

# Quiz 2

Exam time: **2018/11/14 Wed. 8:55-9:40**

Exam room:

**S1:**

Dong Zhong Yuan 2-205: 517370910073-518370910072;

Dong Zhong Yuan 2-101: 518370910073-518370990041;

**S2:**

Dong Zhong Yuan 2-201: 518021910004-518370910088

Dong Zhong Yuan 2-105: 518370910090-518370990039

Lecture for Session 1 is 8 AM, and is 10 AM for session 2

# Recap

- ❑ Boiling point elevation and freezing point depression (molality,  $i$  factor)
- ❑ Osmosis (molality,  $i$  factor)
- ❑ Chemical equilibrium is a dynamic equilibrium
- ❑ Equilibrium constant

## Origins of K and $\Delta G$

$$\Delta G^\circ = \sum nG^\circ (\text{products}) - \sum nG^\circ (\text{reactants}) \quad (\text{Eq. 20 Ch. 8})$$

For standard  $\Delta G^\circ$ , meaning formed from its elements or  $\Delta G_f^\circ$  at 1 bar, 298 K (25°C) per mol.

$\Sigma$  = sum up, and  $n$  = stoichiometric coefficients, moles

$$\Delta G = \sum nG (\text{products}) - \sum nG (\text{reactants})$$

Here  $\Delta G$  is under nonstandard (variable) conditions.

We substitute the two above equations into:

$$G(J) = G^\circ(J) + RT \ln a_J$$

From here we wave a wand, skip a few steps to get (next):

## Origins of $K$ and $\Delta G$

Here we get an equation that applies to gases as well as solutions:

$$G_r = G^\circ_r + RT \ln \frac{(a_c)^c (a_D)^d}{(a_A)^a (a_B)^b}$$

$a$  = activity, either a gas or solute in a solution (molarity)

$r$  = the overall reaction

We now introduce  $Q = \frac{(a_c)^c (a_D)^d}{(a_A)^a (a_B)^b}$  and this is called the **reaction quotient** and apply it to the above:

$$G_r = G^\circ_r + RT \ln Q$$

## Origins of $K$ and $\Delta G$

$$G_r = G_r^\circ + RT \ln Q$$

Don't confuse  $Q$  with  $K$ .

$K$  is a constant, it is known.

$Q$  is unknown and must be found.  $Q$  can be larger or smaller than  $K$ ; again it must be calculated.

Example 5G.2 The standard Gibbs free energy of reaction for:  $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$  is  $\Delta G_r^\circ = -141.74 \text{ kJ}\cdot\text{mol}^{-1}$  at  $25.00^\circ\text{C}$ . What is the Gibbs free energy of reaction when the partial pressure of each gas is 100. bar and in what direction is the spontaneous?

$$G_r = G_r^\circ + RT \ln \frac{(a_c)^c (a_D)^d}{(a_A)^a (a_B)^b} \quad R = 8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$Q = \frac{(a_c)^c (a_D)^d}{(a_A)^a (a_B)^b} = \frac{(a_{\text{SO}_3})^2}{(a_{\text{SO}_2})^2 (a_{\text{O}_2})} = \frac{(100.)^2}{(100.)^2 (100.)} = 1.00 \times 10^{-2}$$

$$\begin{aligned} G_r &= G_r^\circ + RT \ln Q, \\ -141.74 \text{ kJ}\cdot\text{mol}^{-1} &+ (.008314 \text{ kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(25.00 + 273.15)\text{K} \ln 1.00 \times 10^{-2} \\ &= -153.16 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

When  $\Delta G < 0$ , the reaction is spontaneous

When  $\Delta G > 0$ , the reaction is nonspontaneous

When  $\Delta G = 0$ , the reaction is equilibrium

Therefore when  $\Delta G < 0$ , the reaction is spontaneous

## The Direction of Reaction Depending on $Q$

$$Q = \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b} \quad \text{reaction quotient}$$

Whereas  $K$  is a constant and known,  $Q$  is unknown and must be found or calculated.

The only way to know if a reaction reached equilibrium is to measure the quantity of products and reactants, then plug numbers into the reaction quotient,  $Q$ , and compare that to  $K$  to see if the reaction reached equilibrium.

## The Direction of Reaction Depending on $Q$

$$Q = \frac{(a_c)^c (a_D)^d}{(a_A)^a (a_B)^b} \quad \text{reaction quotient}$$

If  $Q < K$ ,  $\Delta G$  is negative, the concentrations of products are too low, and the reaction has a tendency to proceed toward products.

If  $Q = K$ ,  $\Delta G$  is zero, the mixture has its equilibrium, and there is no tendency to change in either direction.

If  $Q > K$ ,  $\Delta G$  is positive, the reverse reaction is spontaneous, and the products decompose into reactants.

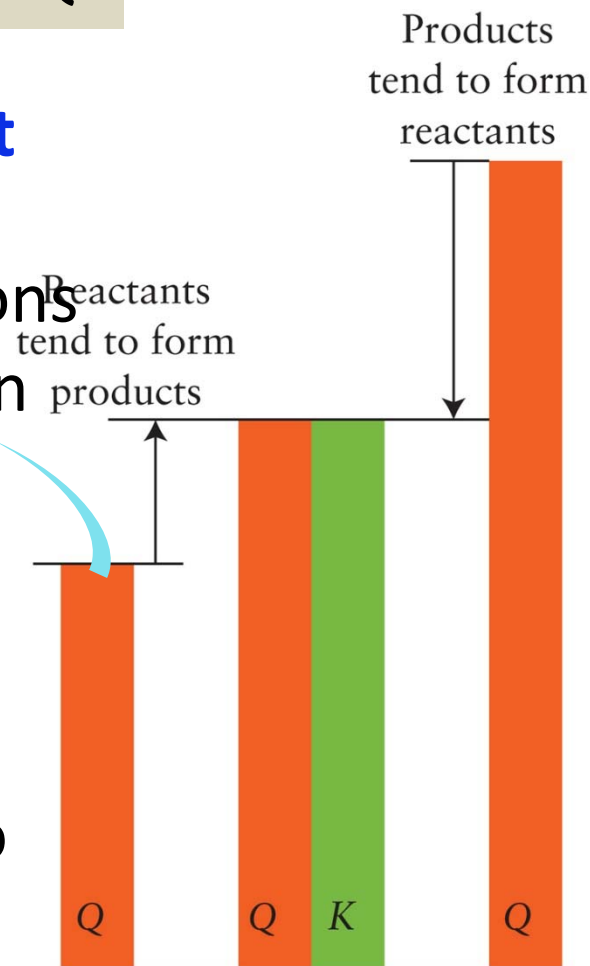


Figure 51.2  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman



Example 5I.2 A mixture of hydrogen, iodine, and hydrogen iodide, each at 55 kPa, was introduced into a container heated to 783 K. At this temperature,  $K = 46$  for  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$ . Predict whether HI has a tendency to form or to decompose into  $\text{H}_2(\text{g})$  and  $\text{I}_2(\text{g})$ .

We want to find  $Q$ , and compare it to  $K$ , in this case  $K = 46$ .

$$\text{For } \text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g}), \quad Q = \frac{(\text{products})}{(\text{reactants})}$$

$$\frac{(P_{\text{HI}})^2}{(P_{\text{H}_2})(P_{\text{I}_2})}, \frac{(55)^2}{(55)(55)} = 1.0$$

Since  $Q < K$ , the reaction will start to form more products, HI (so that the numerator becomes larger).

## Origins of $K$ and $\Delta G$

When  $Q = K$

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

Remember that  $\Delta G^\circ$  is under *standard* conditions, and  $\Delta G$  is under *nonstandard* conditions or variable conditions.

Once  $Q = K$  the reaction is at equilibrium, meaning all “conditions” are *standard* or the conditions are no longer “variable,” therefore  $\Delta G = 0$ . This leads to

$$0 = \Delta G^\circ + RT \ln K \quad \text{or} \quad \Delta G^\circ = -RT \ln K$$

This of course links the thermodynamic tables  $\Delta G^\circ$  to  $K$ .

