

CHEM2100J Chemistry Autumn 2024

Chapter 10 Chemical Equilibrium

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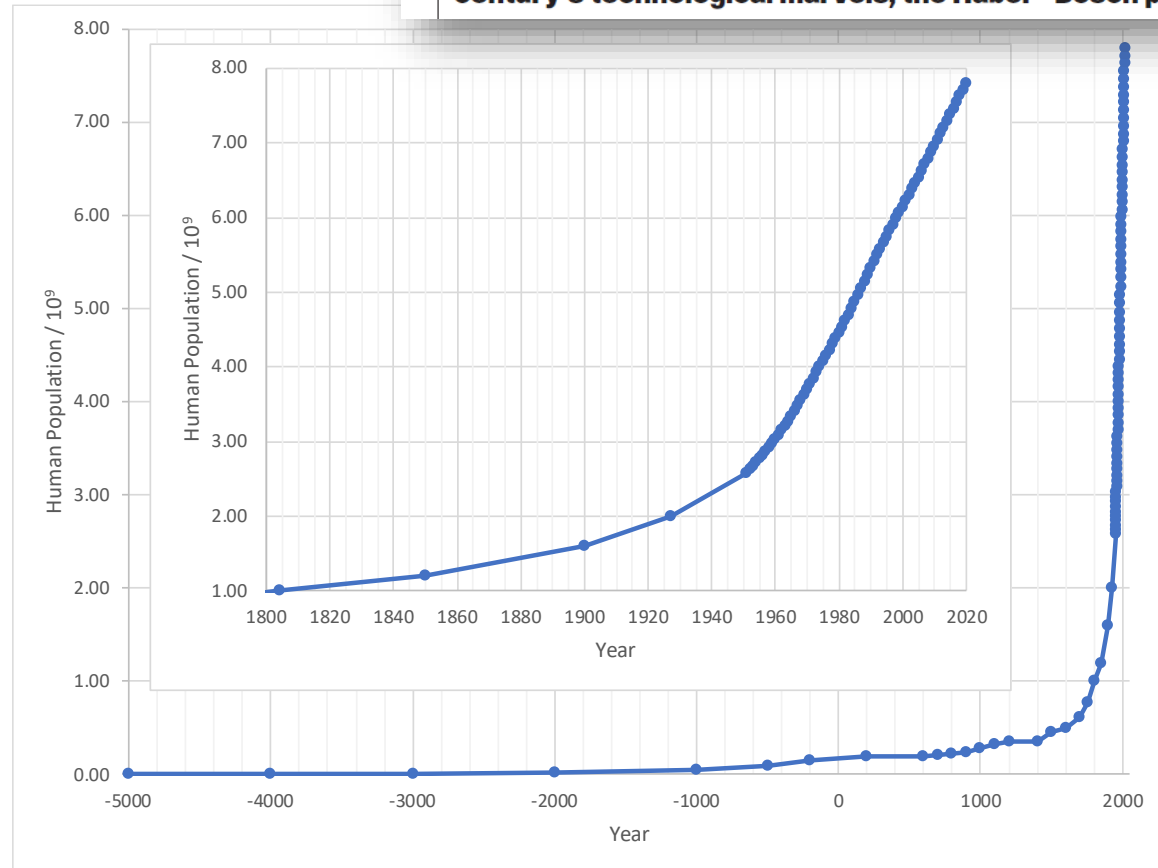
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Nature, 1999

millennium essay

Detonator of the population explosion

Without ammonia, there would be no inorganic fertilizers, and nearly half the world would go hungry. Of all the century's technological marvels, the Haber–Bosch process has made the most difference to our survival.



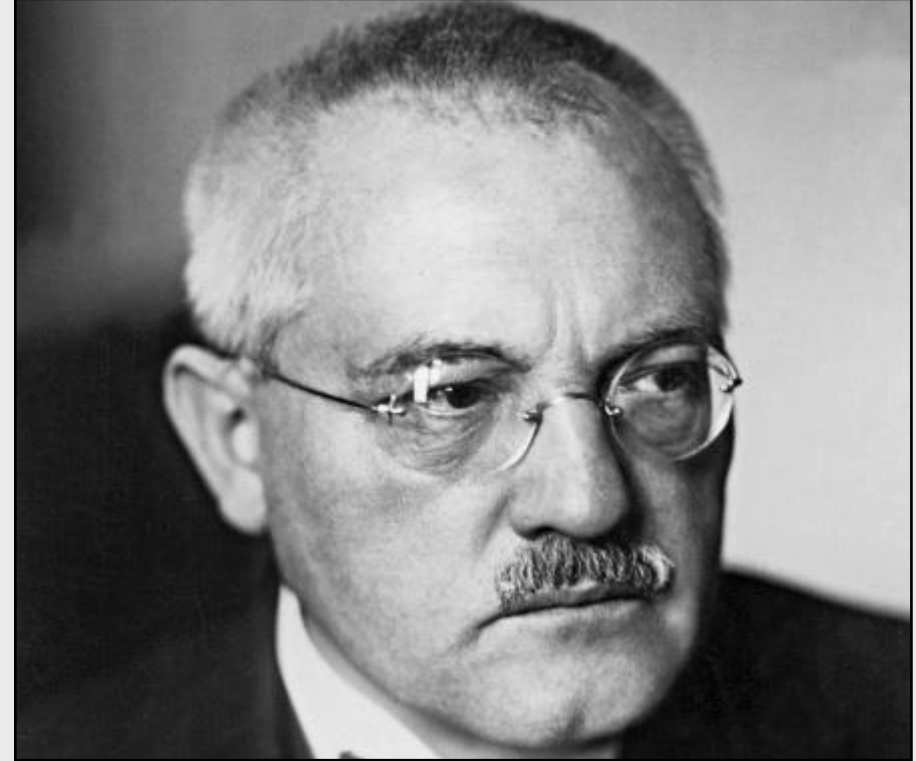
Haber (right) invented the process while Bosch brought the necessary engineering skills.

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Fritz Haber & Carl Bosch



Fritz Haber
1918 Nobel in Chemistry



Carl Bosch
1931 Nobel in Chemistry
High-pressure Chemistry

N₂ Fixation



Even though nitrogen is common (78% of air is N₂), twentieth century methods were unable to convert nitrogen into **nitrates** and ammonia.

Finally, a German chemist, **Fritz Haber**, and a chemical engineer, **Carl Bosch**, found a way to **improve the yield** by **changing the reaction conditions**.

Synthetic Ammonia



Fritz Haber and **Carl Bosch** were the *first* to produce ammonia, originally thought *impossible to make* on a large scale, by **changing the reaction conditions**.

Instead of following “normal stoichiometry” rules, they

1. added **overwhelming** quantities of reactants, *and*
2. continually **starved** the reaction by removing product.



This feat was possible by understanding the nature of equilibrium reactions.

Equilibrium Reactions are Dynamic

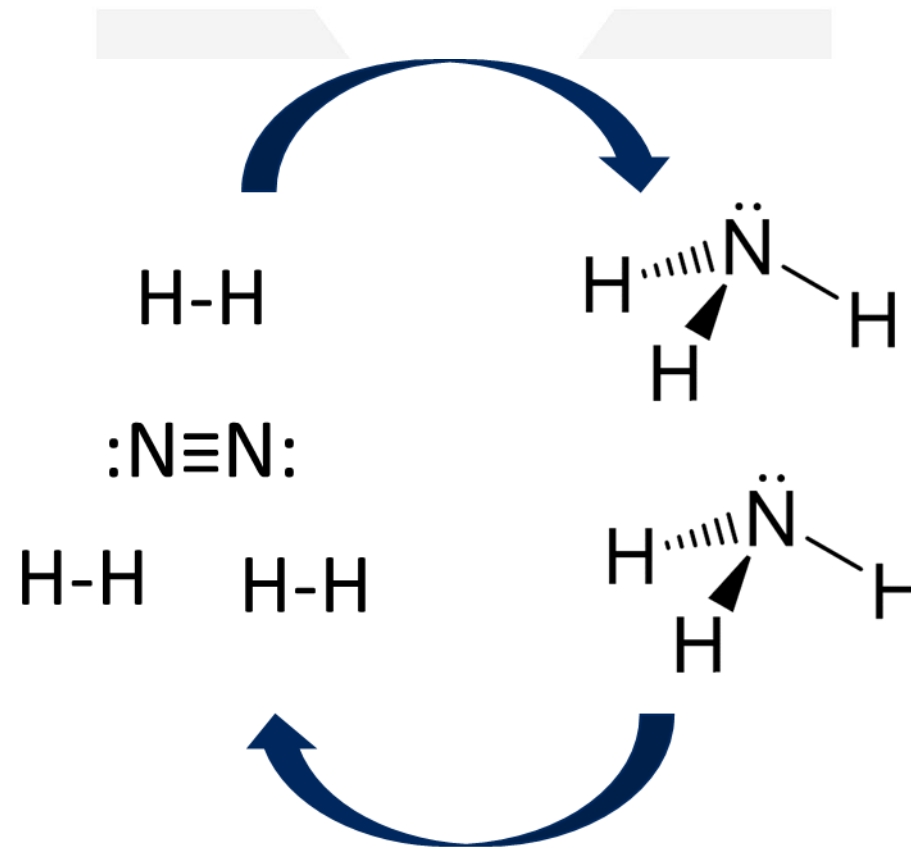


Both forward and reverse reactions occur at the same rate.

As fast as reactants make products, products will react to make reactants, all at the same **speed**.

Though this appears to be a static reaction, in reality the reaction races to make both *reactants and products*.

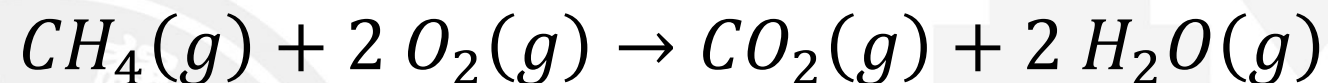
“ \rightleftharpoons ” means the reaction is in chemical equilibrium



Reactions NOT at Equilibrium



Burning methane, CH_4 , in oxygen is a one-way reaction:



Here we only make products.

Just like time as we experience it moves only in one direction.

Reactions at Equilibrium



The *criteria* for dynamic chemical equilibrium are:

1. The forward and reverse reactions are both taking place.
2. The forward rate equals the reverse rate (so there appears to be no net change in concentration).

Rates of breaking and making bonds are the same.

