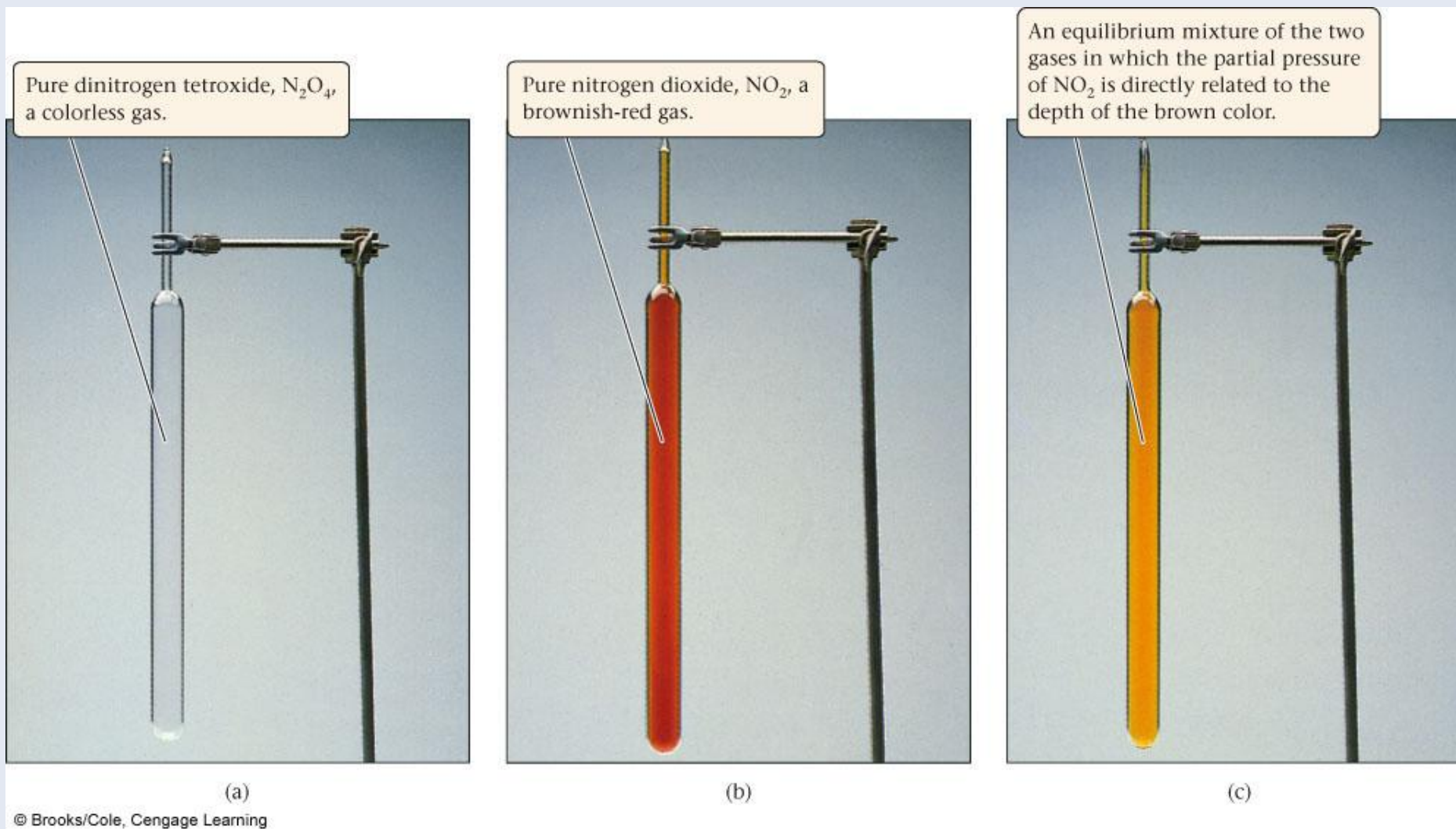


Table 12.1 – Numeric Data on Equilibrium

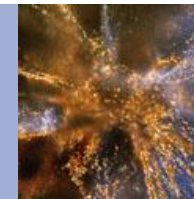


Table 12.1

Establishment of Equilibrium in the System
 $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$ (at 100°C)

Time	0	20	40	60	80	100
$P_{\text{N}_2\text{O}_4}$ (atm)	1.00	0.60	0.35	0.22*	0.22	0.22
P_{NO_2} (atm)	0.00	0.80	1.30	1.56	1.56	1.56

*Boldface numbers are equilibrium pressures.