Example 5G.3 At 25°C, the standard Gibbs free energy of reaction for  $\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{I}_2(\text{s}) \rightleftharpoons \text{HI}(\text{g})$  is  $+1.70 \text{ kJ}\cdot\text{mol}^{-1}$ ; calculate the equilibrium constant for this reaction.

Solving for  $\Delta G^\circ = -RT \ln K$

$$R = 8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\ln K = \frac{G^\circ}{-RT},$$
$$\frac{+1.70 \text{ kJ}\cdot\text{mol}^{-1}}{-(0.008314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(25.00 + 273.15)\text{K}} = -0.685$$

From  $e^{\ln x} = x$

$$e^{-0.685} = 0.504$$

$$K = 0.504$$

## The Extent of Reaction: What Does $K$ Mean?

Reactants  $\rightleftharpoons$  Products

$$K = \left\{ \frac{\text{partial pressure of **Products**}}{\text{partial pressure of **Reactants**}} \right\}_{\text{equil}}$$

For  $K$ 's larger than 1, we expect more products.

For instance a  $K$  of  $1 \times 10^6$ , a large number, written  $\frac{1,000,000}{1}$  and we notice that the **numerator** is much larger than the *denominator* so we would have more products at equilibrium.

## The Extent of Reaction: What Does $K$ Mean?

$$K = \left\{ \frac{\text{partial pressure of **Products**}}{\text{partial pressure of **Reactants**}} \right\}_{equil}$$

And smaller than 1, for instance a  $K$  of 1 millionth, a small number 0.000001,  $1 \times 10^{-6}$  is written as  $\frac{1}{1,000,000}$  and now we notice the **denominator** is much larger than the *numerator*, so we would have more reactants at equilibrium.

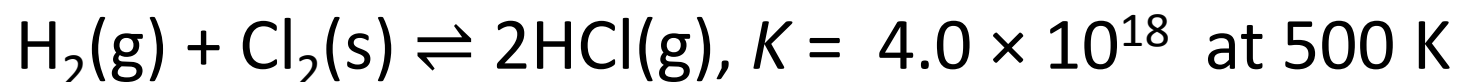
## The Extent of Reaction: What Does $K$ Mean?

Reactants  $\rightleftharpoons$  Products

$$K = \frac{(\text{products})}{(\text{reactants})}$$

$$\Delta G^\circ = -RT \ln K$$

A strongly **negative  $\Delta G^\circ$**  equilibrium is when the reaction is mainly products.  $K$  would also very large.



The main component being HCl in the reaction vessel.

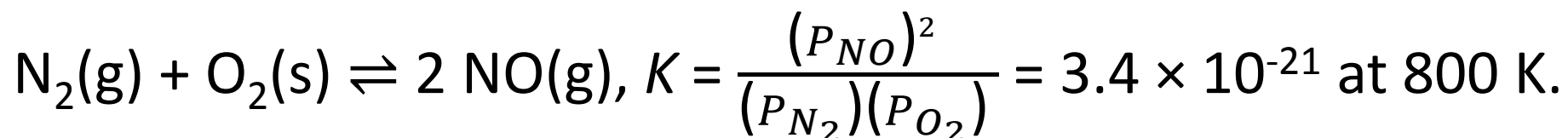
As expected  $\Delta G^\circ = -95.30$

## The Extent of Reaction: What Does $K$ mean

$$\Delta G^\circ = -RT \ln K$$

$$K = \frac{(products)}{(reactants)}$$

A  **$\Delta G^\circ$  largely positive** equilibrium is reached rapidly, after the reaction has produced only some products.  $K$  would also be very small.



Here, at equilibrium, the main components are the reactants  $\text{N}_2$  and  $\text{O}_2$ . As expected  $\Delta G^\circ = +104.20$

## Summary of the Meaning of $K$

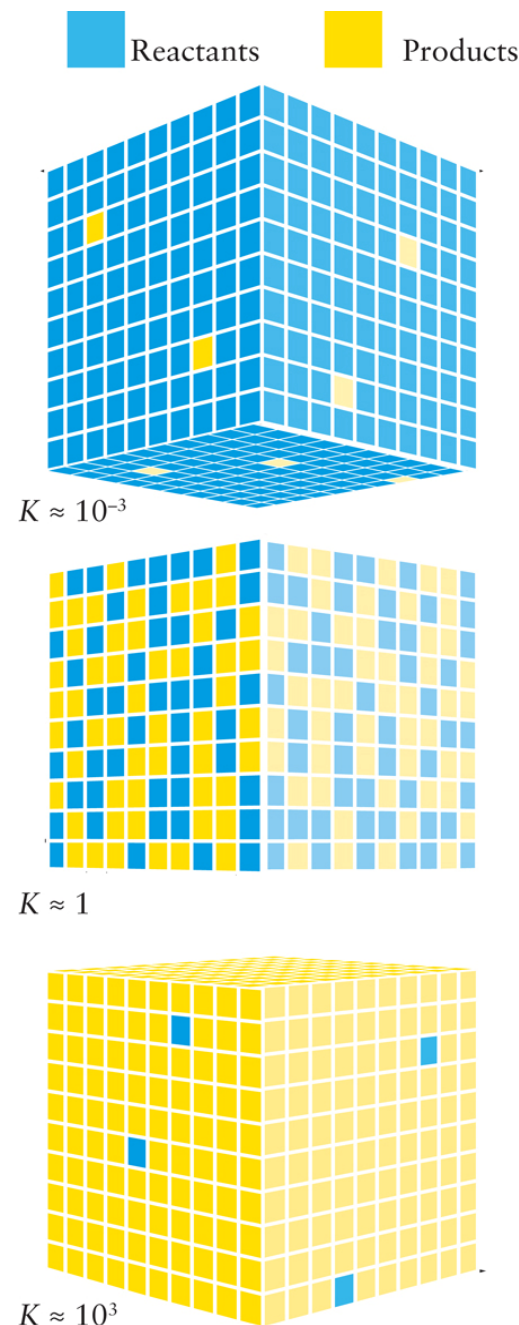
Reactants  $\rightleftharpoons$  Products

$$K = \frac{(products)}{(reactants)}$$
$$\Delta G^\circ = -RT \ln K$$

$K \ll 1$  **favors reactants** at equilibrium  
( $\Delta G^\circ$  is very positive);

When  $10^{-3} < K < 10^3$  **neither** products nor reactants are favored; when  $(-10 < \Delta G^\circ < 10)$  then *temperature* will be a factor;

$K \gg 1$  **favors products** at equilibrium ( $\Delta G^\circ$  is very negative).

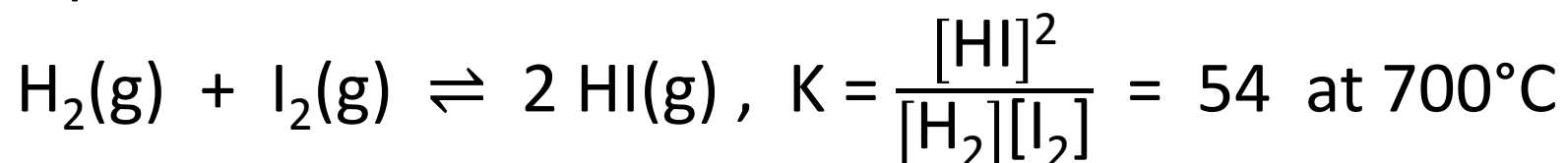


**Figure 5I.1**  
Atkins, *Chemical Principles: The Quest for Insight*,  
W. H. Freeman & Company, © 2016 by P. W. Atkin



## Alternative Forms of the Equilibrium Constant

The following algebraic manipulations are helpful for deriving different forms of equilibrium constant expressions.



Multiply the equation by 2,  $2 \text{H}_2(\text{g}) + 2 \text{I}_2(\text{g}) \rightleftharpoons 4 \text{HI}(\text{g})$ ,

$$K = \frac{[\text{HI}]^4}{[\text{H}_2]^2[\text{I}_2]^2} = 54^2 = 2900$$

Reversing the equation,  $2 \text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ ,

$$K = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{1}{54} = 0.019$$

## Alternative Forms of the Equilibrium Constant

Combine multiple equations and multiply  $K$ 's to find overall equilibrium constant.