Forward **rate** \rightleftharpoons Reverse **rate**



“ \rightleftharpoons ” means the reaction is in chemical equilibrium

Equilibrium

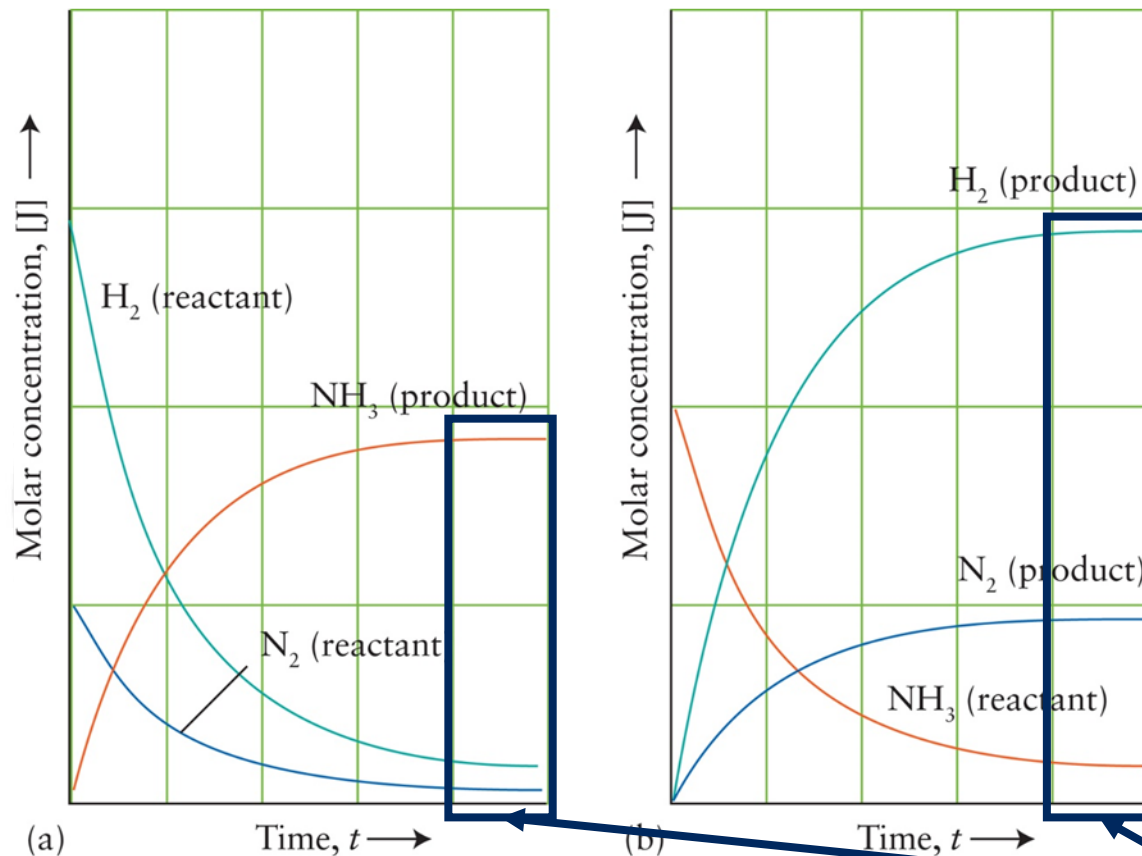
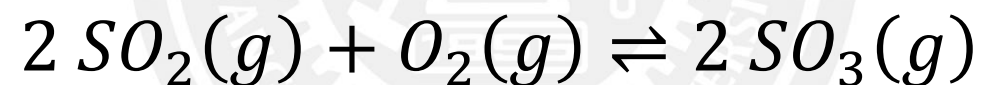


Figure 5G.1
Atkins, *Chemical Principles: The Quest for Insight*, 7e
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Note, it's **impossible** to **make more product** when at equilibrium. The reaction just **appears to have stopped moving**.

Equilibrium is
reached

Cato Guldberg (mathematician), and Peter Waage (chemist), discovered in 1864 the mathematical equilibrium relationship



	$p_{\text{SO}_2} / \text{bar}$	$p_{\text{O}_2} / \text{bar}$	$p_{\text{SO}_3} / \text{bar}$	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

K is the same **regardless** of initial compositions

This is known as the **equilibrium constant** (K) and summarizes the law of mass action as:

$$K_p = \left\{ \frac{\text{partial pressure of } \textcolor{blue}{Products}}{\text{partial pressure of } \textcolor{red}{Reactants}} \right\}_{\text{equilibrium}}$$

In general, for the reaction $\textcolor{red}{a} A(g) + \textcolor{red}{b} B(g) \rightleftharpoons \textcolor{blue}{c} C(g) + \textcolor{blue}{d} D(g)$:

$$K_p = \frac{(p_C)^c \cdot (p_D)^d}{(p_A)^a \cdot (p_B)^b}$$

p : partial pressure

Example



Write the equilibrium constant for the ammonia synthesis reaction:



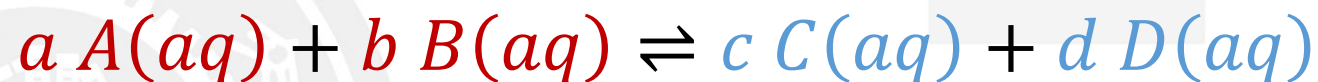
$$K_p = \frac{p_{products}}{p_{reactants}} = \frac{(p_C)^c \cdot (p_D)^d}{(p_A)^a \cdot (p_B)^b}$$

$$K_p = \frac{(p_{NH_3})^2}{(p_{H_2})^3 \cdot p_{N_2}}$$

The partial pressure p is used as reactants and products are **gases**.

From thermodynamics we know there is a relationship between pressure and concentration of liquids (Henry's law, $s = k_H \cdot p_{gas}$).

Changing from (g) to (aq)



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

Note: The brackets [] symbolize the concentration c in $\text{mol} \cdot \text{L}^{-1}$.

Equilibrium Measurements



$$K_p = \frac{(p_C)^c \cdot (p_D)^d}{(p_A)^a \cdot (p_B)^b}$$

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

Notice that the p in the K_p stands for equilibrium constant in terms of pressure, and in K_c , the c means concentration in terms of $\text{mol}\cdot\text{L}^{-1}$.

Also, $K_p \neq K_c$, something we'll look at shortly.

Equilibrium Measurements



It can be shown empirically or thermodynamically that pure **liquids** or **solids** **do not** appear in K .

Consider the equilibrium expression for:



Both $CaCO_3(s)$ and $CaO(s)$ do not appear in the equilibrium expression:

$$K_p = p_{CO_2}$$

Activity

It is common when deriving equations to simplify expressions without units, so the **empirical form** of partial pressure, p_B or concentration $[B]$, are reported as the activity of partial pressure $a_B = p_B$, or the activity of concentration $a_B = [B]$.

(Empirically it is just a pure number without units).

Ideal gas	$a_B = \frac{p_B}{1 \text{ bar}}$
Solute in a dilute solution	$a_B = \frac{[B]}{1 \frac{\text{mol}}{\text{L}}}$
Pure solid or pure liquid	$a_B = 1$ Unchanging throughout the reaction so are not included in an equilibrium

Equilibrium Constant



Each reaction has its **own characteristic equilibrium constant** at **its own temperature**.

The *extraordinary empirical result* is that, regardless of the initial composition, the *reaction adjusts* so that the activities give **the same characteristic value of K** for each reaction at that temperature.

$H_2(g) + Cl_2(g) \rightleftharpoons 2 HCl(g)$	
T / K	K_p
300	4.0×10^{31}
500	4.0×10^{18}
1000	5.1×10^8
$I_2(g) \rightleftharpoons 2 I(g)$	
T / K	K_p
800	2.1×10^{-3}
1000	0.26
1200	6.8

In Chapter 8, Gibbs free energy tells us the tendency “if,” **not** how fast, the reaction reaches equilibrium:

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

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

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

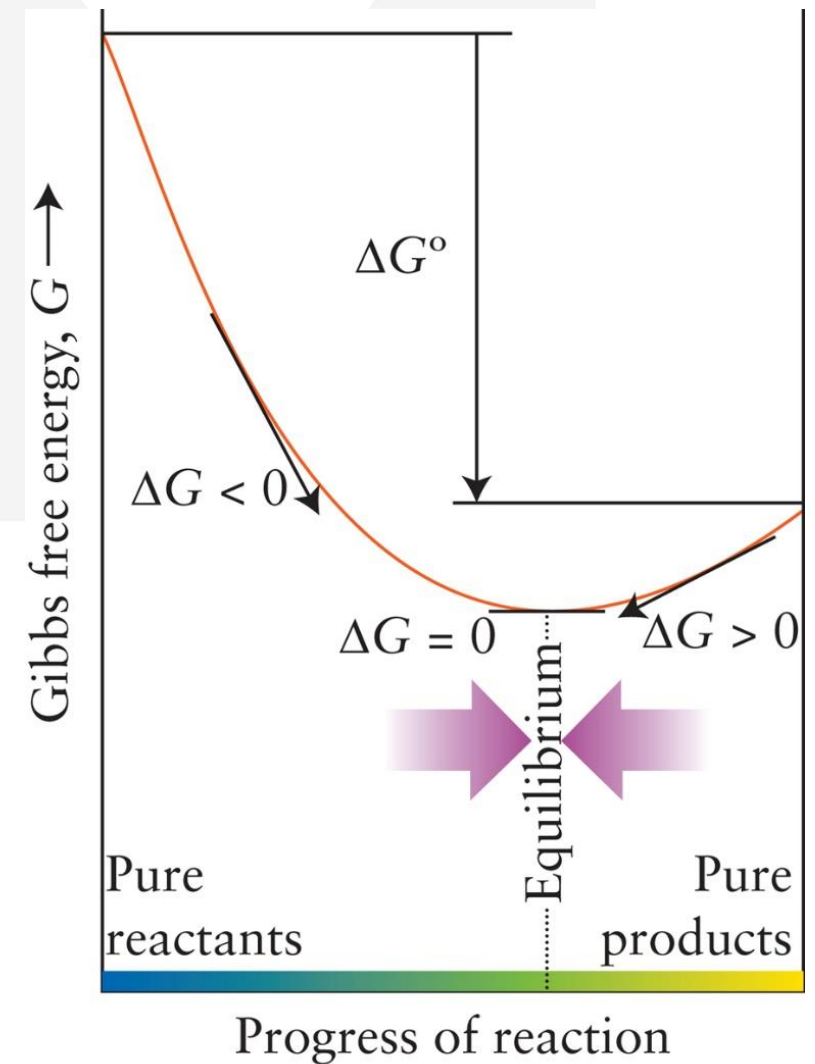
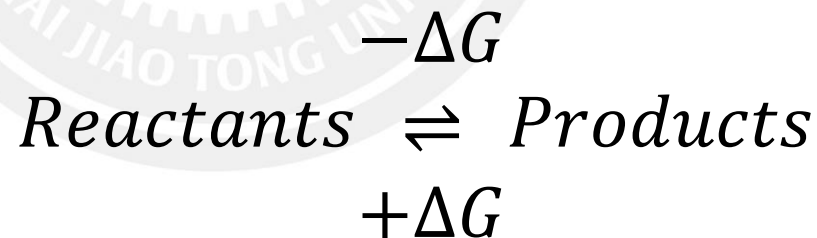


Figure 5G.4

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Origins of K and ΔG



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

(see textbook for derivation)

$$\Delta G_r = \Delta G_r^\circ + RT \cdot \ln \left(\frac{(a_C)^c \cdot (a_D)^d}{(a_A)^a \cdot (a_B)^b} \right)$$

a : Activity (either partial pressure of a gas or concentration of a solute in a solution)

r : Overall reaction

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

$$\Delta G_r = \Delta G_r^\circ + RT \cdot \ln(Q)$$

Origins of K and ΔG



$$\Delta G_r = \Delta G_r^\circ + RT \cdot \ln(Q)$$

Be careful not to confuse Q (reaction quotient) with K (equilibrium constant).

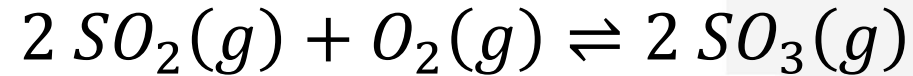
K is a **constant**, it is known.