Figure 12.2 – Graphical Display of Equilibrium

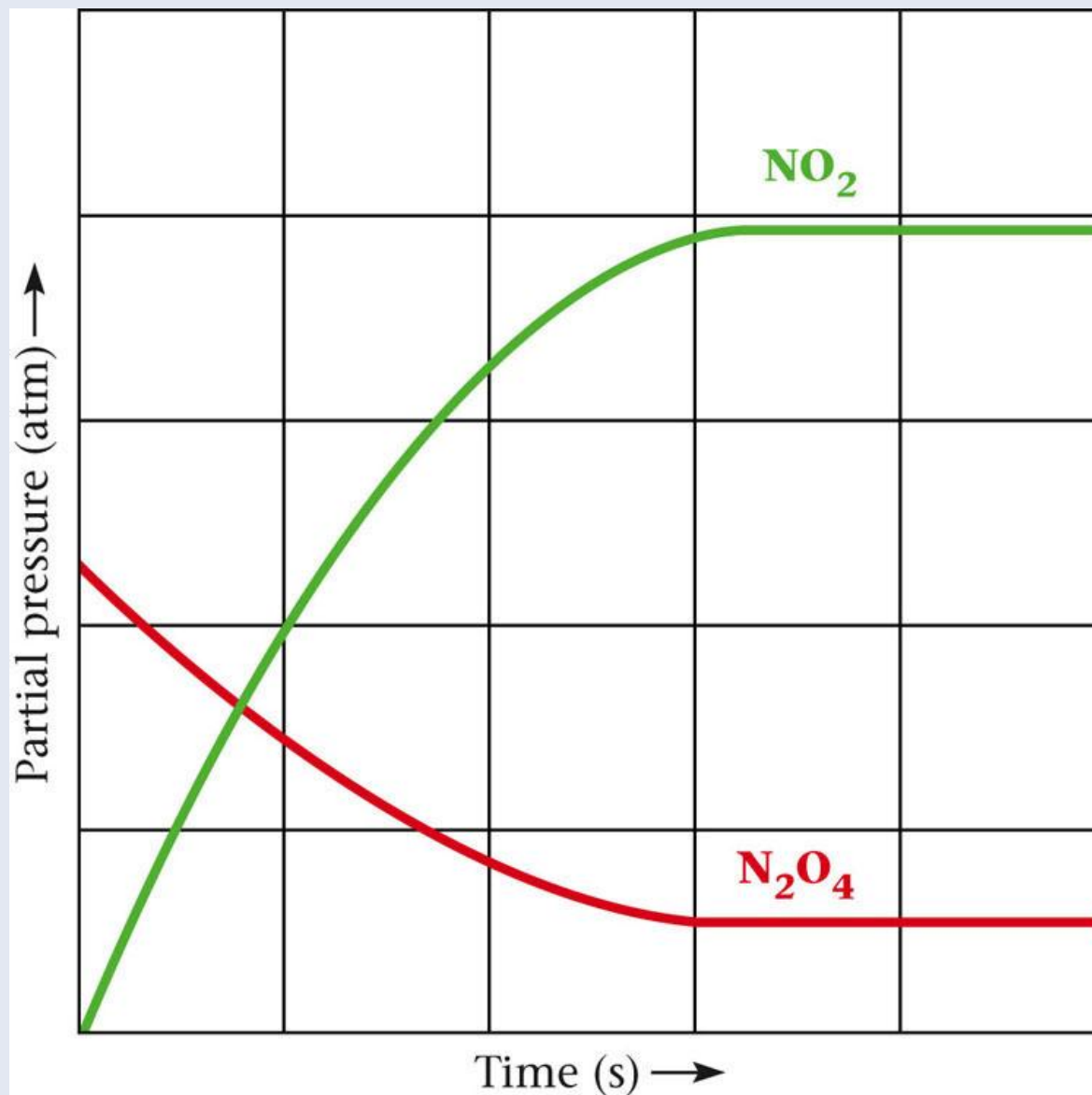


Table 12.2

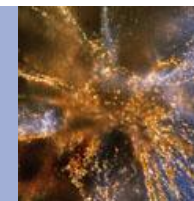


Table 12.2

Equilibrium Measurements in the $\text{N}_2\text{O}_4\text{--NO}_2$ System at 100°C

		Original Pressure (atm)	Equilibrium Pressure (atm)
Expt. 1	N_2O_4	1.00	0.22
	NO_2	0.00	1.56
Expt. 2	N_2O_4	0.00	0.07
	NO_2	1.00	0.86
Expt. 3	N_2O_4	1.00	0.42
	NO_2	1.00	2.16

Common Ground



- What do the three experiments in Table 12.2 have in common?
 - The original pressures differ
 - A specific ratio of product to reactant is common to all three experiments
- The reaction quotient
 - We can define a ratio of product to reactant:

$$\frac{P_{NO_2}^2}{P_{N_2O_4}}$$

- For all three experiments, the value of this quotient is 11

The Equilibrium Constant



- When we use the values for the pressure of each gas at equilibrium with the quotient we just defined, we arrive at the ***equilibrium constant***
- The value of the equilibrium constant is ***independent of the starting concentration or pressure*** of the reactants and products
- The value of the equilibrium constant is ***dependent on the temperature***

12.2 Equilibrium Constant Expression



- For a reaction where
 - $aA (g) + bB (g) \rightleftharpoons cC (g) + dD (g)$
 - A, B, C, D all gases
 - a, b, c, d are the coefficients of the balanced equation

- K is the equilibrium constant

$$K = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

- All partial pressures must be expressed in atmospheres
- Product terms are in the numerator
- Reactant terms are in the denominator
- Coefficients of reactants and product are used as powers
- This K can be termed K_p (pressure equilibrium constant)

Equilibrium Constant and Concentration



- For the same $aA (aq) + bB (aq) \rightleftharpoons cC (aq) + dD (aq)$
- **K_c is the concentration equilibrium constant**

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

- If Δn_g is the change in the number of moles of gas from left to right (i.e., n_g (product) – n_g (reactant)), then
- **K_p is the pressure equilibrium constant**

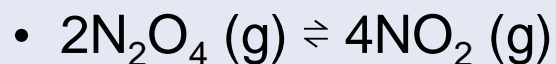
$$K_p = K_c (RT)^{\Delta n}$$

1.Changing the Chemical Equation, 1



- K depends on the equation written to describe the chemical reaction underlying the equilibrium
- Changing the reaction changes K
- If the reactions is multiplied by a number, n, then K is raised to that power:

- For n = 2



$$K = \frac{(P_{\text{NO}_2})^4}{(P_{\text{N}_2\text{O}_4})^2}$$

- For n = $\frac{1}{2}$ (i.e., divide the reaction by two):



$$K = \frac{(P_{\text{NO}_2})}{(P_{\text{N}_2\text{O}_4})^{\frac{1}{2}}}$$

Changing the Chemical Equation, 2



- For the forward and reverse reactions, the K expressions are the reciprocals of each other
 - For $2\text{NO}_2 (\text{g}) \rightleftharpoons \text{N}_2\text{O}_4 (\text{g})$,

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

2. Adding Chemical Equations



- If a reaction can be expressed as the sum of two or more reactions, the K for the overall reaction is the product of the K values for the individual reactions
- Consider
 - $\text{SO}_2 (\text{g}) + \frac{1}{2}\text{O}_2 (\text{g}) \rightleftharpoons \text{SO}_3 (\text{g}) \quad K = 2.2$
 - $\text{NO}_2 (\text{g}) \rightleftharpoons \text{NO} (\text{g}) + \frac{1}{2}\text{O}_2 (\text{g}) \quad K = 4.0$
- For
 - $\text{SO}_2 (\text{g}) + \text{NO}_2 (\text{g}) \rightleftharpoons \text{SO}_3 (\text{g}) + \text{NO} (\text{g}) \quad K = 8.8$