For example, if  $K$ 's are known for Equations 1 and 2 but not 3. We can manipulate 1 and 2 to get 3's  $K$ .



$$K_1 = \frac{P_{\text{PCl}_3}^2}{P_{\text{P}}^2 P_{\text{Cl}_2}^3}$$

$$K_2^2 = \frac{P_{\text{PCl}_5}^2}{P_{\text{PCl}_3}^2 P_{\text{Cl}_2}^2}$$

Eq. 1 can remain unchanged.

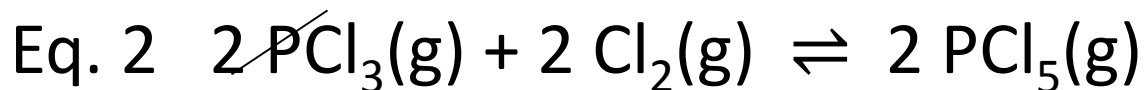


## Alternative Forms of the Equilibrium Constant

Next combine Eq. 1 and Eq. 2 and cancel like species.

Combine  $K_1$  and  $K_2$  ( $K_2$  is now square,  $K_2^2$ )

$$K_1 = \frac{P_{\text{PCl}_3}^2}{P_{\text{P}}^2 P_{\text{Cl}_2}^3}$$



$$K_2^2 = \frac{P_{\text{PCl}_5}^2}{P_{\text{PCl}_3}^2 P_{\text{Cl}_2}^2}$$

$$K_1(K_2)^2 = K_3 = \frac{P_{\text{PCl}_5}^2}{P_{\text{P}}^2 P_{\text{Cl}_2}^5}$$

Example 5I.1 Suppose that, in an equilibrium mixture of HCl, Cl<sub>2</sub>, and H<sub>2</sub>, the partial pressure of H<sub>2</sub> is 4.2 mPa and that of Cl<sub>2</sub> is 8.3 mPa. What is the partial pressure of HCl (in bar) given  $K = 4.0 \times 10^{18}$  at 500 K for  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$ ?

$$K = \frac{(P_{\text{HCl}})^2}{(P_{\text{H}_2})(P_{\text{Cl}_2})} = 4.0 \times 10^{18}, 1 \text{ bar} = 10^5 \text{ Pa}$$

$$\text{Converting from mPa to bar, } \frac{1 \text{ bar}}{10^5 \text{ Pa}} \times \frac{1 \text{ Pa}}{10^3 \text{ mPa}} \times \frac{4.2 \text{ mPa}}{1} = 4.2 \times 10^{-8} \text{ bar}$$

$$4.0 \times 10^{18} = \frac{(P_{\text{HCl}})^2}{(P_{\text{H}_2})(P_{\text{Cl}_2})}, \text{ Solving for HCl, } (P_{\text{HCl}})^2 = 4.0 \times 10^{18} (P_{\text{H}_2})(P_{\text{Cl}_2})$$

$$P_{\text{HCl}} = \sqrt{4.0 \times 10^{18} (P_{\text{H}_2})(P_{\text{Cl}_2})}, \sqrt{4.0 \times 10^{18} \times (4.2 \times 10^{-8}) \times (8.3 \times 10^{-8})} \\ = 120 \text{ bar HCl}$$

## Using Equilibrium Constants

Equilibrium constants are “**constants**” and are therefore, **powerful predicting tools**! Next we look at:

1. Calculating  $K$ 's from knowing equilibrium concentrations.
2. Calculating equilibrium concentrations from knowing  $K$ 's.

	$P_{SO_2}$ (bar)	$P_{O_2}$ (bar)	$P_{SO_3}$ (bar)	$K$
Exp 1	0.660	0.390	0.0840	0.0415
Exp 2	0.110	0.0110	0.00750	0.0423
Exp 3	1.44	1.98	0.410	0.0409

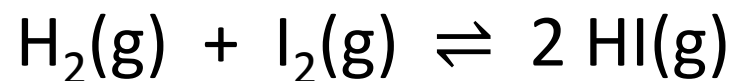
**Regardless** of the initial compositions, the final  $K$  is always the same.

Example:  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$ . Starting with 1 bar each of  $\text{H}_2$  and  $\text{I}_2$ , the equilibrium pressure of  $\text{HI}$  was found to be 0.8 bar. What are the final pressures of  $\text{H}_2$  and  $\text{I}_2$ ?

- We start by building an equilibrium table and plugging in the given data;
- **Initially** 1 bar each of  $\text{H}_2$  and  $\text{I}_2$  and no  $\text{HI}$ ;
- **Equilibrium** was 0.8 bar of  $\text{HI}$ ;

This is enough information to solve the rest of the table.

	$\text{H}_2$	$\text{I}_2$	$\text{HI}$
<b>initial</b>	1	1	0
<b>change</b>			
<b>equil. (final)</b>			0.8



	$\text{H}_2$	$\text{I}_2$	$\text{HI}$
initial	1	1	0
change	$\frac{1}{2} 0.8 = - 0.4$	$\frac{1}{2} 0.8 = - 0.4$	$+ 0.8$
equil.	$1 - 0.4 = 0.6$	$1 - 0.4 = 0.6$	0.8

To go from 0 to 0.8, it must have **changed** by 0.8; notice it is “+” because it was created.

The **changes** are all related by **stoichiometry**; note the “-” because it is consumed.

The **equilibriums of**  $\text{H}_2$  and  $\text{I}_2$  are found by combining the **initial** and **changes**.

Example:  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$ . Starting with 1 bar each of  $\text{H}_2$  and  $\text{I}_2$ , the equilibrium pressure of  $\text{HI}$  was found to be 0.8 bar. What are the final pressures of  $\text{H}_2$  and  $\text{I}_2$ ?

**A cleaned-up table.**

	$\text{H}_2$	$\text{I}_2$	$\text{HI}$
initial	1	1	0
change	- 0.4	- 0.4	+ 0.8
equil.	0.6	0.6	0.8

At equilibrium,  $P_{\text{H}_2} = P_{\text{I}_2} = 0.6 \text{ bar}$ , and  $P_{\text{HI}} = 0.8 \text{ bar}$ .

We can calculate  $K$ :

$$K = \frac{(0.8 \text{ bar})^2}{(0.6 \text{ bar})(0.6 \text{ bar})} = 2$$



Example:  $3 \text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$ . Starting with 0.5 bar each of  $\text{H}_2$  and  $\text{N}_2$ , it was found at equilibrium that the pressure of  $\text{NH}_3$  was 0.02 bar. What are the final pressures of  $\text{H}_2$  and  $\text{N}_2$ ?

- Make an equilibrium table with starting values.
- Calculate the one change we know, here  $\text{NH}_3$ .
- Using stoichiometry, calculate the changes in  $\text{H}_2$  and  $\text{N}_2$ .
- Combine the initial and change to find the final.

It is important to remember that “-” means consumed (going away) and “+” means being produced (making it).

	$\text{H}_2$	$\text{N}_2$	$\text{NH}_3$
<b>initial</b>	0.50	0.50	0
<b>change</b>	$(3/2) 0.02 = - 0.03$	$(1/2) 0.02 = - 0.01$	<b>+</b> 0.02
<b>equil.</b>	$0.50 - 0.03 = 0.47$	$0.50 - 0.01 = 0.49$	0.02

Example:  $3 \text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$ . Starting with 0.5 bar each of  $\text{H}_2$  and  $\text{N}_2$ , it was found at equilibrium that the pressure of  $\text{NH}_3$  was 0.02 bar. What are the final pressures of  $\text{H}_2$  and  $\text{N}_2$ ?

	$\text{H}_2$	$\text{N}_2$	$\text{NH}_3$
<b>initial</b>	0.50	0.50	0
<b>change</b>	- 0.03	- 0.01	+ 0.02
<b>equil.</b>	0.47	0.49	0.02

At equilibrium  $P_{\text{H}_2} = 0.47$  bar,  $P_{\text{N}_2} = 0.49$  bar, and  $P_{\text{NH}_3} = 0.02$  bar.