Q is **unknown** and must be found for every moment of a reaction. Q can be smaller or larger than K . It has to be **calculated**.

Example



The standard Gibbs free energy of reaction for:



is $\Delta G_r^\circ = -141.74 \frac{\text{kJ}}{\text{mol}}$ at 25.00 °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 reaction spontaneous?

$$\Delta G_r = \Delta G_r^\circ + RT \cdot \ln \left(\frac{(a_C)^c \cdot (a_D)^d}{(a_A)^a \cdot (a_B)^b} \right) = \Delta G_r^\circ + RT \cdot \ln \left(\frac{(a_{SO_3})^2}{(a_{SO_2})^2 \cdot (a_{O_2})} \right)$$

$$\Delta G_r = -141.74 \frac{\text{kJ}}{\text{mol}} + 8.314 \times 10^{-3} \frac{\text{kJ}}{\text{mol} \cdot \text{K}} \times (273.15 + 25.00)\text{K} \times \ln \left(\frac{(100)^2}{(100)^2 \times (100)} \right) = -153.16 \frac{\text{kJ}}{\text{mol}}$$

$\Delta G_r < 0$, therefore the reaction is spontaneous and SO_3 will be formed.

Reaction quotient

$$Q = \frac{(a_C)^c \cdot (a_D)^d}{(a_A)^a \cdot (a_B)^b}$$

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 calculate the reaction quotient, Q , and compare it to K to see if the reaction reached equilibrium.

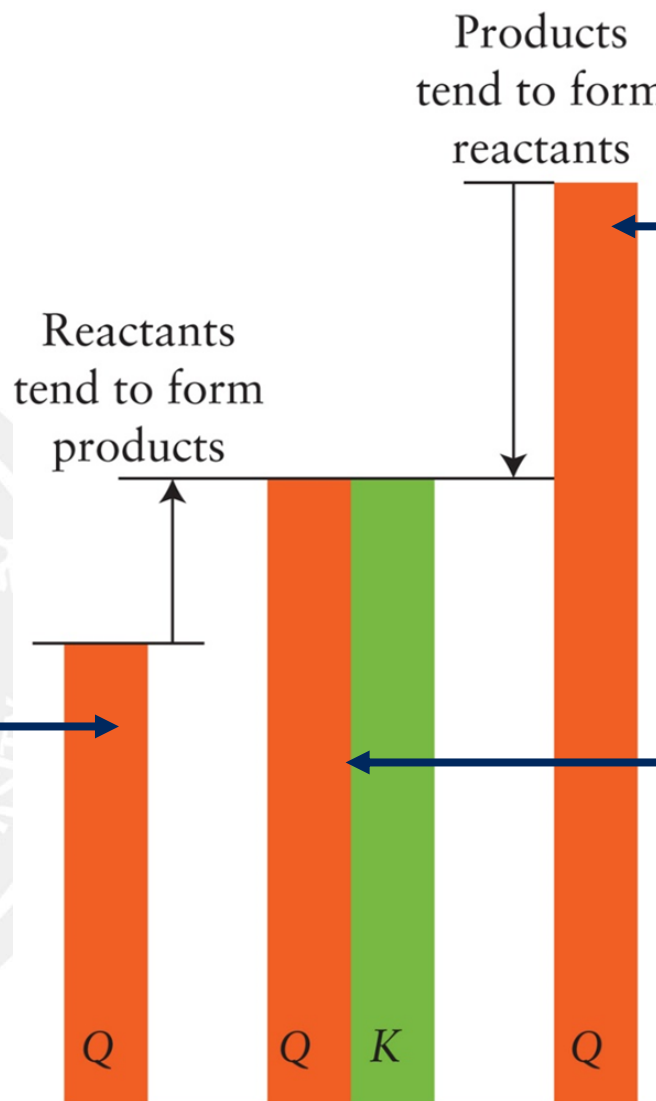
The Direction of Reaction Depending on Q



Reaction quotient

$$Q = \frac{(a_C)^c \cdot (a_D)^d}{(a_A)^a \cdot (a_B)^b}$$

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



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

If $Q = K$, $\Delta G = 0$, the mixture has reached its equilibrium, and there is no tendency to change in either direction.

Figure 51.2
Atkins, *Chemical Principles: The Quest for Insight*, 7e
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Example



A mixture of hydrogen, iodine, and hydrogen iodide, each at 55 kPa, was introduced into a container heated to 783 K. At this temperature, $K_p = 46$ for $H_2(g) + I_2(g) \rightleftharpoons 2 HI(g)$. Predict whether HI has a tendency to form or to decompose into $H_2(g)$ and $I_2(g)$.

$$Q = \frac{p_{products}}{p_{reactants}} = \frac{(a_C)^c \cdot (a_D)^d}{(a_A)^a \cdot (a_B)^b}$$

$$Q = \frac{(a_{HI})^2}{(a_{H_2}) \cdot (a_{I_2})} = \frac{(55)^2}{(55) \cdot (55)} = 1.0$$

Since $Q = 1.0 < 46 = K_p$, the reaction will move forward and form more products ($HI(g)$).

Origins of K and ΔG , When $Q = K$



$$\Delta G_r = \Delta G_r^\circ + RT \cdot \ln(Q)$$

Once $Q = K$, the reaction is at equilibrium, therefore $\Delta G_r = 0$. This leads to:

$$0 = \Delta G_r^\circ + RT \cdot \ln(K)$$

$$\Delta G_r^\circ = -RT \cdot \ln(K)$$

This links the thermodynamic tables for ΔG_r° to K .

Example

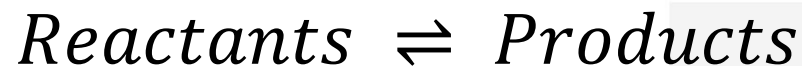


At 25 °C, $\Delta G_r^\circ = +1.70 \frac{\text{kJ}}{\text{mol}}$ for $\frac{1}{2} H_2(g) + \frac{1}{2} I_2(s) \rightleftharpoons HI(g)$. Calculate the equilibrium constant for this reaction.

$$\Delta G_r^\circ = -RT \cdot \ln(K)$$

$$K_p = e^{-\frac{\Delta G_r^\circ}{RT}} = e^{-\frac{1.70 \frac{\text{kJ}}{\text{mol}}}{8.314 \times 10^{-3} \frac{\text{kJ}}{\text{mol} \cdot \text{K}} \times (273.15 + 25.00) \text{K}}} = 0.504$$

The Extent of Reaction: What Does K Mean?

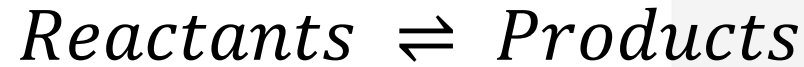


$$K_p = \left\{ \frac{\text{partial pressure of } \textcolor{blue}{\text{Products}}}{\text{partial pressure of } \textcolor{red}{\text{Reactants}}} \right\}_{\text{equilibrium}}$$

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

For instance, for a large K of 1×10^6 , also written as $\frac{1,000,000}{1}$, 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?



$$K_p = \left\{ \frac{\text{partial pressure of } \textcolor{blue}{\text{Products}}}{\text{partial pressure of } \textcolor{red}{\text{Reactants}}} \right\}_{\text{equilibrium}}$$

For K 's smaller than 1, we expect more reactants than products.

For instance, for a small K of 1×10^{-6} , also written as $\frac{1}{1,000,000}$, 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?

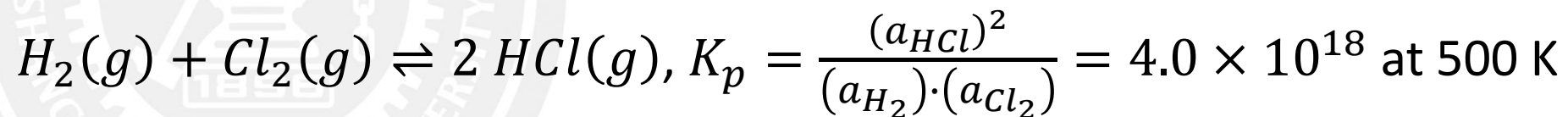


Reactants \rightleftharpoons Products

$$K = \frac{a_{\text{Products}}}{a_{\text{Reactants}}}$$

$$\Delta G_r^\circ = -RT \cdot \ln(K)$$

An equilibrium with a **strongly negative ΔG_r°** occurs when the reaction is mainly products. K would also very large.



The main component expected in the reaction vessel would be HCl. As expected,
 $\Delta G_r^\circ = -95.30 \frac{\text{kJ}}{\text{mol}}$.

The Extent of Reaction: What Does K Mean?

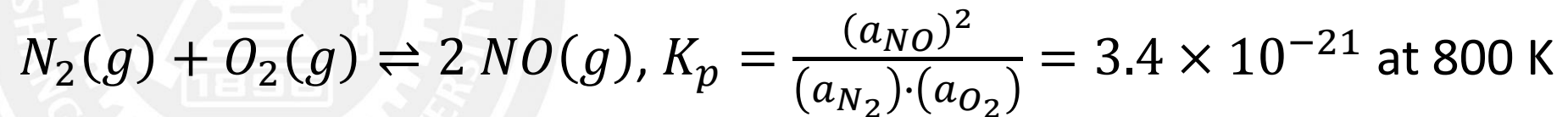


Reactants \rightleftharpoons Products

$$K = \frac{a_{\text{Products}}}{a_{\text{Reactants}}}$$

$$\Delta G_r^\circ = -RT \cdot \ln(K)$$

An equilibrium with a **strongly positive ΔG_r°** occurs when the reaction is mainly reactants. K would also very small.



The main component expected in the reaction vessel would be N_2 and O_2 . As expected, $\Delta G_r^\circ = +104.20 \frac{\text{kJ}}{\text{mol}}$.