Table 12.3

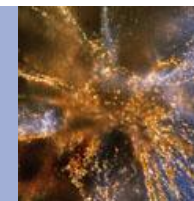
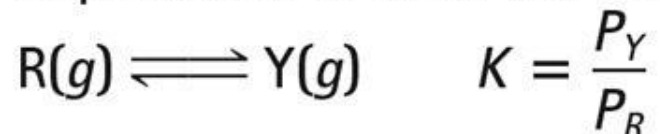


Table 12.3 Dependence of K on the Form of the Chemical Reaction



Form of Equation	K Expression	Relation to K	Rule
$Y(g) \rightleftharpoons R(g)$	$K' = \frac{P_R}{P_Y}$	$K' = \frac{1}{K}$	Reciprocal Rule
$nR(g) \rightleftharpoons nY(g)$	$K'' = \frac{(P_Y)^n}{(P_R)^n}$	$K'' = K^n$	Coefficient Rule
$R(g) \rightleftharpoons A(g)$	$K_1 = \frac{P_A}{P_R}$		
$A(g) \rightleftharpoons Y(g)$	$K_2 = \frac{P_Y}{P_A}$		
$R(g) \rightleftharpoons Y(g)$		$K = K_1 \times K_2$	Rule of Multiple Equilibria

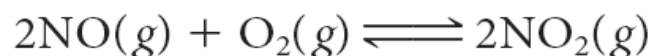
Example 12.1

Graded

Consider the air pollutants NO and NO₂, contributors to photochemical smog. Both can be formed by the reaction between atmospheric nitrogen and oxygen. At 25°C,



- * (a) Write the equilibrium constant expression for the formation of two moles of NO at 25°C.
- ** (b) Calculate K for the formation of one mole of NO at 25°C.
- *** (c) Calculate K for the decomposition of one mole of NO₂ at 25°C.
- **** (d) Calculate K for the following reaction at 25°C:



SOLUTION

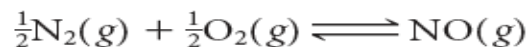
(a) Following the rules described on p. 327, we have

$$K_1 = \frac{(P_{\text{NO}})^2}{(P_{\text{N}_2})(P_{\text{O}_2})}$$



Example 12.1, (Cont'd)

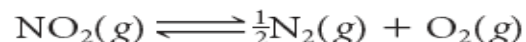
(b) The reaction for the formation of one mole of NO is



The coefficients for this equation are obtained by multiplying those in (1) by $\frac{1}{2}$.
Using the coefficient rule,

$$K = (K_1)^{1/2} = (4.2 \times 10^{-31})^{1/2} = 6.5 \times 10^{-16}$$

(c) The reaction for the decomposition of one mole of NO₂ is



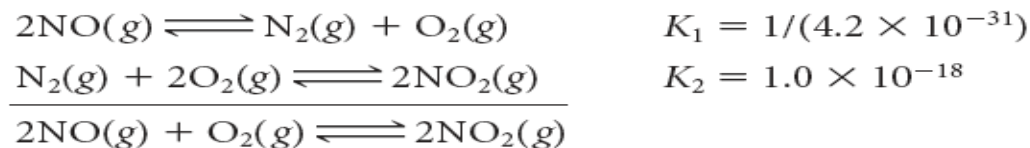
To arrive at this equation, two changes are made:

1. The product (NO₂) and the reactants (N₂ and O₂) have switched sides (reciprocal rule).
2. The coefficients are multiplied by $\frac{1}{2}$ (coefficient rule).

Thus,

$$K = \frac{1}{(K_2)^{1/2}} = \frac{1}{(1.0 \times 10^{-18})^{1/2}} = 1.0 \times 10^9$$

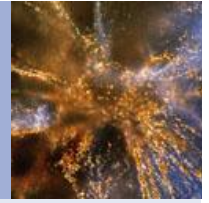
(d) To obtain the equation asked for here, combine two other equations for which you can find equilibrium constants.



The rule of multiple equilibria gives

$$K_3 = K_1 \times K_2 = \frac{1.0 \times 10^{-18}}{4.2 \times 10^{-31}} = 2.4 \times 10^{12}$$

3. Heterogeneous Equilibria



- In mixed-phase systems, note that the liquids and solids present do not change with time
 - Pure solids and pure liquids ***do not appear in equilibrium expressions***
 - The position of equilibrium is independent of the amount of solid or liquid, ***as long as some is present in the reaction mixture***

Carbon-Dioxide-Hydrogen Equilibrium



- $\text{CO}_2 (\text{g}) + \text{H}_2 (\text{g}) \rightleftharpoons \text{CO} (\text{g}) + \text{H}_2\text{O} (\text{l})$ at 25°C
 - The equilibrium vapor pressure of water at 25°C is constant
 - Water is left out of the equilibrium expression since its pressure does not change

$$K = \frac{P_{\text{CO}}}{P_{\text{CO}_2} P_{\text{H}_2\text{O}}}$$

Table 12.4



Table 12.4

Equilibrium Constant Expressions
for $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{l})$

	Expt. 1	Expt. 2	Expt. 3	Expt. 4
Mass $\text{H}_2\text{O}(\text{l})$	8 g	6 g	4 g	2 g
$P_{\text{H}_2\text{O}}$ (atm)	3×10^{-2}	3×10^{-2}	3×10^{-2}	3×10^{-2}
K_{I}	9×10^{-6}	9×10^{-6}	9×10^{-6}	9×10^{-6}
K_{II}	3×10^{-4}	3×10^{-4}	3×10^{-4}	3×10^{-4}

$$K_{\text{I}} = \frac{P_{\text{CO}} \times P_{\text{H}_2\text{O}}}{P_{\text{CO}_2} \times P_{\text{H}_2}} \quad K_{\text{II}} = \frac{P_{\text{CO}}}{P_{\text{CO}_2} \times P_{\text{H}_2}}$$

Example 12.2



Example 12.2

Write the expression for K for

- (a) the reduction of black solid copper(II) oxide (1 mol) with hydrogen to form copper metal and steam.
- (b) the reaction of 1 mol of steam with red-hot coke (carbon) to form a mixture of hydrogen and carbon monoxide, called water gas.