We have the information to calculate  $K$ ,

$$K = \frac{(P_{\text{NH}_3})^2}{(P_{\text{H}_2})^3 P_{\text{N}_2}} \simeq \frac{(0.02)^2}{(0.47)^3 (0.49)} = 7.9 \times 10^{-3}$$

Example 5I.3 Suppose that a mixture of 0.482 mol N<sub>2</sub> and 0.933 mol O<sub>2</sub> is transferred to a reaction vessel of volume 10.0 L and allowed to form N<sub>2</sub>O at 800 K; at this temperature,  $K = 3.2 \times 10^{-28}$  for the reaction  $2 \text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{N}_2\text{O}(\text{g})$ . Calculate the partial pressures of the gases in the equilibrium mixture.

First we find the pressure for each gas using  $PV = nRT$

$$P_{\text{N}_2} = \frac{(0.482 \text{ mol})(8.3145 \times 10^{-2} \text{ L}\cdot\text{bar}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(800.\text{K})}{10.0 \text{ L}} = 3.21 \text{ bar}$$

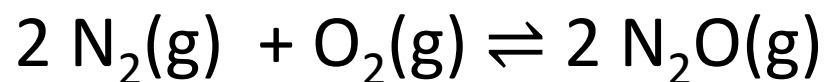
$$P_{\text{O}_2} = \frac{(0.933 \text{ mol})(8.3145 \times 10^{-2} \text{ L}\cdot\text{bar}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(800.\text{K})}{10.0 \text{ L}} = 6.21 \text{ bar}$$

$$P_{\text{N}_2\text{O}} = 0 \text{ (initially).}$$

We make our equilibrium table from known values.

Here we use “ $x$ ” to denote the change in concentration, which is based on **stoichiometry**, remembering that “+” means producing and “-” means going away.

	N <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub> O
initial	3.21	6.21	0
change	-2 $x$	- $x$	+2 $x$
equil.	3.21 - 2 $x$	6.21 - $x$	+2 $x$



Form an equilibrium expression,

$$K = \frac{(2x)^2}{(3.21 - 2x)^2(6.21 - x)} = 3.2 \times 10^{-28}$$

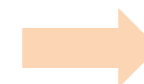
## Example 5I.3 continued

Our equilibrium expression,

$$K = \frac{(2x)^2}{(3.21 - 2x)^2(6.21 - x)} = 3.2 \times 10^{-28}$$

This would be *very difficult to solve quickly* without using Newton's method or software.

Next we look at a method often called an **approximation** that can greatly reduce the time we spend solving complex problems.



Previously we found  $K$  is  $3.2 \times 10^{-28}$ , which is in fact very very small.

This means this is a “reactant-favored” reaction but more importantly, it tells us that  $K$  is so small that the amount of disassociation—that is  $x$  is very very small, so small we can ignore it in this case.

	$N_2$	$O_2$	$N_2O$
initial	3.21	6.21	0
change	$-2x$	$-x$	$+2x$
equil.	$3.21 - 2x$	$6.21 - x$	$+2x$

In reality, the disassociation is small because of  $K$ , that 3.21 and 6.21 are much LARGER, so that our table actually looks like this.

	$N_2$	$O_2$	$N_2O$
initial	3.21	6.21	0
change	$-2x$	$-x$	$+2x$
equil.	3.21	6.21	$+2x$

This approximation greatly simplifies our  $K$  expression from

$$K = \frac{(2x)^2}{(3.21 - 2x)^2(6.21 - x)} = 3.2 \times 10^{-28}$$

to

$$3.2 \times 10^{-28} = \frac{(2x)^2}{(3.21)^2(6.21)} =$$

$$x = \sqrt{\frac{3.2 \times 10^{-28}(3.21)^2(6.21)}{2}}$$

$$x = 7.2 \times 10^{-14}$$

Now we can solve for our final concentrations.

Substituting our  $x$  back into our table to find our final concentrations.

$$x = 7.2 \times 10^{-14}$$

	N <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub> O
initial	3.21	6.21	0
change	-2 $x$	- $x$	+2 $x$
equil.	3.21 - 2 $x$	6.21 - $x$	+2 $x$

$$\text{N}_2: 3.21 - 2x, \quad 3.21 - 2(7.2 \times 10^{-14}) = 3.21 \text{ bar N}_2$$

$$\text{O}_2: 6.21 - x, \quad 6.21 - (7.2 \times 10^{-14}) = 6.21 \text{ bar O}_2$$

$$\text{N}_2\text{O}: 2x, \quad 2(7.2 \times 10^{-14}) = 1.4 \times 10^{-13} \text{ bar N}_2\text{O}$$



Question: **When** can we “throw”  $x$  out?

When  $K$  is small, and the starting concentrations are large, we assume disassociation, “ $x$ ”, is negligible.

$$K = 3.2 \times 10^{-28}$$

	$N_2$	$O_2$	$N_2O$
initial	3.21	6.21	0
change	<u><math>-2x</math></u>	<u><math>-x</math></u>	$+2x$
equil.	$3.21 - \underline{2x}$	$6.21 - \underline{x}$	$+2x$

	$N_2$	$O_2$	$N_2O$
initial	3.21	6.21	0
change	$-2x$	$-x$	$+2x$
equil.	3.21	6.21	$+2x$

Question: When can we “throw”  $x$  out?

< 5% rule

The 5% rule says we can **ignore “ $x$ ”** when there is **less than 5% decomposition or ionization change** (the definition of a weak acid).

Previously:  $x = 7.2 \times 10^{-14}$ , our initial concentration 3.21 M.

% ionization =  $0.2 \times 10^{-12}$  which  $\lll 5\%$ .

	N <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub> O
initial	3.21	6.21	0
change	-2 $x$	- $x$	+2 $x$
e Equil.	3.21 - 2 $x$	6.21 - $x$	+2 $x$

A note of good practice is, once solving for  $x$ , **always plug  $x$  back into the original equilibrium table** to make sure you're below 5% **and** to get your final values.

Example 51.4 Suppose that we place 3.12 g of  $\text{PCl}_5$  in a reaction vessel of volume 500 mL and reach equilibrium at  $250^\circ\text{C}$ , when  $K = 78.3$  for the reaction

$\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ . All three substances are gases at  $250^\circ\text{C}$ . Find the composition of the equilibrium mixture in bar.

Because we're given  $K$ , we have enough information to find the pressure of  $\text{PCl}_5$ .

Using  $PV = nRT$ , we need mole first.

Mole  $\text{PCl}_5$ ,

$$P = \frac{nRT}{V}, \quad \frac{\frac{3.12 \text{ g}}{208.24 \text{ g}\cdot\text{mol}^{-1}} (8.3145 \times 10^{-2} \text{ L}\cdot\text{bar}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) 523 \text{ K}}{0.500 \text{ L}} =$$

1.30 bar

Example 51.4  $K = 78.3$  for  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ .

	$\text{PCl}_5$	$\text{PCl}_3$	$\text{Cl}_2$
initial	1.30	0	0
change	-x	+x	+x
equil.	$1.30 - x$	x	x

$K = \frac{x^2}{1.30 - x} = 78.3$ . However,  $K$  is very large, which means “ $x$ ” in  $1.30 - x$  will be *substantial*;  **$\text{PCl}_5$  will dissociate noticeably.**

We simplify to:

$78.3(1.30 - x) = x^2$ , or  $x^2 + 78.3x - 102$ ; the only way to solve this is with the quadratic equation.