Summary



Reactants \rightleftharpoons Products

$$K = \frac{a_{\text{Products}}}{a_{\text{Reactants}}}$$

$$\Delta G_r^\circ = -RT \cdot \ln(K)$$

$K \ll 1$ **favours reactants** at equilibrium ($\Delta G_r^\circ \gg 0$)

When $10^{-3} < K < 10^3$ **neither** products nor reactants are favoured; when $-10 < \Delta G_r^\circ < 10$ the *temperature* will be the deciding factor

$K \gg 1$ **favours products** at equilibrium ($\Delta G_r^\circ \ll 0$)

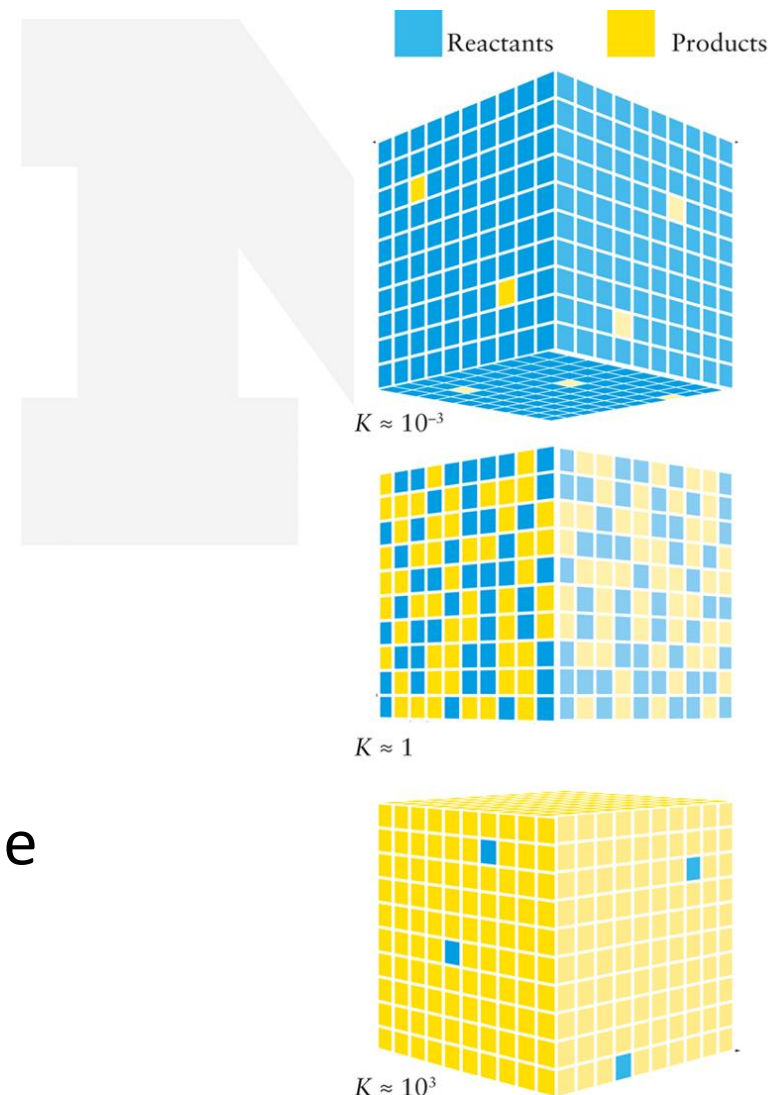
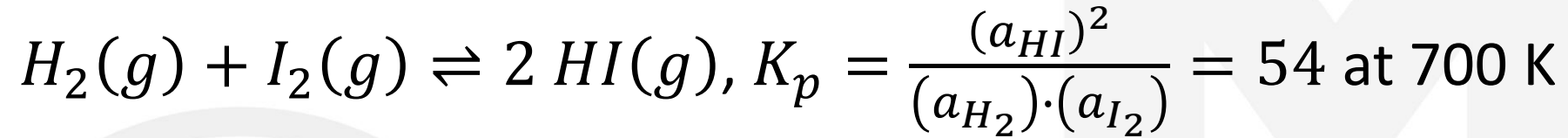


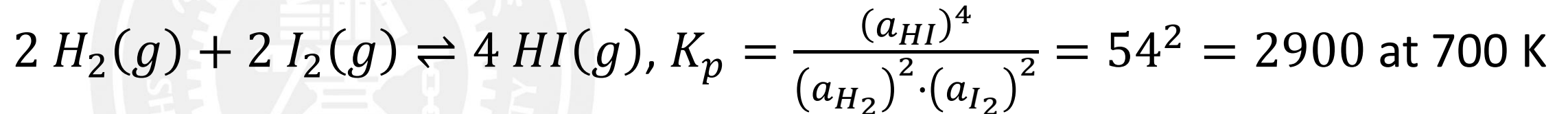
Figure 5I.1

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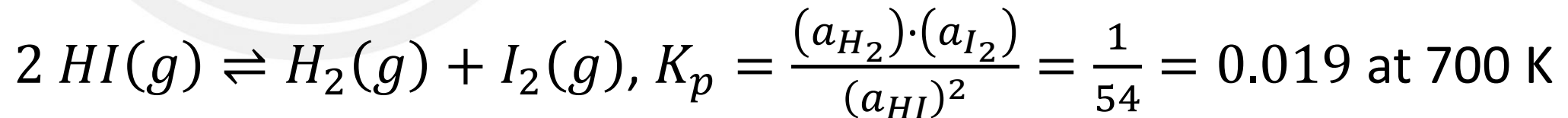
The following algebraic manipulations are helpful for deriving different forms of equilibrium constant expressions.



Multiplying the equation by 2:



Reversing the equation:

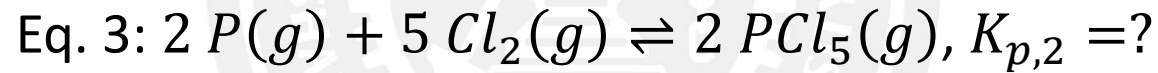
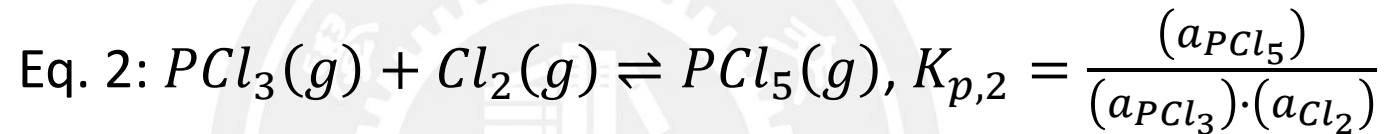
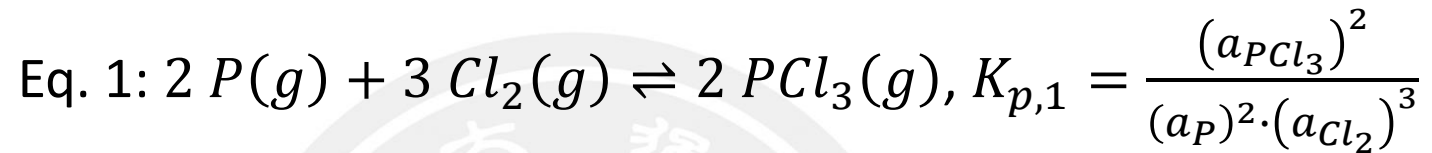


Alternative Forms of the Equilibrium Constant

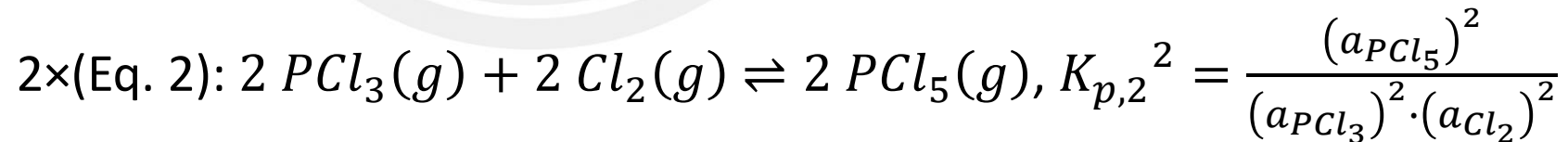


Multiple equilibrium constants can be combined to find an **overall equilibrium constant**.

Example:



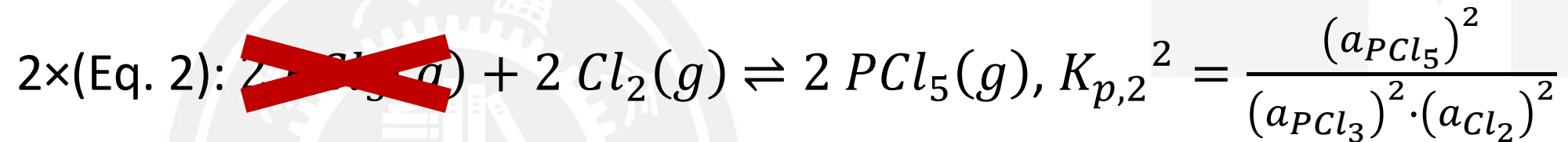
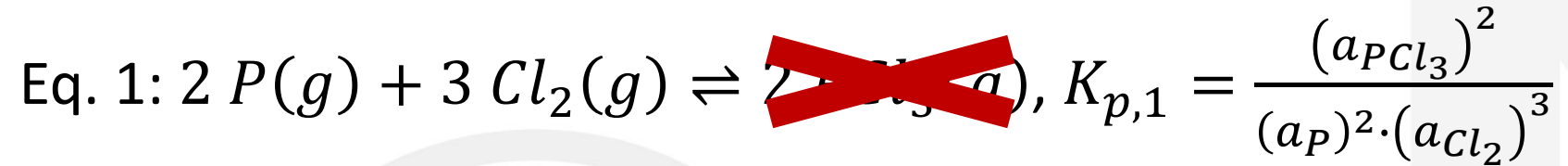
Eq. 1 can remain unchanged. Eq. 2 has to be multiplied by 2:



Alternative Forms of the Equilibrium Constant



Combining Eq. 1 and 2×(Eq. 2) yields:

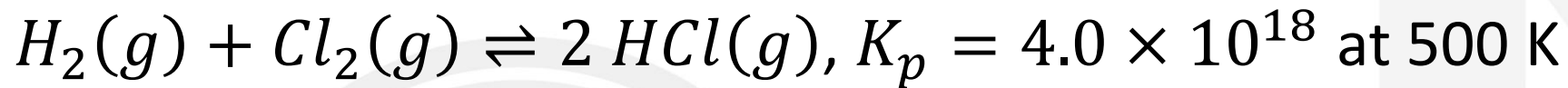


$$K_{p,3} = K_{p,1} \cdot K_{p,2}^2 = \frac{(a_{PCl_3})^2}{(a_P)^2 \cdot (a_{Cl_2})^3} \cdot \frac{(a_{PCl_5})^2}{(a_{PCl_3})^2 \cdot (a_{Cl_2})^2} = \frac{(a_{PCl_5})^2}{(a_P)^2 \cdot (a_{Cl_2})^5}$$

Example



Suppose that, in an equilibrium mixture of HCl, Cl₂, and H₂, the partial pressure of H₂ is 4.2 mPa and that of Cl₂ is 8.3 mPa. What is the partial pressure of HCl (in bar)?



$$K_p = \frac{(a_{HCl})^2}{(a_{H_2}) \cdot (a_{Cl_2})} = \frac{\left(\frac{p_{HCl}}{1 \text{ bar}}\right)^2}{\left(\frac{p_{H_2}}{1 \text{ bar}}\right) \cdot \left(\frac{p_{Cl_2}}{1 \text{ bar}}\right)}$$

$$p_{HCl} = \sqrt{K_p \cdot \left(\frac{p_{H_2}}{1 \text{ bar}}\right) \cdot \left(\frac{p_{Cl_2}}{1 \text{ bar}}\right)} \times 1 \text{ bar} = \sqrt{4.0 \times 10^{18} \times \left(\frac{4.2 \times 10^{-8} \text{ bar}}{1 \text{ bar}}\right) \cdot \left(\frac{8.3 \times 10^{-8} \text{ bar}}{1 \text{ bar}}\right)} \times 1 \text{ bar} = 120 \text{ bar}$$

Using Equilibrium Constants



Equilibrium constants are
“**constants**” and are therefore,
powerful predicting tools!

Next, we look at:

1. Calculating K from knowing equilibrium concentrations.
2. Calculating equilibrium concentrations from knowing K .

	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

The final K is always the same, **regardless** of initial compositions

Example



Starting with 1 bar each of H_2 and I_2 , the equilibrium pressure of HI was found to be 0.8 bar. What are the final pressures of H_2 and I_2 ?

- We start by building an equilibrium table and plugging in the given data;
- **Initially** 1 bar each of H_2 and I_2 and no HI;
- **Equilibrium** was 0.8 bar of HI;

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

	H_2	I_2	HI
initial	1	1	0
change			
equilibrium (final)			0.8

Example



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 **equilibria of** H_2 and I_2 are found by combining the **initial** and **changes**.