Strategy First write the chemical equation for the equilibrium system. Then write the expression for K , leaving out pure liquids and solids. Remember that gases are represented by their partial pressures.

SOLUTION

(a) The reaction is $\text{CuO}(s) + \text{H}_2(g) \rightleftharpoons \text{Cu}(s) + \text{H}_2\text{O}(g)$

The expression for K is $K = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}$

(b) The reaction is $\text{C}(s) + \text{H}_2\text{O}(g) \rightleftharpoons \text{H}_2(g) + \text{CO}(g)$

The expression for K is $K = \frac{P_{\text{H}_2} \times P_{\text{CO}}}{P_{\text{H}_2\text{O}}}$

Recap



- In the equilibrium expression, always include
 - Terms for gases, raised to the coefficient of each
 - Terms for aqueous species (molecules or ions), raised to the coefficient of each
- Always exclude
 - Terms for pure liquids and pure solids

12.3 Determination of K



- K can be evaluated numerically by experiment
- One of two sets of data will be used
 - Equilibrium pressures, which may be used directly to determine the value for K
 - Original pressures, which must be algebraically linked to the equilibrium pressure ultimately used to determine the value for K

Example 12.3

Ammonium chloride is sometimes used as a flux in soldering because it decomposes on heating:



The HCl formed removes oxide films from metals to be soldered. In a certain equilibrium system at 400°C, 22.6 g of NH₄Cl is present; the partial pressures of NH₃ and HCl are 2.5 atm and 4.8 atm, respectively. Calculate K at 400°C.

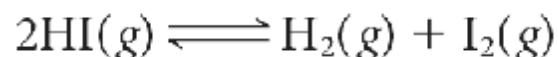
Strategy First write the expression for K . Then substitute equilibrium partial pressures into that expression and solve.

SOLUTION

$$K = (P_{\text{NH}_3})(P_{\text{HCl}}) = 2.5 \times 4.8 = 12$$

Example 12.4

Consider the equilibrium system



Originally, a system contains only HI at a pressure of 1.00 atm at 520°C. The equilibrium partial pressure of H₂ is found to be 0.10 atm. Calculate

- (a) P_{I_2} and P_{HI} at equilibrium (b) K

Strategy To solve this problem, you must—

- carefully distinguish *original* from *equilibrium* partial pressures.
- learn how to relate the equilibrium partial pressures of H₂, I₂, and HI using the coefficients of the balanced equation.
- make a table to summarize your reasoning.

SOLUTION

- (a) Start by creating the following table and enter the pertinent information obtained from the statement of the problem. (That will be the red entries in the following table.)

	$2\text{HI}(g)$	\rightleftharpoons	$\text{H}_2(g)$	+	$\text{I}_2(g)$
P_0 (atm)	1.00		0		0
ΔP (atm)					
P_{eq} (atm)			0.10		

P_0 = initial pressure, P_{eq} = equilibrium pressure, ΔP = change in pressure

Note that H_2 and I_2 are being made (pressure increases), and HI is being used up. Furthermore, ΔP for $\text{H}_2(g)$ must be 0.10 atm to get from an original pressure of zero to an equilibrium partial pressure of 0.10 atm. Your table should then look like:

	$2\text{HI}(g)$	\rightleftharpoons	$\text{H}_2(g)$	+	$\text{I}_2(g)$
P_0 (atm)	1.00		0		0
ΔP (atm)	–		+0.10		+
P_{eq} (atm)			0.10		



Example 12.4, (Cont'd)



Note from the balanced equation that one mole of I_2 is formed for every mole of H_2 . Putting it another way, as the reaction proceeds from left to right, the increase in the number of moles of I_2 is the same as that for H_2 :

$$\Delta n_{I_2} = \Delta n_{H_2}$$

Because $P = nRT/V$, it follows that for an equilibrium system at constant T and V , pressure is directly proportional to amount in moles, and the above relationship must hold for partial pressures as well:

$$\Delta P_{I_2} = \Delta P_{H_2}$$

By similar reasoning, because two moles of HI are required to form one mole of H_2 ,

$$\Delta n_{HI} = -2\Delta n_{H_2}$$

and

$$\Delta P_{HI} = -2\Delta P_{H_2}.$$

Example 12.4, (Cont'd)



The table now looks like:

	$2\text{HI}(g)$	\rightleftharpoons	$\text{H}_2(g)$	+	$\text{I}_2(g)$
P_0 (atm)	1.00		0		0
ΔP (atm)	$-2(0.10)$		+0.10		+1(0.10)
P_{eq} (atm)	0.80		0.10		0.10

From this table, you see that $P_{\text{HI}} = 0.80$ atm and $P_{\text{I}_2} = 0.10$ atm.

$$(b) \quad K = \frac{P_{\text{H}_2} \times P_{\text{I}_2}}{P_{\text{HI}}^2} = \frac{(0.10)(0.10)}{(0.80)^2} = 0.016$$

Reality Check

1. Note that the numbers for ΔP are related through the coefficients of the balanced equation (2HI , I_2 , H_2)
2. You might expect that K would be rather small (0.016). Recall that at equilibrium, P_{I_2} is 0.100 atm, only one-tenth of the original pressure of HI (1.00 atm).