Example 51.4  $K = 78.3$  for the reaction  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ .

$$x^2 + 78x - 102, \text{ using } \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$\frac{-78 \pm \sqrt{78^2 - 4(102)}}{2} \text{ we solve and find } x = -79.6 \text{ and } 1.28$$

Since a “-” means the opposite of “+” or perhaps anti-mass, which has no meaning in chemistry. Therefore,  $x = 1.28$  bar

	$\text{PCl}_5$	$\text{PCl}_3$	$\text{Cl}_2$
initial	1.30	0	0
change	-x	+x	+x
equil.	$1.30 - x$	x	x

$$\text{PCl}_5 = 1.30 - x, \quad 1.30 - 1.28 = 0.02 \text{ bar}$$

$$\text{PCl}_3 = x, \quad = 1.28 \text{ bar}$$

$$\text{Cl}_2 = x, \quad = 1.28 \text{ bar}$$

$$\% \text{ change} = \frac{1.28}{1.30} \times 100 = 98.5$$

# The Response of Equilibria to Changes in Conditions

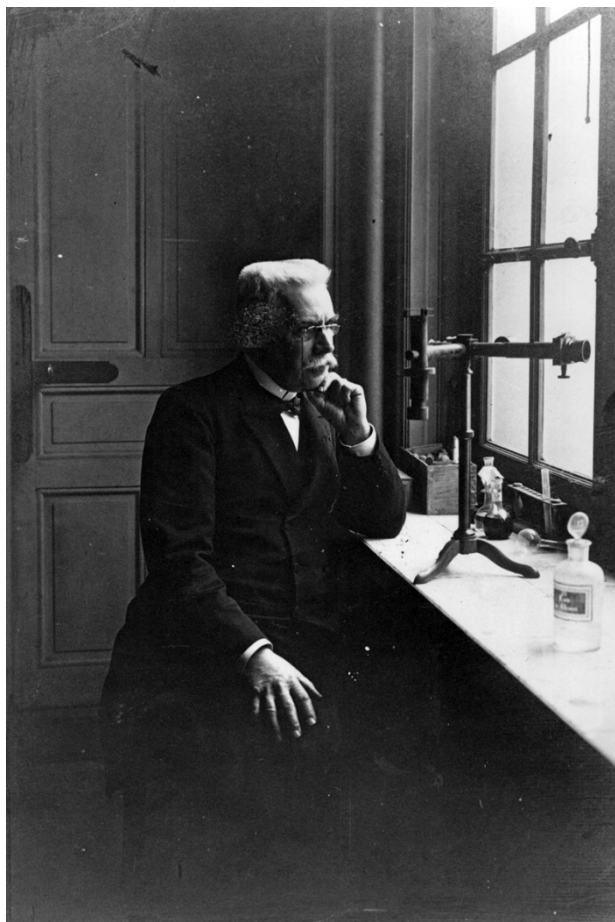


Figure 5J.3  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
Academie des Sciences, Paris, France/Archives Charmet/ Bridgeman Images.

Because chemical equilibria are dynamic, they respond to changes or disturbances in concentrations, pressure, and temperature.

After the initial change in  $\underline{G}$  (and  $K$ ) the composition reaches  $\Delta G = 0$  again.

The French chemist Henri Le Chatelier first noticed equilibrium disturbances re-approach equilibrium, and is now called *Le Chatelier's principle*.

# The Response of Equilibria to Changes in Conditions

In this example the reaction is coming into equilibrium.

1. The reaction approaches equilibrium.

2. Hydrogen is added.

3. The reaction again approaches equilibrium.

Symbolically: Adding ( $\uparrow$ )  $\text{H}_2$  shifts the reaction to produce more  $\uparrow \text{NH}_3$

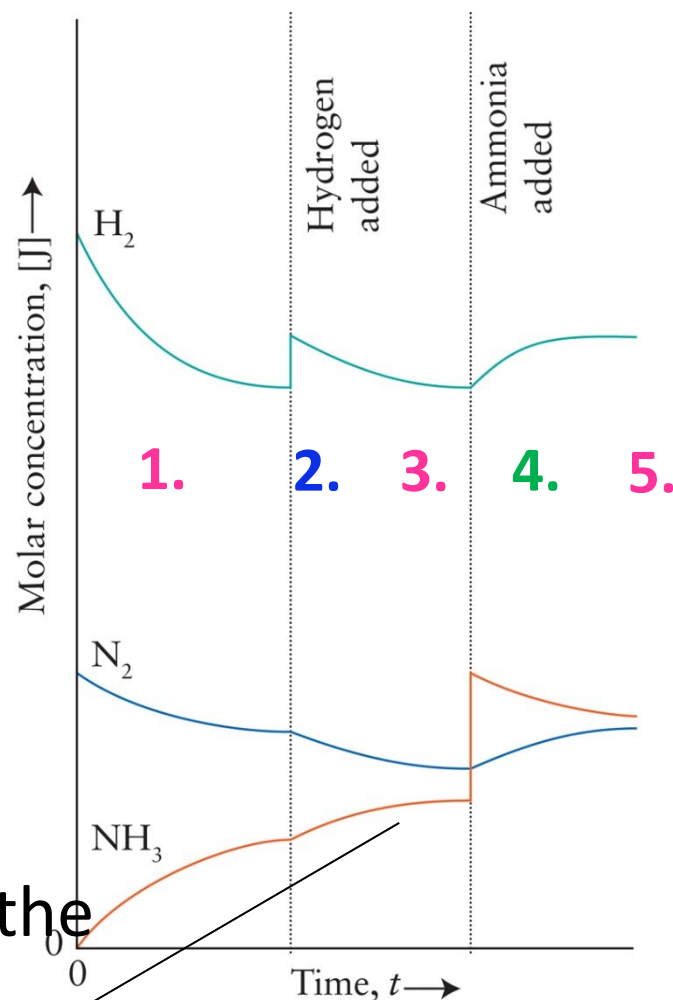
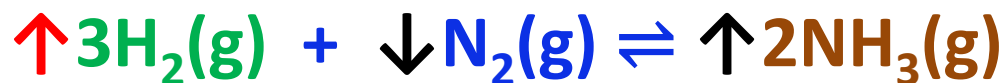


Figure 5J.4

Atkins, *Chemical Principles: The Quest for Insight*, 7e  
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# The Response of Equilibria to Changes in Conditions

4. Ammonia is added.

5. The reaction approaches equilibrium.

**Adding  $\text{NH}_3$**  shifts the reaction to produce more  $\uparrow \text{H}_2$  and  $\uparrow \text{N}_2$

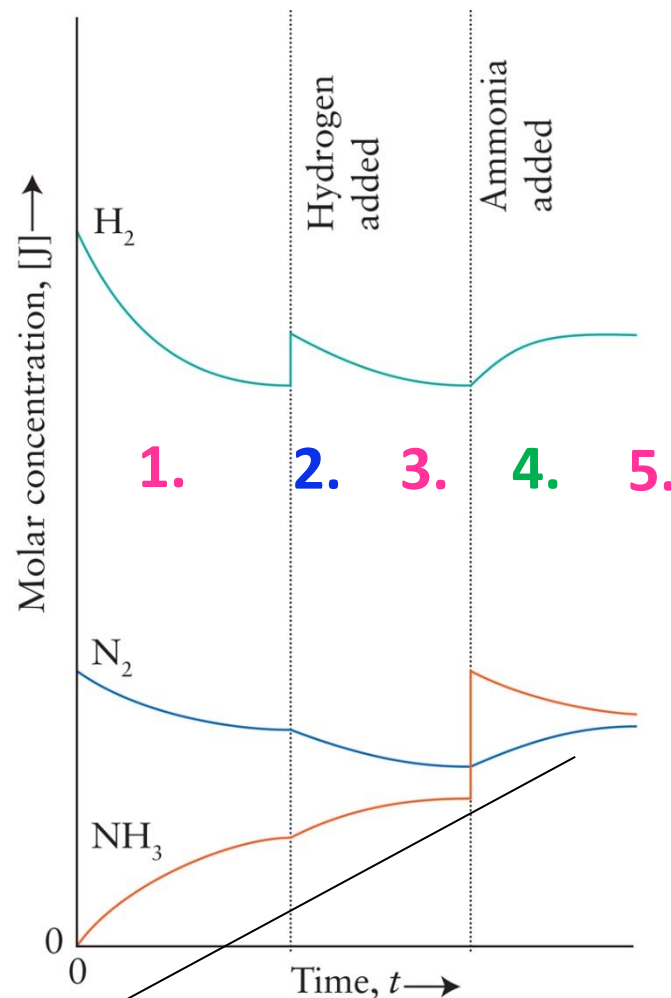
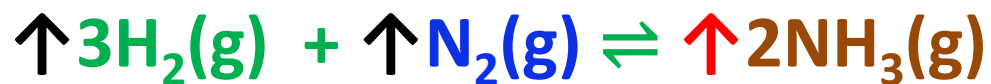
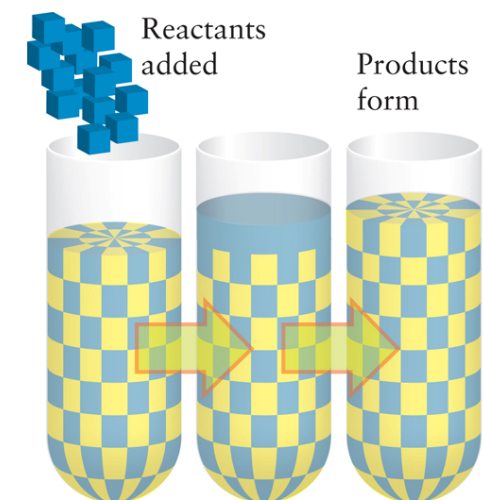