	H_2	I_2	HI
initial	1	1	0
change	$\frac{1}{2} \times 0.8 = -0.4$	$\frac{1}{2} \times 0.8 = -0.4$	+ 0.8
equilibrium (final)	$1 - 0.4 = 0.6$	$1 - 0.4 = 0.6$	0.8

Example



At equilibrium:

$$p_{H_2} = p_{I_2} = 0.6 \text{ bar}$$

$$p_{HI} = 0.8 \text{ bar}$$

Calculating K_p :

$$K_p = \frac{(a_{HI})^2}{(a_{H_2}) \cdot (a_{I_2})} = \frac{(0.8)^2}{(0.6) \times (0.6)} = 1.78$$

A cleaned-up table

	H ₂	I ₂	HI
initial	1	1	0
change	-0.4	-0.4	+ 0.8
equilibrium (final)	0.6	0.6	0.8

Example



Starting with 0.5 bar each of H_2 and N_2 , it was found at equilibrium that the pressure of NH_3 was 0.02 bar. What are the final pressures of H_2 and N_2 ?

- 1) Make an equilibrium table with starting values.
- 2) Calculate the one change we know, here NH_3 .
- 3) Using stoichiometry, calculate the changes in H_2 and N_2 .
- 4) Combine the initial and change to find the final.

	H_2	N_2	NH_3
initial	0.50	0.50	0
change	$\frac{3}{2} \times 0.02 = -0.03$	$\frac{1}{2} \times 0.02 = -0.01$	+0.02
equilibrium (final)	0.47	0.49	0.02

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

Example



At equilibrium:

$$p_{H_2} = 0.47 \text{ bar}$$

$$p_{N_2} = 0.49 \text{ bar}$$

$$p_{NH_3} = 0.02 \text{ bar}$$

Calculating K_p :

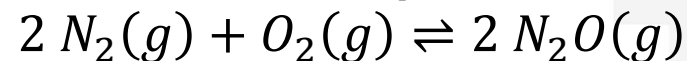
$$K_p = \frac{(a_{NH_3})^2}{(a_{H_2})^3 \cdot (a_{N_2})} = \frac{(0.02)^2}{(0.47)^3 \times (0.49)} = 7.9 \times 10^{-3}$$

	H ₂	N ₂	NH ₃
initial	0.50	0.50	0
change	-0.03	-0.01	+0.02
equilibrium (final)	0.47	0.49	0.02

Example



Suppose that a mixture of 0.482 mol N_2 and 0.933 mol O_2 is transferred to a reaction vessel of volume 10.0 L and allowed to form N_2O at 800 K; at this temperature, $K_p = 3.2 \times 10^{-28}$ for the reaction:



Calculate the partial pressures of the gases in the equilibrium mixture.

Initial partial pressures using $pV = nRT$:

$$p_{N_2} = \frac{0.482 \text{ mol} \times 8.314 \frac{\text{N} \cdot \text{m}}{\text{mol} \cdot \text{K}} \times 800 \text{ K}}{10.0 \times 10^{-3} \text{ m}^3} = 3.21 \times 10^5 \frac{\text{N}}{\text{m}^2} = 3.21 \text{ bar}$$

$$p_{O_2} = \frac{0.933 \text{ mol} \times 8.314 \frac{\text{N} \cdot \text{m}}{\text{mol} \cdot \text{K}} \times 800 \text{ K}}{10.0 \times 10^{-3} \text{ m}^3} = 6.21 \times 10^5 \frac{\text{N}}{\text{m}^2} = 6.21 \text{ bar}$$

$$p_{N_2O} = 0$$

Example



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.

Equilibrium expression:

$$K_p = \frac{(a_{\text{N}_2\text{O}})^2}{(a_{\text{N}_2})^2 \cdot (a_{\text{O}_2})} = \frac{(2\mathbf{x})^2}{(3.21 - 2\mathbf{x})^2 \times (6.21 - \mathbf{x})} = 3.2 \times 10^{-28}$$

	N ₂	O ₂	N ₂ O
initial	3.21	6.21	0
change	-2 x	- x	+2 x
equilibrium (final)	3.21-2 x	6.21- x	+2 x

Example



$$K_p = \frac{(a_{N_2O})^2}{(a_{N_2})^2 \cdot (a_{O_2})} = \frac{(2x)^2}{(3.21 - 2x)^2 \times (6.21 - x)} = 3.2 \times 10^{-28}$$

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

Next, we look at an **approximation** that can greatly reduce the time we spend solving complex problems.

Approximation



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

This means this is a “**reactant-favoured**” 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.

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 ₂ O
initial	3.21	6.21	0
change	-2 x	- x	+2 x
equilibrium (final)	3.21-2 x	6.21- x	+2 x

	N ₂	O ₂	N ₂ O
initial	3.21	6.21	0
change	-2 x	- x	+2 x
equilibrium (final)	3.21	6.21	+2 x

Approximation



This approximation greatly simplifies our equilibrium expression:

$$K_p = \frac{(a_{N_2O})^2}{(a_{N_2})^2 \cdot (a_{O_2})} = \frac{(2x)^2}{(3.21 - 2x)^2 \times (6.21 - x)} = 3.2 \times 10^{-28}$$

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

$$x = \sqrt{\frac{3.2 \times 10^{-28} \times (3.21)^2 \times (6.21)}{4}} = 7.2 \times 10^{-14}$$

This allows us to solve for the final concentrations.

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

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

$$a_{\text{equil}, N_2}: 3.21 - 2 \times (7.2 \times 10^{-14}) = 3.21$$

$$a_{\text{equil}, O_2}: 6.21 - (7.2 \times 10^{-14}) = 6.21$$

$$a_{\text{equil}, N_2O}: 2 \times (7.2 \times 10^{-14}) = 1.4 \times 10^{-13}$$

	N_2	O_2	N_2O
initial	3.21	6.21	0
change	$-2x$	$-x$	$+2x$
equilibrium (final)	$3.21-2x$	$6.21-x$	$+2x$

Remember:

$$a_B = \frac{p_B}{1 \text{ bar}}$$

Question: When Can We „Throw“ x Out?



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

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

	N ₂	O ₂	N ₂ O
initial	3.21	6.21	0
change	-2 x	- x	+2 x
equilibrium (final)	3.21-2 x	6.21- x	+2 x

	N ₂	O ₂	N ₂ O
initial	3.21	6.21	0
change	-2 x	- x	+2 x
equilibrium (final)	3.21	6.21	+2 x

Question: When Can We „Throw“ x Out?



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

Previously:

$x = 7.2 \times 10^{-14}$, with an initial partial pressure of 3.21 bar.

$$\text{relative change} = \frac{x}{a_{\text{initial}}}$$

$$\text{relative change} = \frac{7.2 \times 10^{-14}}{3.21} = 2.2 \times 10^{-14}$$

$$2.2 \times 10^{-14} \ll 0.05 = 5\%$$

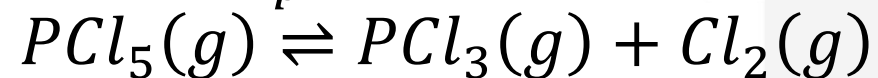
	N ₂	O ₂	N ₂ O
initial	3.21	6.21	0
change	-2 x	- x	+2 x
equilibrium (final)	3.21-2 x	6.21- x	+2 x

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



Suppose that we place 3.12 g of PCl_5 in a reaction vessel of volume 500 mL and reach equilibrium at 250 °C, when $K_p = 78.3$ for the reaction



All three substances are gases at 250 °C. Find the composition of the equilibrium mixture in bar.

$$M_{\text{PCl}_5} = 208.24 \frac{\text{g}}{\text{mol}}$$

$$p_{\text{PCl}_5} = \frac{n_{\text{PCl}_5} RT}{V} = \frac{\frac{m_{\text{PCl}_5}}{M_{\text{PCl}_5}} \cdot RT}{V}$$

$$p_{\text{PCl}_5} = \frac{\frac{3.12 \text{ g}}{208.24 \frac{\text{g}}{\text{mol}}} \times 8.314 \frac{\text{N} \cdot \text{m}}{\text{mol} \cdot \text{K}} \times (273.15 + 250) \text{K}}{0.500 \times 10^{-3} \text{ m}^3} = 1.30 \times 10^5 \frac{\text{N}}{\text{m}^2} = 1.30 \text{ bar}$$

Example



$$K_p = \frac{x^2}{1.30 - x} = 78.3$$

However, K_p is very large, which means “ x ” in $1.30 - x$ will be *substantial*; **PCl₅** will **dissociate noticeably**.

We simplify to:

$$x^2 = 78.3 \times (1.30 - x)$$

$$0 = x^2 + 78.3x - 102$$

The only way to solve this is with the quadratic formula.

	PCl ₅	PCl ₃	Cl ₂
initial	1.30	0	0
change	- x	+ x	+ x
equilibrium (final)	1.30- x	x	x

Example



$$0 = x^2 + 78.3x - 102$$

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

$$x = \frac{-78.3 \pm \sqrt{78.3^2 - 4 \times 1 \times (-102)}}{2 \times 1}$$

$$x = 1.28 \text{ or } x = -79.6$$

Since negative pressures are physically meaningless, we discard the negative solution and remain with $x = 1.28$.

$$a_{\text{equil}, \text{PCl}_5} = 1.30 - 1.28 = 0.02$$

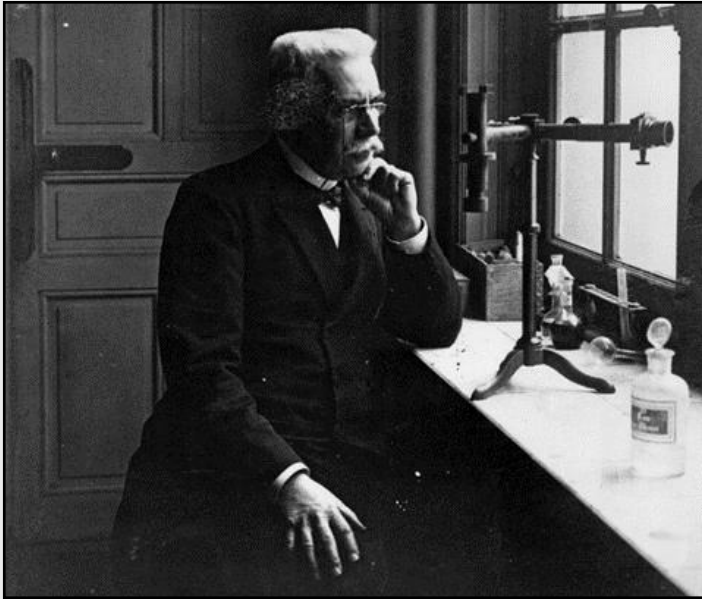
$$a_{\text{equil}, \text{PCl}_3} = x = 1.28$$

$$a_{\text{equil}, \text{Cl}_2} = x = 1.28$$

	PCl_5	PCl_3	Cl_2
initial	1.30	0	0
change	-1.28	+1.28	+1.28
equilibrium (final)	0.02	1.28	1.28

$$\text{relative change} = \frac{1.28}{1.30} = 0.985$$

The Response of Equilibria to Change



Henri Le Chatelier

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

After the initial change in G_r (and K) the composition reaches $\Delta G_r = 0$ again.