Fundamentals of Equilibrium Problems



- As a system approaches equilibrium, changes in partial pressures of reactants and products are related to each other through the coefficients of the balanced equation
 - The same holds for changes to molar amounts
 - The balanced equation is the key to setting up and solving equilibrium problems

12.4 Applications of the Equilibrium Constant



- The magnitude of the equilibrium constant translates directly into the extent of reaction
 - Reactions are feasible as written only if K is large enough that an appreciable amount of product forms
 - Consider the reaction
 - $\text{N}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightleftharpoons 2\text{NO} (\text{g})$
 - $K = 1 \times 10^{-30}$ at 25°C
 - This reaction does not proceed to any great extent at this temperature, so nitrogen and oxygen in air do not react appreciably at room temperature

1. Synthesis of Ammonia



- $\text{N}_2 (\text{g}) + 3\text{H}_2 (\text{g}) \rightleftharpoons 2\text{NH}_3 (\text{g})$
 - $K = 6 \times 10^5$ at 25°C
 - When the reaction reaches equilibrium, mostly product (ammonia) is present
- Conclusions
 - If K is very small, the mixture contains mostly unreacted reactants at equilibrium
 - If K is large, the mixture contains mostly products at equilibrium

2.Direction of Reaction; the Reaction Quotient, Q



- We can define a new quantity called the reaction quotient, Q
- Q has the same form as the equilibrium expression
 - Values for reactant and product need not be equilibrium pressures
- For $aA (g) + bB (g) \rightleftharpoons cC (g) + dD (g)$

$$Q = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

Q and the Direction of Reaction



- When we start with only reactants
 - $aA (g) + bB (g) \rightleftharpoons cC (g) + dD (g)$
 - P_C and P_D are 0, so $Q = 0$
- When we start with only products
 - P_A and P_B are 0, so $Q = \infty$
- Q can take any value from zero to infinity

Q and the Direction of Reaction, (Cont'd)



- Comparing Q and K
 - When $Q < K$, the reaction proceeds from left to right
 - When $Q > K$, the reaction proceeds from right to left
 - When $Q = K$, the reaction is at equilibrium

Example 12.5

Consider the following system at 100°C:



Predict the direction in which reaction will occur to reach equilibrium, starting with 0.10 mol of N_2O_4 and 0.20 mol of NO_2 in a 2.0-L container.

Strategy First calculate the partial pressures of N_2O_4 and NO_2 , using the ideal gas law as applied to mixtures: $P_i = n_iRT/V$. Then calculate Q . Finally, compare Q and K to predict the direction of reaction.

SOLUTION

$$P_{\text{N}_2\text{O}_4} = \frac{nRT}{V} = \frac{(0.10 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(373 \text{ K})}{2.0 \text{ L}} = 1.5 \text{ atm}$$

Since there are twice as many moles of NO_2 at the same V and T ,

$$P_{\text{NO}_2} = 2(1.5 \text{ atm}) = 3.0 \text{ atm}$$

$$Q = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} = \frac{(3.0)^2}{1.5} = 6.0$$

Because $Q < 11$, reaction must proceed in the forward direction.

Reality Check When reaction occurs in the forward direction, the partial pressure of NO_2 increases, that of N_2O_4 decreases, and Q becomes equal to K .

Equilibrium Partial Pressures



- The equilibrium constant can be used to calculate the partial pressures of the species present at equilibrium
 1. Using the balanced equation, write the K expression
 2. Express the equilibrium partial pressures in terms of a single unknown.

Use the balanced equation to make the expression
 3. Substitute into the expression for K to find the unknown in (2)
 4. Calculate the equilibrium partial pressures using (3)

Example 12.6



Example 12.6 Graded

For the system



K is 0.64 at 900 K. Calculate the equilibrium partial pressures of all species, starting with

* (a) $P_{\text{CO}_2} = P_{\text{H}_2} = 1.00 \text{ atm}$; $P_{\text{CO}} = P_{\text{H}_2\text{O}} = 0$

** (b) $P_{\text{CO}_2} = 2.00 \text{ atm}$, $P_{\text{H}_2} = 1.00 \text{ atm}$; $P_{\text{CO}} = P_{\text{H}_2\text{O}} = 0$

SOLUTION

(a) Follow the four steps described above.

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

Example 12.6, (Cont'd)



- (2) You must express all equilibrium partial pressures in terms of a single unknown, x . A reasonable choice for x is

$$\begin{aligned}x &= \text{change in partial pressure of CO as the system goes to equilibrium} \\ &= \Delta P_{\text{CO}}\end{aligned}$$

All the coefficients in the balanced equation are the same, 1. It follows that all the partial pressures change by the same amount, x .

$$\Delta P_{\text{H}_2\text{O}} = \Delta P_{\text{CO}} = x$$

$$\Delta P_{\text{H}_2} = \Delta P_{\text{CO}_2} = -x$$

(The minus sign arises because H_2 and CO_2 are consumed, whereas CO and H_2O are formed.) The equilibrium table becomes

	$\text{CO}_2(g)$	+	$\text{H}_2(g)$	\rightleftharpoons	$\text{CO}(g)$	+	$\text{H}_2\text{O}(g)$
P_o (atm)	1.00		1.00		0		0
ΔP (atm)	$-x$		$-x$		$+x$		$+x$
P_{eq} (atm)	$1.00 - x$		$1.00 - x$		x		x

Example 12.6, (Cont'd)



(3) Substituting into the expression for K ,

$$0.64 = \frac{(x)(x)}{(1.00 - x)(1.00 - x)}$$

Taking the square root of both sides,

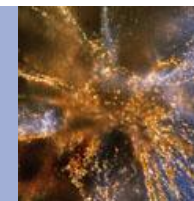
$$(0.64)^{1/2} = 0.80 = \frac{x}{1.00 - x}$$

Solving for x ,

$$x = 0.80 - 0.80x \quad 1.80x = 0.80 \quad x = 0.44$$

(4) Referring back to the equilibrium table,

$$P_{\text{CO}} = P_{\text{H}_2\text{O}} = x = 0.44 \text{ atm}$$
$$P_{\text{CO}_2} = P_{\text{H}_2} = 1.00 - x = 0.56 \text{ atm}$$



Example 12.6, (Cont'd)

(b) Proceeding in the same manner as in (a), the equilibrium table becomes

	$\text{CO}_2(g)$	+	$\text{H}_2(g)$	\rightleftharpoons	$\text{CO}(g)$	+	$\text{H}_2\text{O}(g)$
P_o (atm)	2.00		1.00		0		0
ΔP (atm)	$-x$		$-x$		$+x$		$+x$
P_{eq} (atm)	$2.00 - x$		$1.00 - x$		x		x