Figure 5.14

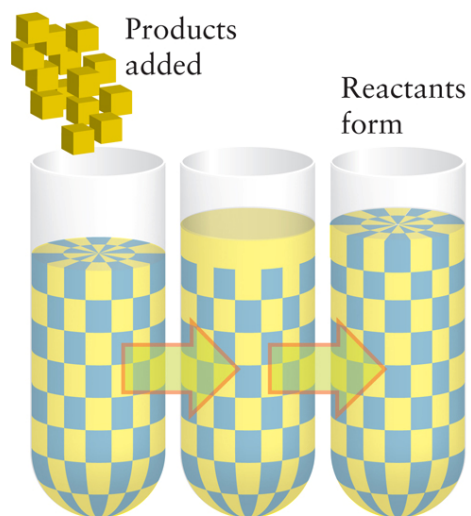
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# The Response of Equilibria to Changes in Conditions



(a)  $K = 1$      $Q < K$      $K = 1$



(b)  $K = 1$      $Q > K$      $K = 1$

In the preceding examples reactants or products were added.

In each case,  $Q$  was disturbed.

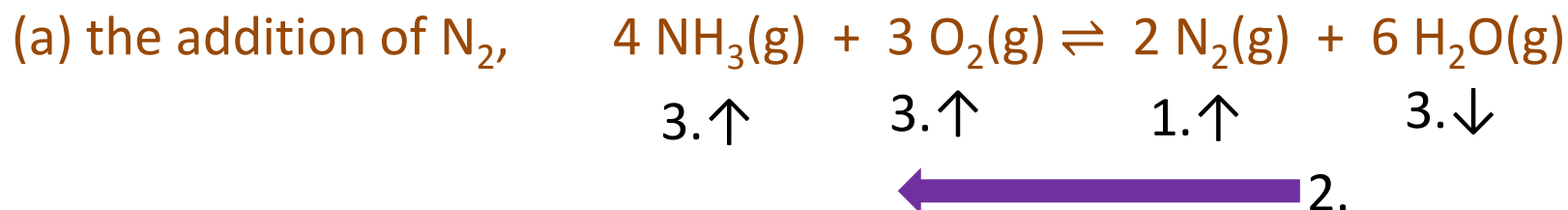
Also, in each case, the reaction reached  $K$  after time.

**Figure 5J.5**  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

Example 5J.1 Consider the equilibrium

$4\text{NH}_3(\text{g}) + 3\text{O}_2(\text{g}) \rightleftharpoons 2\text{N}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$ . Predict the effect on each equilibrium concentration of (a) the addition of  $\text{N}_2$ , (b) the removal of  $\text{NH}_3$ , and (c) the removal of  $\text{H}_2\text{O}$ .

3. Over time  $\text{N}_2$  will  $\downarrow$



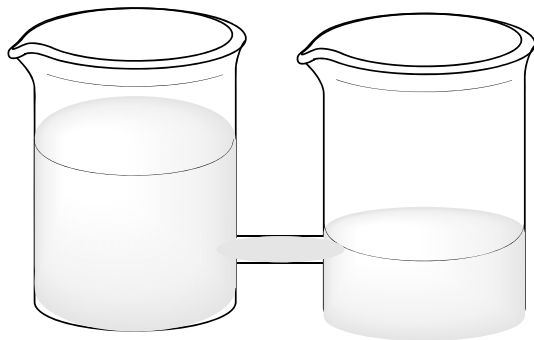
“1.  $\uparrow$ ” is an increase in concentration, and (1) means it was the first event.

“2.  $\leftarrow$ ” means a shift in equilibrium to the left to get rid of excess  $\text{N}_2$ .  
Excess  $\text{N}_2$  will react with  $\text{H}_2\text{O}$  producing more reactants ( $\text{NH}_3$  and  $\text{O}_2$ ).

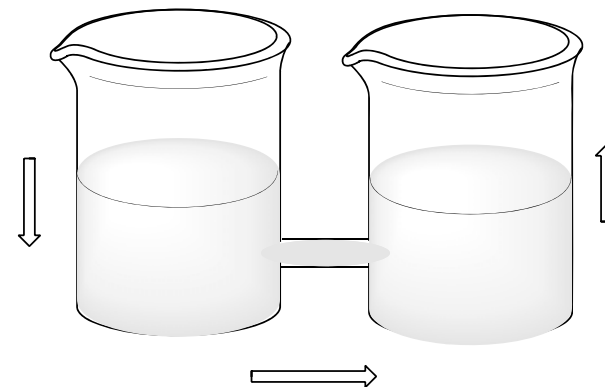
All “3” arrows describe the changes in concentration to reach equilibrium.

A more visual representation of equilibria is what happens to the water level in two beakers joined in such a way to allow water to move freely between the two beakers.

The water level is the same in each beaker, where the water level is representing an equilibrium in the two beakers.

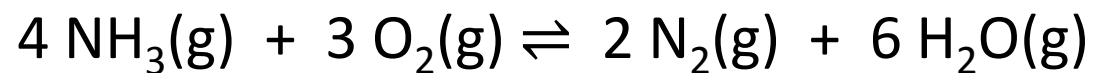


Adding water to the left beaker will cause the water to flow to the right.



The water flows until a new equilibrium is reached.

Example 5J.1 b. Removing a reactant,  $\text{NH}_3$



1. ↓

3. ↑

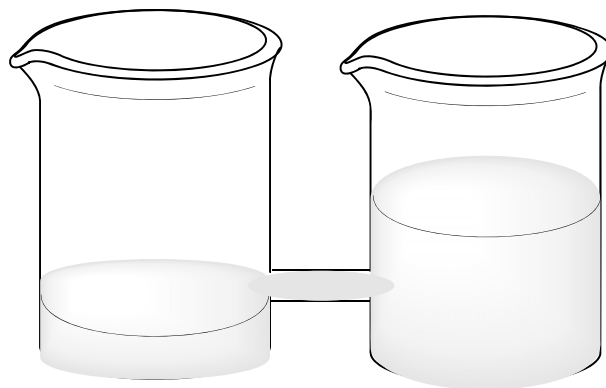
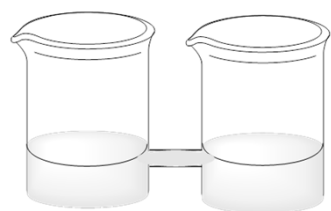
3. ↓

3. ↓

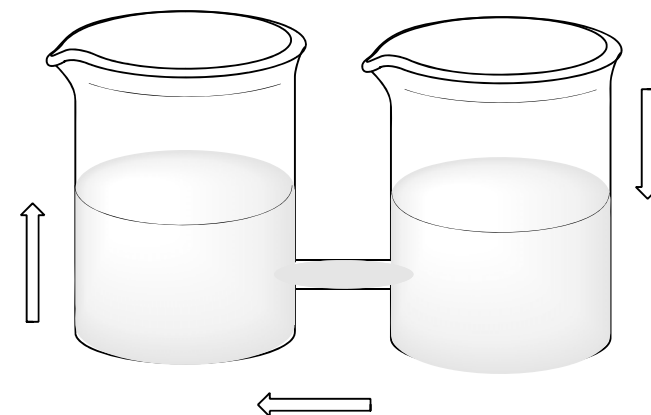
3. Over time  $\text{NH}_3$  will ↑



2. ← will cause the equilibrium to shift to the left, to make more reactants.