The French chemist Henri Le Chatelier first noticed that equilibrium disturbances re-approach equilibrium. This is now known as *Le Chatelier's principle*.

The Response of Equilibria to Change



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) H_2 shifts the reaction to produce more $\uparrow NH_3$

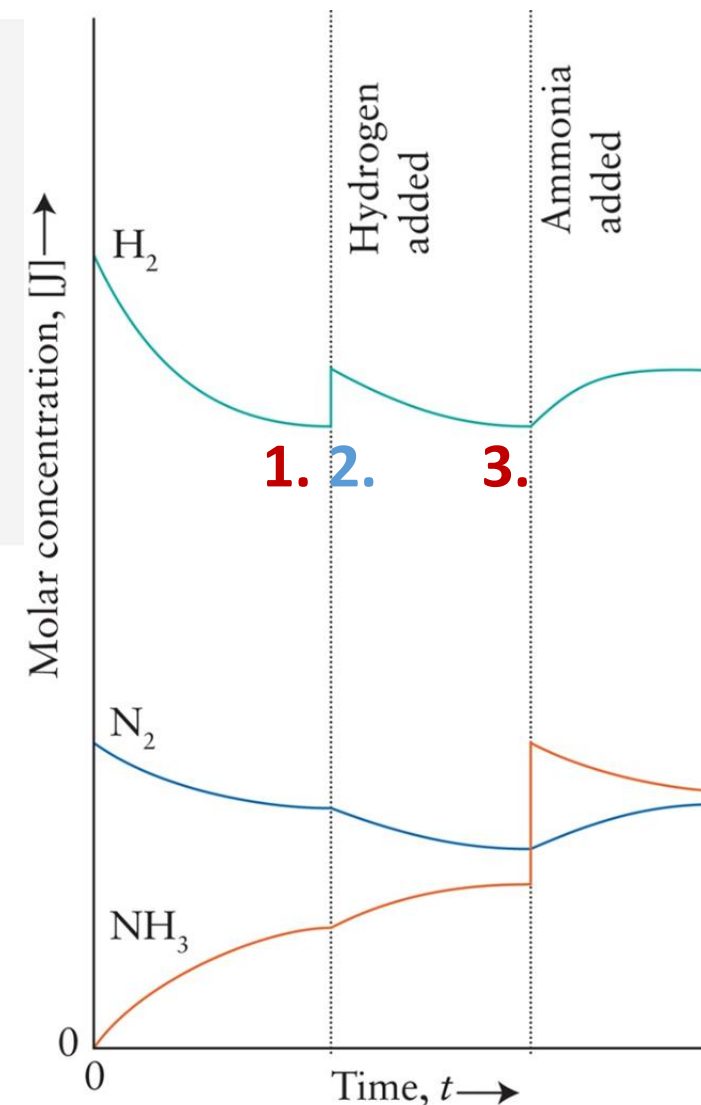
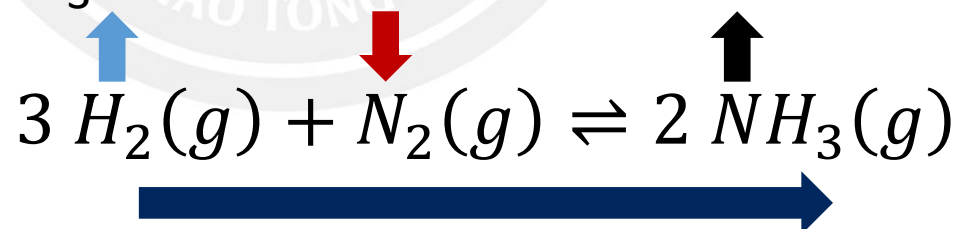


Figure 5J.4

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The Response of Equilibria to Change



4. Ammonia is added.

5. The reaction again approaches equilibrium.

Adding (↑) NH_3 shifts the reaction to produce more ↑ H_2 and ↑ N_2

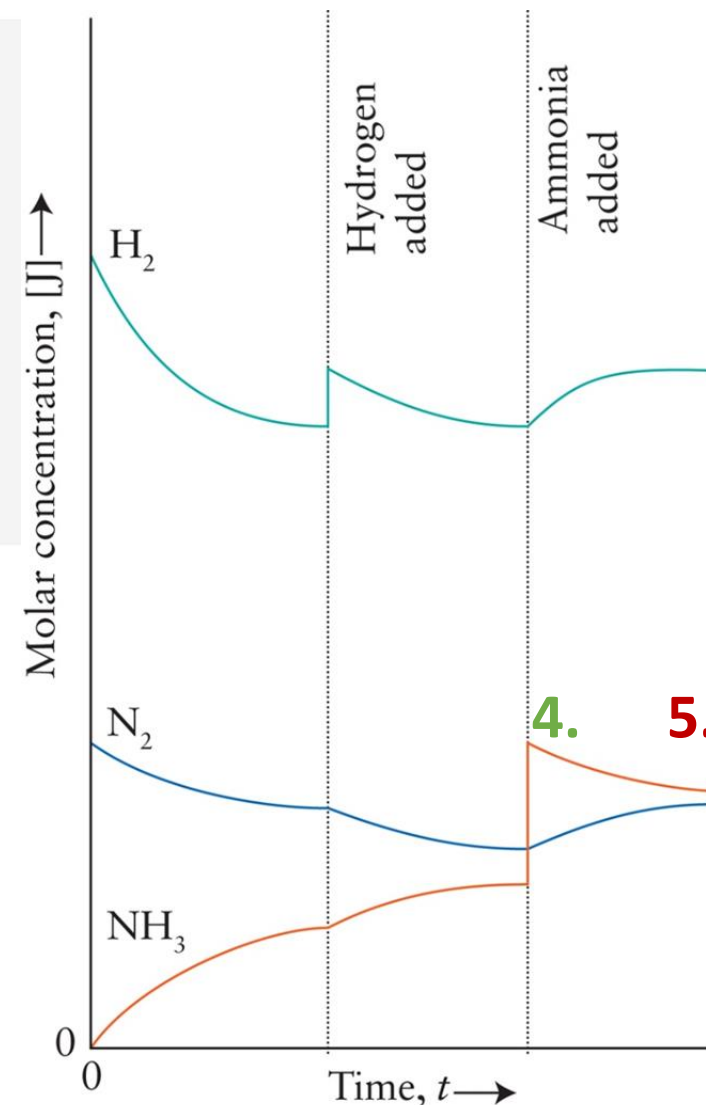
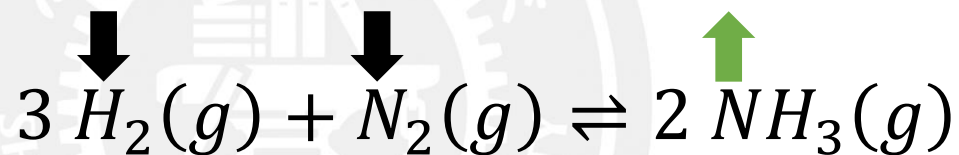
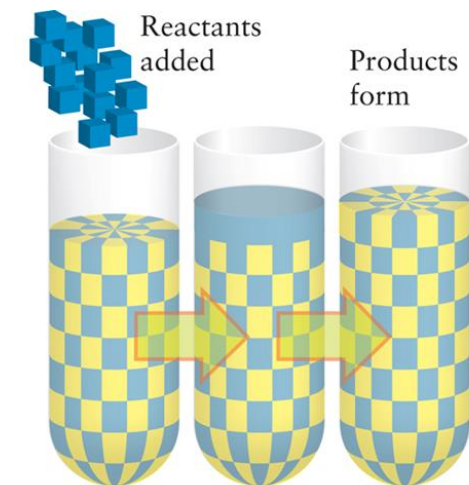


Figure 5J.4

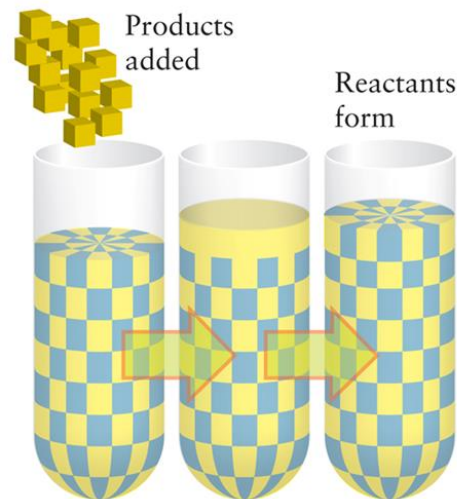
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The Response of Equilibria to Change



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



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

Figure 5J.5

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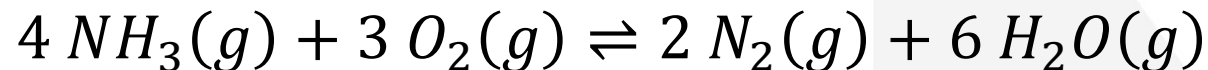
In the preceding examples reactants or products were added.

In each case, Q was disturbed.

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

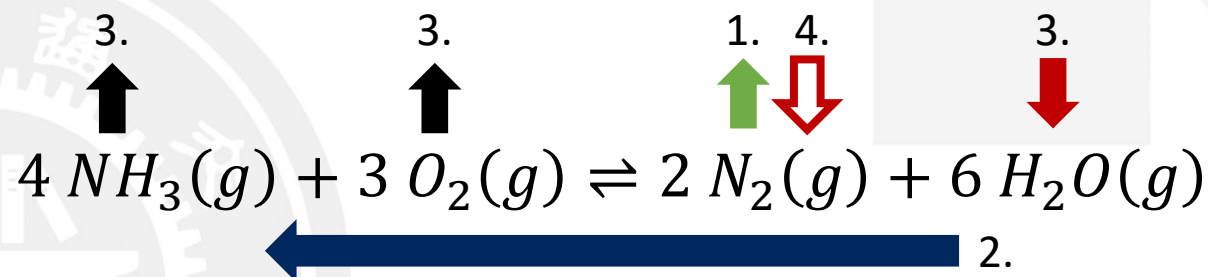
Example

Consider the equilibrium:



Predict the effect on each equilibrium concentration of (a) the addition of N_2 , (b) the removal of NH_3 , and (c) the removal of H_2O .

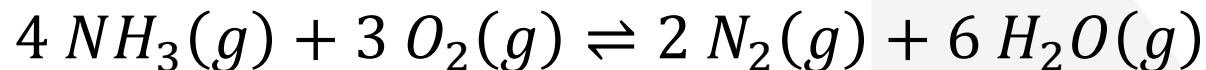
a) Addition of N_2 :



1. The first event is the increase in N_2 ↑
2. This causes the equilibrium to shift left to consume excess N_2 and H_2O to form more reactants (O_2 and NH_3)
3. The concentrations of H_2O decreases, while the concentrations of O_2 and NH_3 increases
4. Over time, the concentration of N_2 decreases again

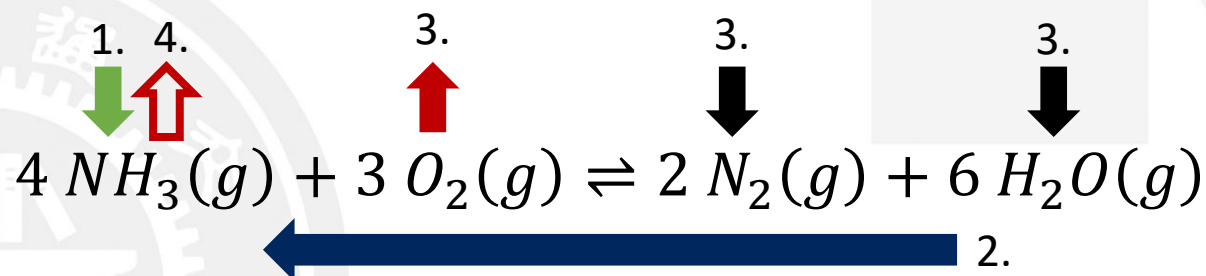
Example

Consider the equilibrium:



Predict the effect on each equilibrium concentration of (a) the addition of N_2 , (b) the removal of NH_3 , and (c) the removal of H_2O .