Substituting into the expression for K ,

$$0.64 = \frac{x^2}{(2.00 - x)(1.00 - x)}$$

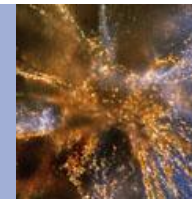
This time, the equation is not as readily solved as in (a) because the right side is not a perfect square. Use the general method of solving a quadratic equation. This involves rearranging to the standard form

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

and applying the quadratic formula

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

Example 12.6, (Cont'd)



Putting the equilibrium constant expression in the desired standard form,

$$x^2 = 0.64(2.00 - x)(1.00 - x)$$

$$x^2 = 1.28 - 1.92x + 0.64x^2$$

$$0.36x^2 + 1.92x - 1.28 = 0$$

So

$$a = 0.36, b = 1.92, c = -1.28$$

Solving

$$x = \frac{-1.92 \pm \sqrt{3.69 + 1.84}}{0.72} = \frac{-1.92 \pm 2.35}{0.72}$$

$$x = 0.60, \text{ or } -5.93$$

Of the two answers, only 0.60 is plausible; a value of -5.93 would imply that CO and H₂ have *negative* partial pressures, which is ridiculous.

Substituting $x = 0.60$ back into the equilibrium table,

$$P_{\text{CO}} = P_{\text{H}_2\text{O}} = 0.60 \text{ atm}; \quad P_{\text{CO}_2} = 1.40 \text{ atm}; \quad P_{\text{H}_2} = 0.40 \text{ atm}$$

To check the arithmetic, substitute these values back into the expression for K :

$$\frac{(0.60)(0.60)}{(0.40)(1.40)} = 0.64 \quad \text{Voila!}$$

12.5 Effect of Changes in conditions on an Equilibrium Systems



- Several changes can disturb a system in equilibrium
 1. Adding or removing a gaseous reactant or product
 2. Compressing or expanding the system
 3. Changing the temperature

1. LeChâtelier's Principle

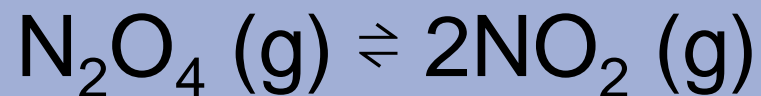


- Henri LeChâtelier (1850-1936)
- If a system at equilibrium is disturbed by a change in concentration, pressure, or temperature, the system will, if possible, shift to partially counteract the change and restore equilibrium

2. Adding or Removing a Gas



- If a chemical equilibrium is disturbed by ***adding*** a gas (reactant or product), the system will ***shift in the direction that consumes the added species.***
- If a chemical equilibrium is disturbed by ***removing*** a gas (reactant or product), the system will ***shift in the direction that restores part of the added species.***



- **Adding N_2O_4** will cause a shift from ***left to right***
- **Adding NO_2** will cause a shift from ***right to left***
- **Removing N_2O_4** will cause a shift from ***right to left***
- **Removing NO_2** will cause a shift from ***left to right***
- It is possible to use K to calculate the extent to which the shift occurs when a reactant or product is added or removed



Example 12.7

Example 12.7

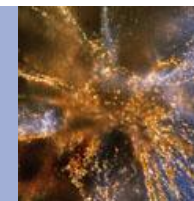
In Example 12.4 you found that the HI–H₂–I₂ system is in equilibrium at 520°C when $P_{\text{HI}} = 0.80$ atm and $P_{\text{H}_2} = P_{\text{I}_2} = 0.10$ atm. Suppose enough HI is added to raise its pressure temporarily to 1.00 atm. When equilibrium is restored, what are P_{HI} , P_{H_2} , and P_{I_2} ?

Strategy This problem is entirely analogous to Example 12.6; the only real difference is that in this case the original pressures are those that prevail immediately after equilibrium is disturbed. Note that

$$Q = \frac{(0.10) \times (0.10)}{(1.00)^2} = 0.010 < K = 0.016$$

so some HI must dissociate to establish equilibrium.

Example 12.7, (Cont'd)



SOLUTION

(1) Recall from Example 12.4 that

$$K = \frac{P_{\text{H}_2} \times P_{\text{I}_2}}{(P_{\text{HI}})^2} = 0.016 \text{ at } 520^\circ\text{C}$$

(2) The partial pressure of HI must decrease; those of H₂ and I₂ must increase. Let x be the increase in partial pressure of H₂. Then

$$\Delta P_{\text{I}_2} = \Delta P_{\text{H}_2} = x \quad \Delta P_{\text{HI}} = -2x$$

The equilibrium table becomes

	2HI(g)	\rightleftharpoons	H ₂ (g)	+	I ₂ (g)
P_o (atm)	1.00		0.10		0.10
ΔP (atm)	-2x		+x		+x
P_{eq} (atm)	1.00 - 2x		0.10 + x		0.10 + x

(3) Substituting into the expression for K ,

$$0.016 = \frac{(0.10 + x)^2}{(1.00 - 2x)^2}$$

Example 12.7, (Cont'd)



To solve this equation, take the square root of both sides:

$$0.13 = \frac{0.10 + x}{1.00 - 2x}$$

from which you should find that $x = 0.024$.

$$(4) P_{\text{H}_2} = P_{\text{I}_2} = 0.10 + x = 0.12 \text{ atm}$$

$$P_{\text{HI}} = 1.00 - 2x = 0.95 \text{ atm}$$

Reality Check Note that the equilibrium partial pressure of HI is intermediate between its value before equilibrium was established (0.80 atm) and that immediately afterward (1.00 atm). This is exactly what Le Châtelier's principle predicts; part of the added HI is consumed to re-establish equilibrium.