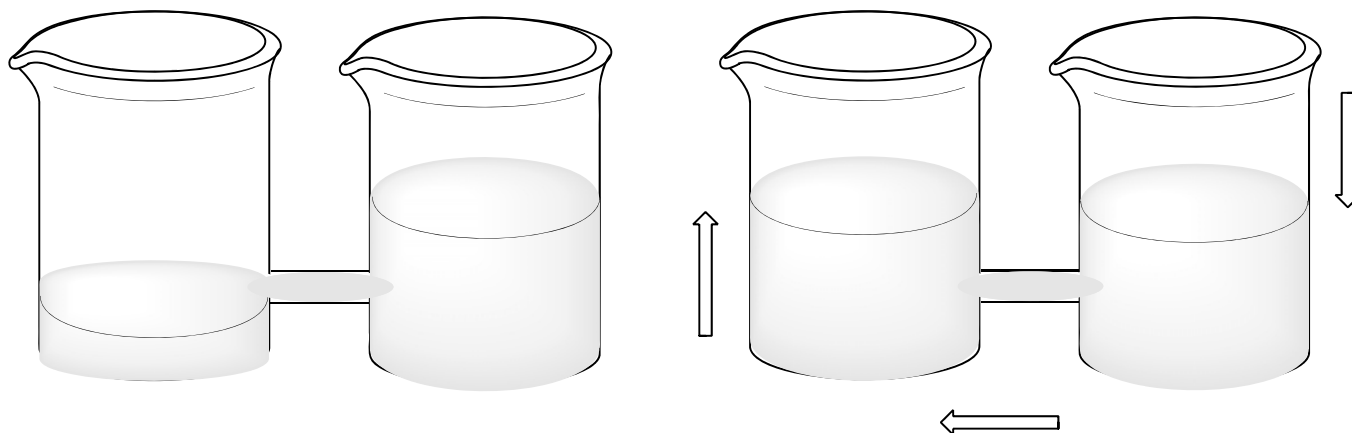
Removing water from the left represents removing a reactant, the water will flow to the left...



representing a shift in equilibrium to the reactant side.

Example 5J.1 Consider the equilibrium

$4 \text{NH}_3(\text{g}) + 3 \text{O}_2(\text{g}) \rightleftharpoons 2 \text{N}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{g})$ . Predict the effect on each equilibrium concentration of (a) the addition of  $\text{N}_2$ , (b) the removal of  $\text{NH}_3$ , (c) the removal of  $\text{H}_2\text{O}$ .



(a) the addition of  $\text{N}_2$ ,



3. ↑

3. ↑

1. ↑

3. ↓

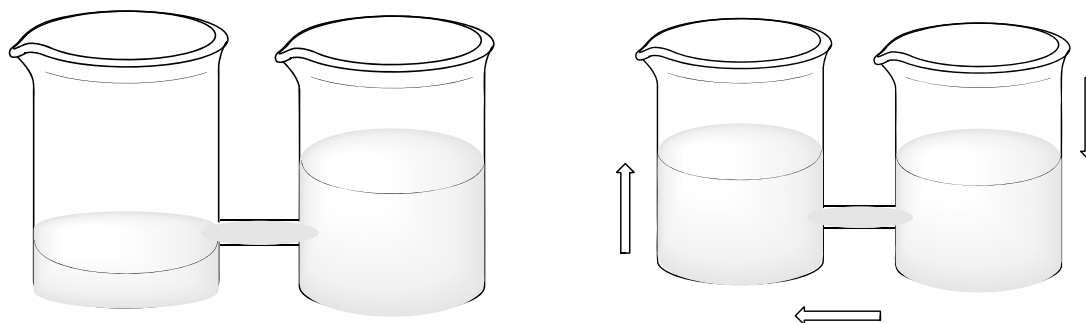
3. Over time  $\text{N}_2$  will ↓



2. ← will cause the equilibrium to shift to the left, to make more reactants.

Example 5J.1 Consider the equilibrium

$4 \text{NH}_3(\text{g}) + 3 \text{O}_2(\text{g}) \rightleftharpoons 2 \text{N}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{g})$ . Predict the effect on each equilibrium concentration of (a) the addition of  $\text{N}_2$ , (b) the removal of  $\text{NH}_3$ , and (c) the removal of  $\text{H}_2\text{O}$ .



(b) the removal of  $\text{NH}_3$ ,  $4 \text{NH}_3(\text{g}) + 3 \text{O}_2(\text{g}) \rightleftharpoons 2 \text{N}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{g})$

1.↓                      3.↑                      3.↓                      3.↓



3. Over time  $\text{NH}_3$  will ↑

2. ← will cause the equilibrium to shift to the left, to make more reactants.

## Forcing Products

Le Chatelier's principle suggests a good way to ensure that a reaction goes on generating a substance: simply *remove products as they are formed*.

(c) the **removal of H<sub>2</sub>O**



3.↓

3.↓

3.↑

1.↓

2. →



Example 5J.2 Using the final values from 5I.4 we add 0.0100 mol  $\text{Cl}_2(\text{g})$  to the container (of volume 500 mL), which is equal to 0.870 bar. Calculate the new composition of the equilibrium mixture,  $K = 78.3$  for the reaction  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ .

Example 5I.4

$\text{PCl}_5 = 0.02 \text{ bar}$

$\text{PCl}_3 = 1.28 \text{ bar}$

$\text{Cl}_2 = 1.28 \text{ bar}$

	$\text{PCl}_5$	$\text{PCl}_3$	$\text{Cl}_2$
initial	0.02	1.28	$1.28 + 0.870$
change	$+x$	$-x$	$-x$
final	$0.02 + x$	$1.28 - x$	$2.15 - x$

When we add to the product side, we expect to produce more reactant.

Now the final.



Example 5J.2 Using the final values from 5I.4 we add 0.0100 mol Cl<sub>2</sub>(g) to the container (of volume 500 mL), which is equal to 0.870 bar. Calculate the new composition of the equilibrium mixture,  $K = 78.3$  for the reaction  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ .

Write the equilibrium expression

$$K = \frac{(1.28 - x)(2.15 - x)}{0.02 + x} = 78.3 \quad \text{solved with software}$$

$$x = 0.01$$

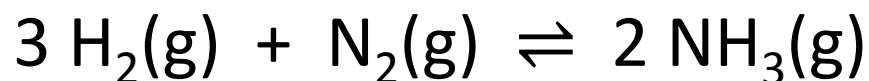
$$\text{PCl}_5 = 0.02 + x, 0.02 + 0.01 = 0.03 \text{ bar}$$

$$\text{PCl}_3 = 1.28 - x, 1.28 - 0.01 = 1.27 \text{ bar}$$

$$\text{Cl}_2 = 2.15 - x, 2.15 - 0.01 = 2.14 \text{ bar}$$

## Compressing a Reaction Mixture

Reducing the volume forces the molecules more closely together. This will shift the equilibrium to the side with the fewest number of moles of gas.



4 moles of gas  $\rightarrow$  2 moles of gas

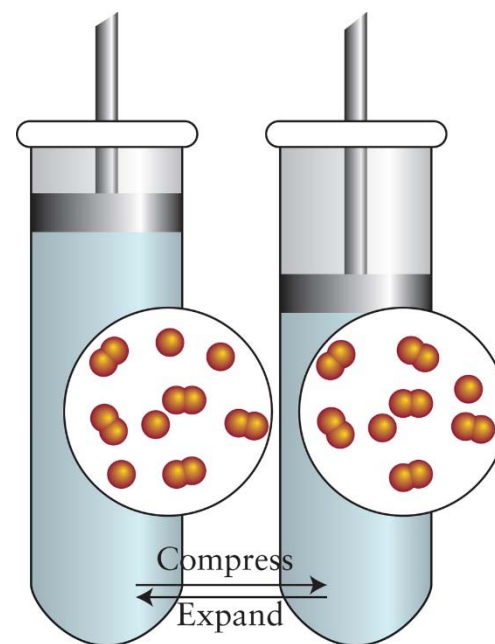
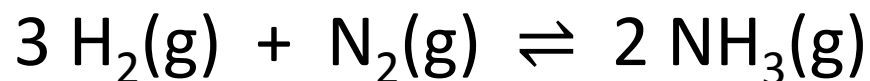


Figure 51.7  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

This results in a shift in equilibria to the side with the fewest moles of gas, thereby reducing the overall pressure.