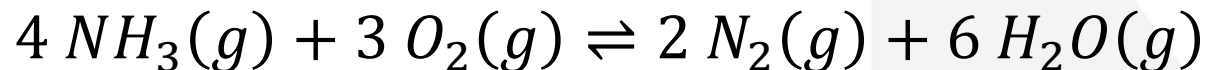
b) Removal of NH_3 :



1. The first event is the removal of NH_3 ↓
2. This causes the equilibrium to shift left to consume N_2 and H_2O to form more reactants (NH_3 and O_2)
3. The concentrations of N_2 and H_2O decreases, while the concentrations of O_2 increases
4. Over time, the concentration of NH_3 increases again

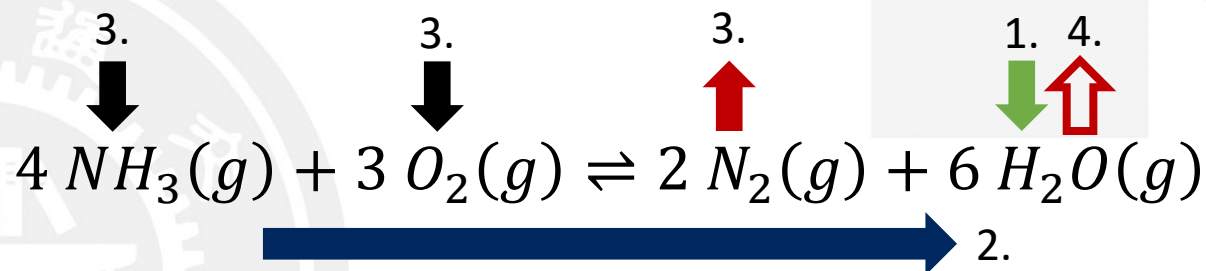
Example

Consider the equilibrium:



Predict the effect on each equilibrium concentration of (a) the addition of N_2 , (b) the removal of NH_3 , and (c) the removal of H_2O .

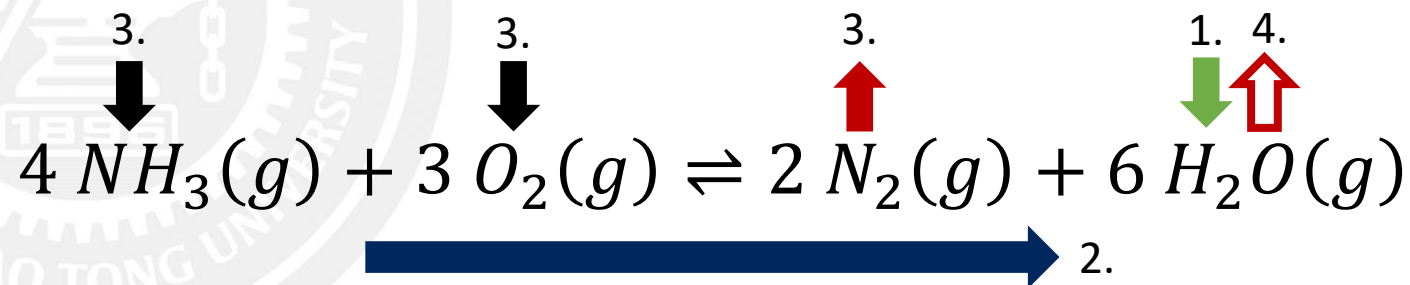
c) Removal of H_2O :



1. The first event is the removal of H_2O ↓
2. This causes the equilibrium to shift right to consume NH_3 and O_2 to form more products (N_2 and H_2O)
3. The concentrations of NH_3 and O_2 decreases, while the concentrations of N_2 increases
4. Over time, the concentration of H_2O increases again

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*.

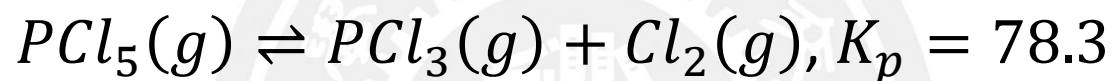
c) Removal of H_2O :



Example



Using the final values from the last Example we **add 0.0100 mol $\text{Cl}_2(g)$** to the container (of volume 500 mL), which is equal to 0.870 bar. Calculate the new composition of the equilibrium mixture.



Last example:

$$a_{\text{equil}, \text{PCl}_5} = 0.02$$

$$a_{\text{equil}, \text{PCl}_3} = 1.28$$

$$a_{\text{equil}, \text{Cl}_2} = 1.28$$

	PCl_5	PCl_3	Cl_2
initial	0.02	1.28	2.15
change	+ x	- x	- x
equilibrium (final)	$0.02+x$	$1.28-x$	$2.15-x$

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

Example

The equilibrium expression:

$$K_p = \frac{(1.28 - x) \cdot (2.15 - x)}{0.02 + x} = 78.3$$

$$0 = x^2 - 81.73x + 1.186$$

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

$$x = \frac{-(-81.73) \pm \sqrt{(-81.73)^2 - 4 \times 1 \times 1.186}}{2 \times 1}$$

$$x = 81.7 \text{ or } x = 0.0145$$

But only $x = 0.0145$ is physically meaningful.

$$a_{\text{equil}, \text{PCl}_5} = 0.02 + 0.0145 = 0.03$$

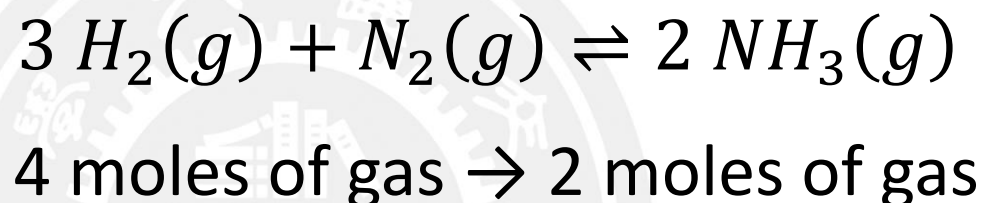
$$a_{\text{equil}, \text{PCl}_3} = 1.28 - 0.0145 = 1.27$$

$$a_{\text{equil}, \text{Cl}_2} = 2.15 - 0.0145 = 2.14$$

	PCl_5	PCl_3	Cl_2
initial	0.02	1.28	2.15
change	+0.0145	-0.0145	-0.0145
equilibrium (final)	0.03	1.27	2.14

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.



This results in a shift of the equilibrium to the side with the smallest amount of gas, thereby reducing the overall pressure.

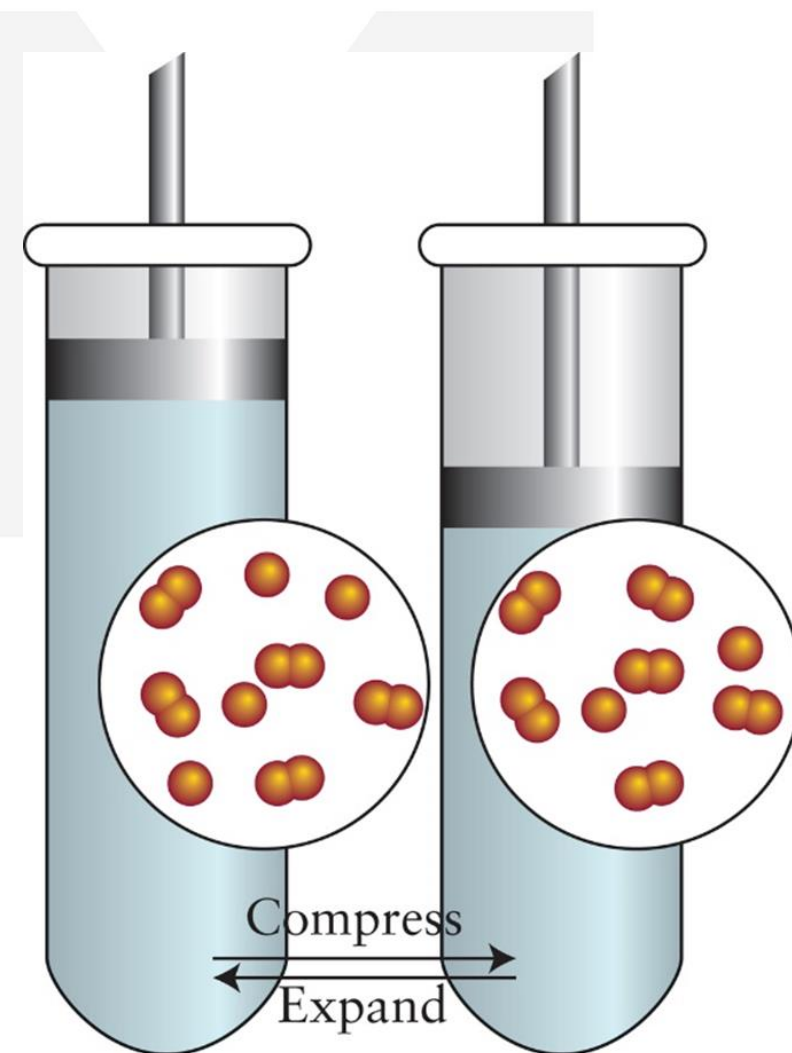
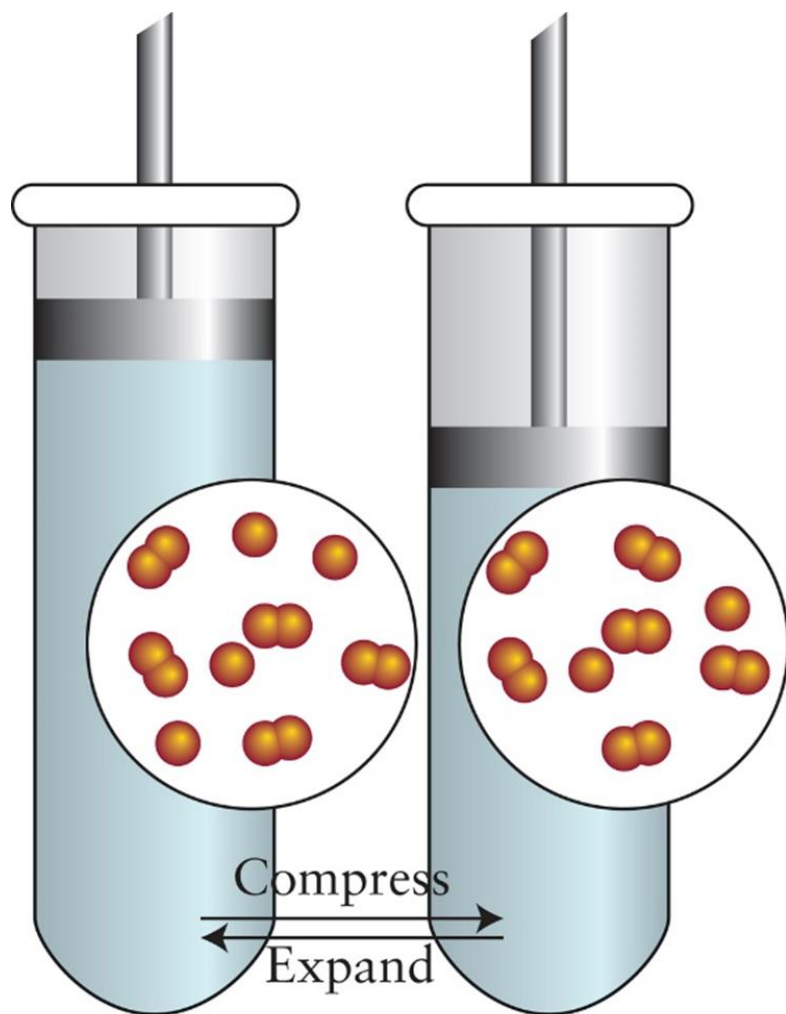
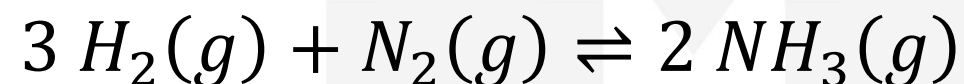


Figure 5J.7
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Compressing a Reaction Mixture



The opposite happens for an increase in volume.