3. Volume Changes



- Consider again the equilibrium
 - $\text{N}_2\text{O}_4 (\text{g}) \rightleftharpoons 2\text{NO}_2 (\text{g})$
- Reducing the volume will increase the pressure
 - Recall that $P = nRT/V$
 - Pressure and volume are inversely related
 - As V becomes smaller, P becomes larger
- Now consider the system response
 - By shifting to the left, two moles of gas are consumed and one is produced
 - The pressure is reduced by shifting to the left, so the stress is counteracted

Figure 12.3

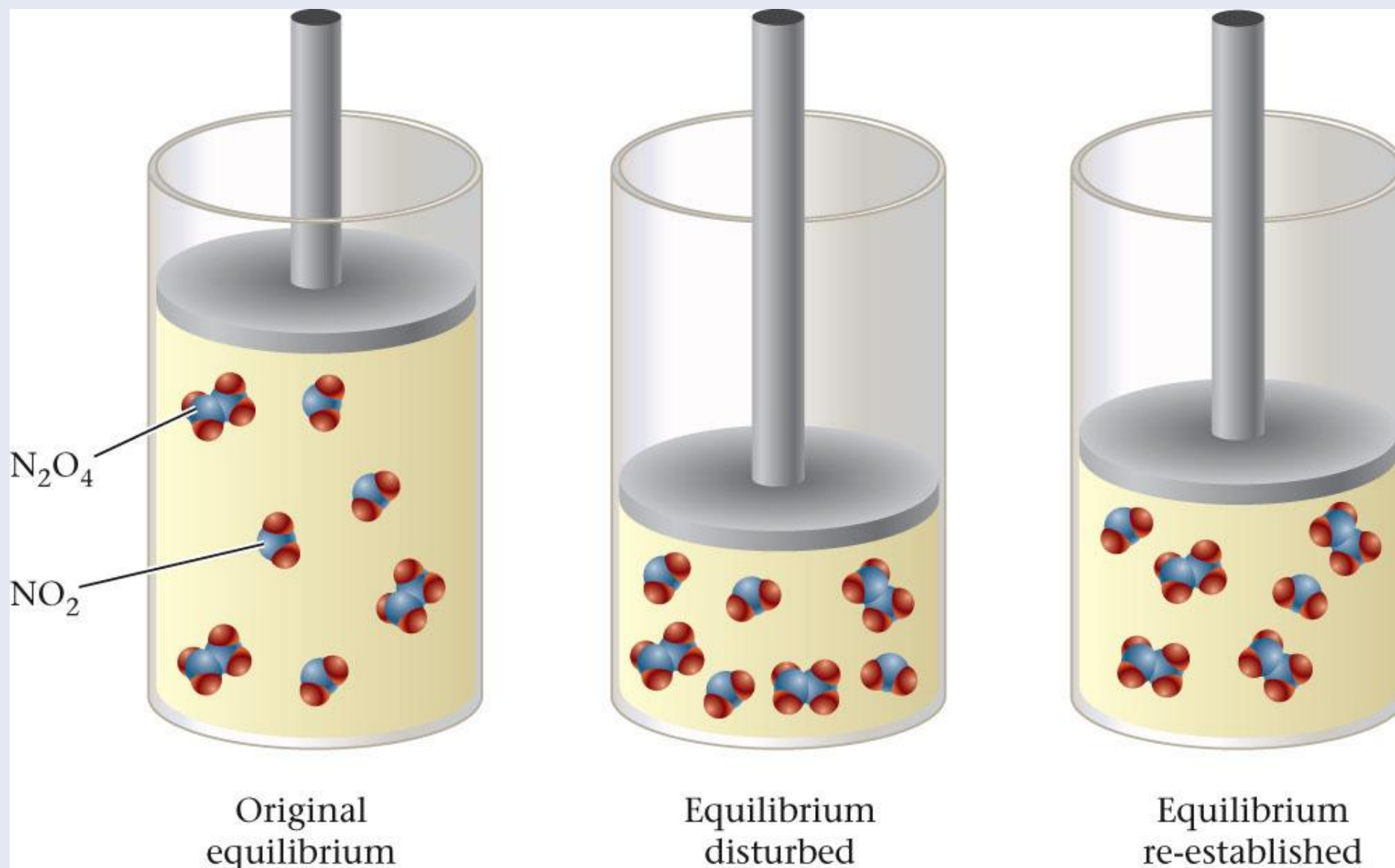
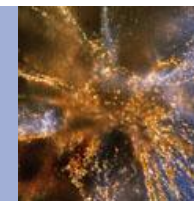


Table 12.6

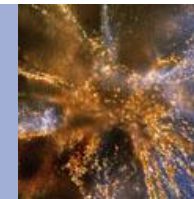


Table 12.6

Effect of Compression on the Equilibrium System $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$; $K = 11$ at 100°C

P_{tot} (atm)	n_{NO_2}	$n_{\text{N}_2\text{O}_4}$	n_{tot}
1.0	0.92	0.08	1.00
2.0	0.82	0.13	0.95
5.0	0.64	0.22	0.86
10.0	0.50	0.29	0.79

Pressure Changes



- When a system is compressed, the ***total pressure increases***, causing the system to shift in the direction that decreases the total number of moles of gas
- When a system is expanded, the ***total pressure decreases***, causing the system to shift in the direction that increases the total number of moles of gas
- If the total number of moles of gas is the same on both sides of the equation, pressure change will have a small or negligible effect on the equilibrium

Table 12.7

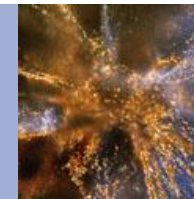
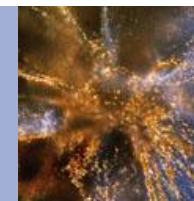


Table 12.7 Effect of Pressure on the Position of Gaseous Equilibria

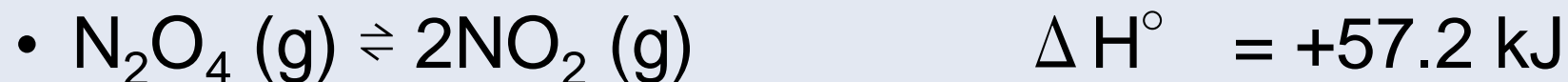
System	Δn_{gas}^*	P_{tot} Increases	P_{tot} Decreases
1. $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$	+1	←	→
2. $\text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \rightleftharpoons \text{SO}_3(g)$	$-\frac{1}{2}$	→	←
3. $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$	-2	→	←
4. $\text{C}(s) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + \text{H}_2(g)$	+1	←	→
5. $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)$	0	0	0

* Δn_{gas} is the change in the number of moles of gas as the forward reaction occurs.