## Compressing a Reaction Mixture

The opposite happens for an increase in volume.



4 moles of gas  $\leftarrow$  2 moles of gas

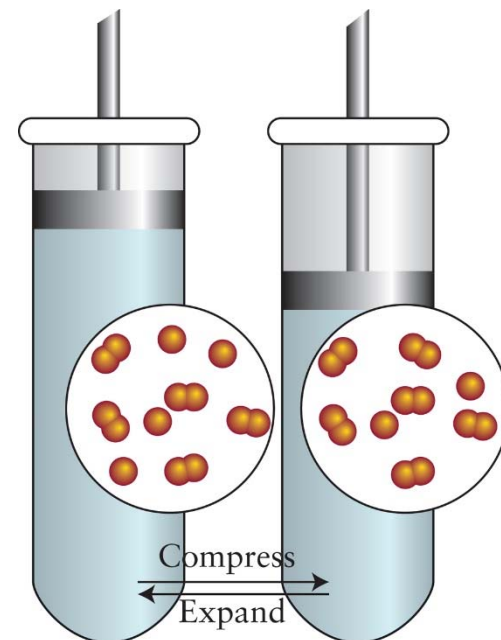
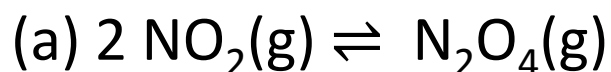


Figure 53.7  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

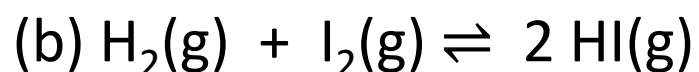
This results in a shift in equilibria to the side with the greatest moles of gas; this follows from gases expanding to fill their entire volume.

Example 5J.3 Predict the effect of compression on the equilibrium composition of the reaction mixtures in which the equilibria (a)  $2 \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$  and (b)  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$  have been established.



2 moles  $\rightarrow$  1 mole

A decrease in volume will force the equilibrium to shift to the side with the fewest moles of gas.



2 moles  $\rightarrow$  2 mole

Note: Adding an **inert gas** does not interfere with the reacting gases, so the reacting gases continue to occupy the same volume, and so their individual molar concentrations and partial pressures **remain unchanged** despite the presence of an inert gas.

## Temperature and Equilibrium

Changes in equilibrium are consistent with Le Chatelier's principle when heat is either removed or added to a reaction.

heat + reactants  $\rightleftharpoons$  products, ***endothermic***  
reactants  $\rightleftharpoons$  products + heat, ***exothermic***

In either case we treat changes in heat like we would a reactant or product.

Example 5J.4 One stage in the manufacture of sulfuric acid is the formation of sulfur trioxide by the reaction of  $\text{SO}_2$  with  $\text{O}_2$  in the presence of a vanadium(V) oxide catalyst. Predict how the equilibrium composition for the sulfur trioxide synthesis will tend to change when the temperature is raised.

For the reaction  $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$  we are missing information about whether the reaction is exothermic or endothermic, so we'll have to calculate,  $\Delta H^\circ$ .

$$\Delta H^\circ = \sum \Delta H^\circ (\text{products}) - \sum \Delta H^\circ (\text{reactants}).$$

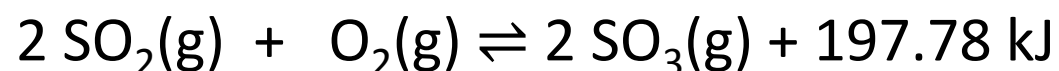
$$\Delta H^\circ = 2 \Delta H^\circ(\text{SO}_3(\text{g})) - [2 \Delta H^\circ(\text{SO}_2(\text{g})) + \Delta H^\circ(\text{O}_2(\text{g}))].$$

$$\Delta H^\circ = 2(-395.75 \text{ kJ}) - [2(-296.83 \text{ kJ}) + (0)].$$

$$\Delta H^\circ = -197.78 \text{ kJ}, \text{ exothermic.}$$

Example 5J.4 One stage in the manufacture of sulfuric acid is the formation of sulfur trioxide by the reaction of  $\text{SO}_2$  with  $\text{O}_2$  in the presence of a vanadium(V) oxide catalyst. Predict how the equilibrium composition for the sulfur trioxide synthesis will tend to change when the temperature is raised.

$$\Delta H^\circ = -197.78 \text{ kJ}, \text{ exothermic}$$



↑ raising the temperature

← Will shift the equilibrium to the product side

In the end    ↑  $\text{SO}_2$     ↑  $\text{O}_2$     ↓  $\text{SO}_3$     ↓ heat

## The Effect of Temperature on the Equilibrium Constant

The relation between the equilibrium constant and the standard Gibbs free energy of reaction,

$$\Delta G_1^\circ = -RT_1 \ln K_1 \quad \text{and for the second component}$$
$$\Delta G_2^\circ = -RT_2 \ln K_2$$

These are rearranged into  $\ln K_1 = \frac{\Delta G_1^\circ}{-RT_1}$  and  $\ln K_2 = \frac{\Delta G_2^\circ}{-RT_2}$

Combined into  $\ln K_2 - \ln K_1 = \frac{-1}{R} \left\{ \frac{\Delta G_2^\circ}{T_2} - \frac{\Delta G_1^\circ}{T_1} \right\}$

Since  $\Delta G = \Delta H - T\Delta S$



## The Effect of Temperature on the Equilibrium Constant

Combined into  $\ln K_2 - \ln K_1 = \frac{-1}{R} \left\{ \frac{\Delta G_1^\circ}{T_1} - \frac{\Delta G_2^\circ}{T_2} \right\}$

Since  $\Delta G = \Delta H - T\Delta S$

Substituting,  $\ln K_2 - \ln K_1 = \frac{-1}{R} \left\{ \frac{\Delta H_1^\circ - T_1 \Delta S_1^\circ}{T_1} - \frac{\Delta H_2^\circ - T_2 \Delta S_2^\circ}{T_2} \right\}$

Since  $\Delta H$  and  $\Delta S$  are independent of range of temperatures, we have our final form,

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

here we see  $K_2$  over  $K_1$  and no “-” on the right.

Example 5J.5 The equilibrium constant  $K$  for the synthesis of ammonia is  $6.8 \times 10^5$  at 298 K. Predict its value at 400 K,  
 $3 \text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$ .

We use,  $\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$  and we will solve for  $K_2$ .

Calculate  $\Delta H^\circ = 2 \Delta H^\circ(\text{NH}_3(\text{g})) - [3 \Delta H^\circ(\text{H}_2(\text{g})) + \Delta H^\circ(\text{N}_2(\text{g}))]$

$\Delta H^\circ = 2 (-46.11 \text{ kJ}) - [2 (0) + (0)]$ ,  $\Delta H^\circ = -92.22 \text{ kJ}$  or  $-92,220 \text{ J}$

$$\ln \frac{K_2}{6.8 \times 10^5} = \frac{-92,220 \text{ J}}{8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} \left( \frac{1}{298 \text{ K}} - \frac{1}{400. \text{ K}} \right)$$

$$K_2 = 6.8 \times 10^5 e^{\frac{-92,220 \text{ J}}{8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} \left( \frac{1}{298 \text{ K}} - \frac{1}{400. \text{ K}} \right)}$$

$$K_2 = 6.8 \times 10^5 e^{-9.49} = 51$$

**HUGE Decrease in  $K$  ( $\sim 10^4$  times)!**