4 moles of gas \leftarrow 2 moles of gas

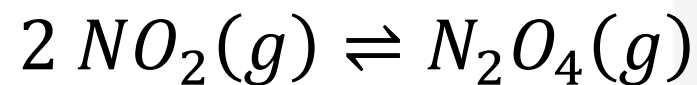
This results in a shift of the equilibrium to the side with the greatest amount of gas; this follows from gases expanding to fill their entire volume.

Figure 5J.7
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Example



Predict the effect of compression on the equilibrium composition of the reaction mixtures in which the equilibria have been established:



2 moles \rightarrow 1 mole



2 moles \rightarrow 2 moles

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



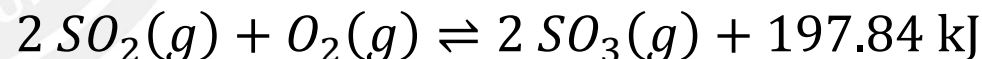
One stage in the manufacture of sulfuric acid is the formation of sulfur trioxide by the reaction of SO_2 with O_2 in the presence of a vanadium(V) oxide catalyst. Predict how the equilibrium composition for the sulfur trioxide synthesis will tend to change when the temperature is raised.

For the reaction $2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g)$ we are missing information about whether the reaction is exothermic or endothermic, so we need to calculate, ΔH° .

$$\Delta H^\circ = \sum (n \cdot \Delta H_{f, \text{products}}^\circ) - \sum (n \cdot \Delta H_{f, \text{reactants}}^\circ) = n \cdot \Delta H_{f, \text{SO}_3(g)}^\circ - (n \cdot \Delta H_{f, \text{SO}_2(g)}^\circ + n \cdot \Delta H_{f, \text{O}_2(g)}^\circ)$$

$$\Delta H^\circ = 2 \text{ mol} \times \left(-395.75 \frac{\text{kJ}}{\text{mol}} \right) - \left[2 \text{ mol} \times \left(-296.83 \frac{\text{kJ}}{\text{mol}} \right) + 1 \text{ mol} \times \left(0 \frac{\text{kJ}}{\text{mol}} \right) \right] = -197.84 \text{ kJ}$$

exothermic



Raising the temperature will shift the equilibrium to the reactant side.

The Effect of Temperature on K



The relation between the equilibrium constant and the standard Gibbs free energy of a reaction for two temperatures:

$$\Delta G_1^\circ = -RT_1 \cdot \ln(K_1) \text{ and } \Delta G_2^\circ = -RT_2 \cdot \ln(K_2)$$

$$\ln(K_1) = \frac{\Delta G_1^\circ}{-RT_1} \text{ and } \ln(K_2) = \frac{\Delta G_2^\circ}{-RT_2}$$

Combine:

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

Substituting $\Delta G = \Delta H - T \cdot \Delta S$:

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

The Effect of Temperature on K



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

Assuming ΔH° and ΔS° are independent of the temperature in the considered range:

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

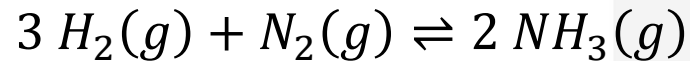
Van't Hoff Equation:

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

Example



The equilibrium constant K for the synthesis of ammonia is 6.8×10^5 at 298 K. Predict its value at 400 K.



$$\Delta H^\circ = \sum (n \cdot \Delta H_{f,products}^\circ) - \sum (n \cdot \Delta H_{f,reactants}^\circ) = n \cdot \Delta H_{f,NH_3(g)}^\circ - (n \cdot \Delta H_{f,H_2(g)}^\circ + n \cdot \Delta H_{f,N_2(g)}^\circ)$$

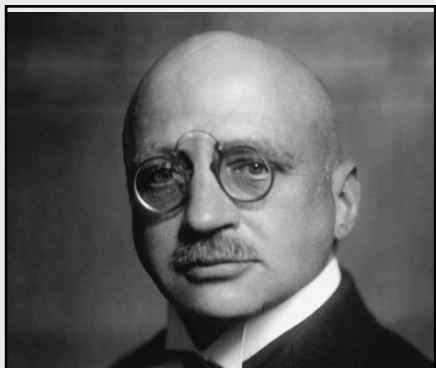
$$\Delta H^\circ = 2 \text{ mol} \times \left(-46.11 \frac{\text{kJ}}{\text{mol}} \right) - \left[3 \text{ mol} \times \left(0 \frac{\text{kJ}}{\text{mol}} \right) + 1 \text{ mol} \times \left(0 \frac{\text{kJ}}{\text{mol}} \right) \right] = -92.22 \text{ kJ} \left(\frac{1}{\text{mol}} \right)$$

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

$$K_2 = K_1 \cdot e^{-\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)} = 6.8 \times 10^5 \times e^{-\frac{-92.22 \times 10^3 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}} \left(\frac{1}{400 \text{ K}} - \frac{1}{298 \text{ K}} \right)} = 51$$

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

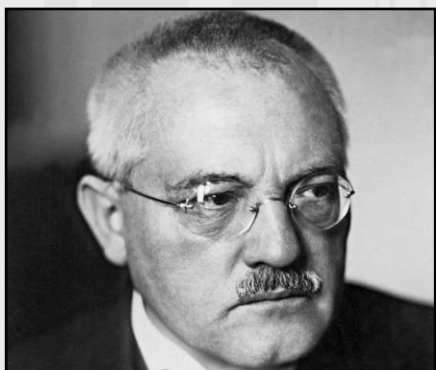
Catalysts and Haber's Achievement



Fritz Haber
1918 Nobel in Chemistry

A **catalyst** increases the rate of a chemical reaction without being consumed itself; more on this in Chapter 14.

A catalyst can speed up the rate of a reaction until it reaches equilibrium, but it does not affect the composition at equilibrium.



Carl Bosch
1931 Nobel in Chemistry
High-pressure Chemistry

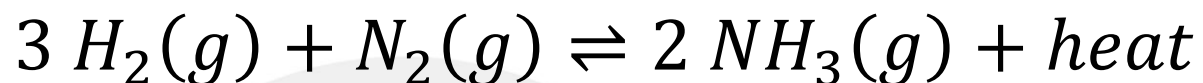
The thermodynamic justification is that the equilibrium constant depends only on the temperature and the value of ΔG° :

$$\Delta G_1^\circ = -RT_1 \cdot \ln(K_1)$$

Catalysts and Haber's Achievement

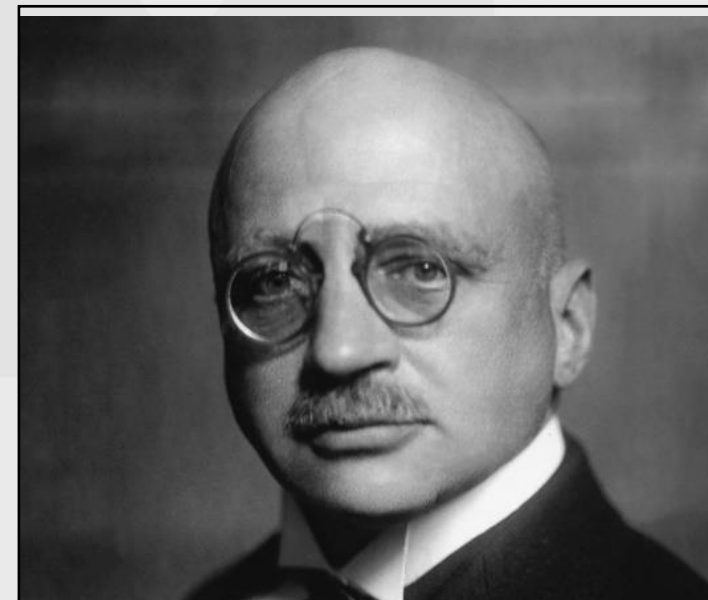


Haber was the first to correctly identify the optimal conditions for making one of the most important reactions known, ammonia:



To increase the yield, he found that:

1. compressing the gases forms more product
2. removing the ammonia encourages more product to form
3. running the reaction at as low a temperature as possible because the reaction is exothermic



Fritz Haber
1918 Nobel in Chemistry

Catalysts and Haber's Achievement

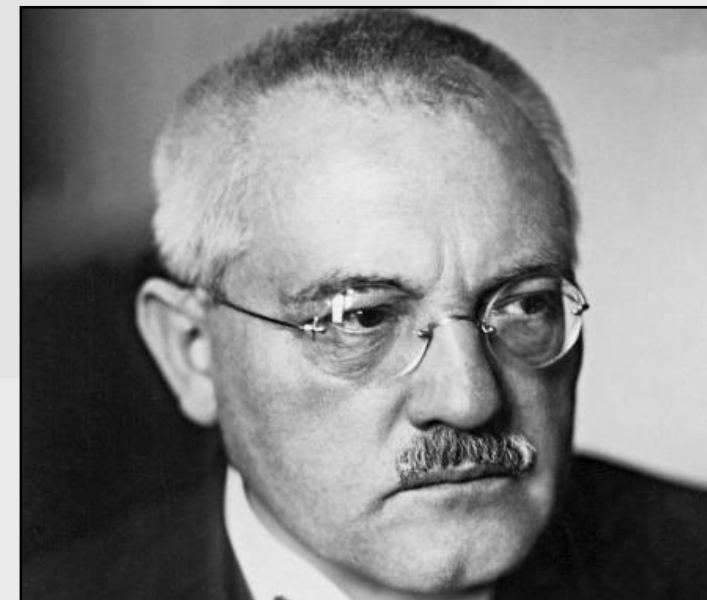


The Haber process is still in use today.

An improvement by Carl Bosch added a **cheap iron catalyst**, which overcame some problems with explosions when running this reaction at too high a pressure.



Figure 53.8
Atkins, Chemical Principles: The Quest for Insight, 7e
ZD GONG/EPA/Newscom.



Carl Bosch
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