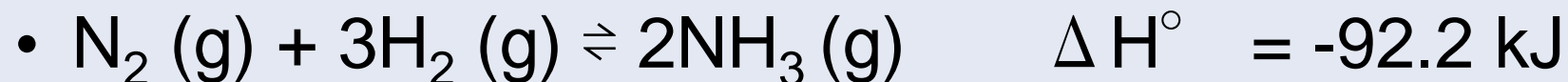
Changes in Temperature



- In increase in temperature favors the endothermic reaction



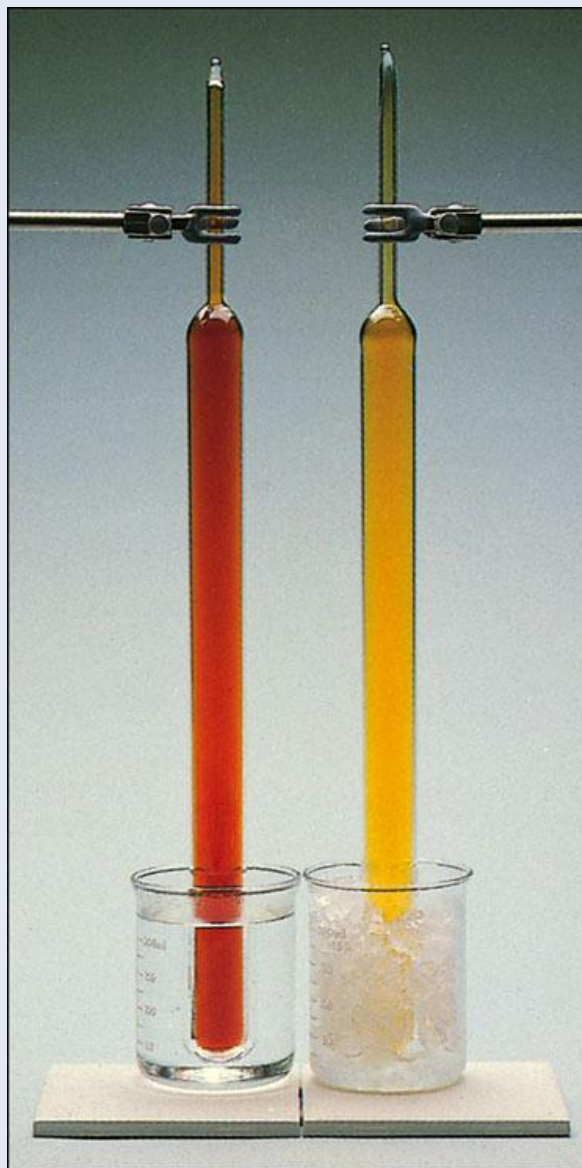
- Increasing the temperature favors NO_2



- Increasing the temperature favors N_2 and H_2

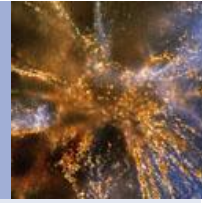
- The ***reverse reaction is endothermic***

Figure 12.4



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Two-Point Equilibrium Constant Equation



- van't Hoff Equation

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^\circ}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

- Same form as the Clausius-Clapeyron and Arrhenius rate-constant equations
- K_2 and K_1 are equilibrium constants corresponding to T_2 and T_1
- ΔH° is the enthalpy change for the reaction

Applying the van't Hoff Equation



- $\text{N}_2 (\text{g}) + 3\text{H}_2 (\text{g}) \rightleftharpoons 2\text{NH}_3 (\text{g}) \quad \Delta H^\circ = -92.2 \text{ kJ}$
 - $K = 6 \times 10^5$ at 25°C
 - Calculate K at 100°C
 - Convert temperatures to Kelvin and ΔH° to J
 - K at $100^\circ \text{C} = 4 \times 10^2$
 - Note that K becomes smaller as T increases because of the negative enthalpy change
 - For reactions with positive ΔH° , K increases with temperature

Example 12.8



Example 12.8

Consider the following systems:

- (a) $2\text{CO}(g) + \text{O}_2(g) \longrightarrow 2\text{CO}_2(g)$ $\Delta H = -566 \text{ kJ}$
(b) $\text{H}_2(g) + \text{I}_2(g) \longrightarrow 2\text{HI}(g)$ $\Delta H = -2.7 \text{ kJ}$
(c) $\text{H}_2(g) + \text{I}_2(s) \longrightarrow 2\text{HI}(g)$ $\Delta H = +53.0 \text{ kJ}$
(d) $\text{I}_2(g) \longrightarrow 2\text{I}(g)$ $\Delta H = +36.2 \text{ kJ}$

What will happen to the position of the equilibrium if the system is compressed (at constant temperature)? Heated at constant pressure?

Strategy An increase in pressure tends to drive the equilibrium in such a direction as to decrease the number of moles of *gas*. Endothermic reactions are favored by an increase in temperature.

SOLUTION

- (a) increase in P \longrightarrow ; increase in T \longleftarrow
(b) increase in P has no effect; increase in T \longleftarrow (slightly!)
(c) increase in P \longleftarrow ; increase in T \longrightarrow
(d) increase in P \longleftarrow ; increase in T \longrightarrow

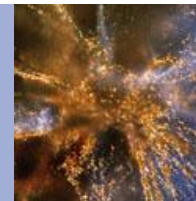
Final Notes



- We have examined three changes in conditions:
 1. Adding or removing a gas
 2. Compressing or expanding the system
 3. Changing the temperature

- Of these, only one change leads to a change in the value of the equilibrium constant K

Changing K



- The ***only way to change the equilibrium constant*** is to ***change the temperature*** of the reaction

Key Concepts



1. Write the expression for the equilibrium constant
2. Calculate the equilibrium constant from experimental data
3. Use the equilibrium constant to predict the extent to which a reaction will take place
4. Use the equilibrium constant to predict the effect that disturbing a system in equilibrium will have