Chapter 15
Chemical Equilibrium

Equilibrium or Steady State?
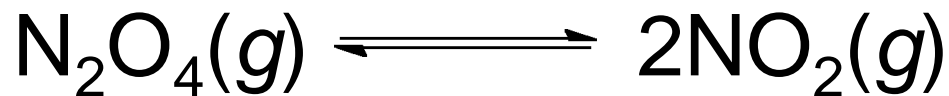

$$A \longrightarrow B \longrightarrow C$$

$$\frac{\mathrm{d}[B]}{\mathrm{d}t} = 0$$

15 – Chemical equilibrium
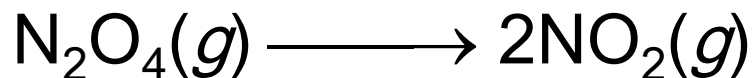
The Principle of Detailed Balance

- **Chemical equilibrium** occurs when each elementary process is equilibrated by its reverse process (e.g., $k_1[\text{A}] = k_{-1}[\text{B}]$ and $k_2[\text{B}] = k_{-2}[\text{C}]$).

- The reversibility of all elementary processes is required.

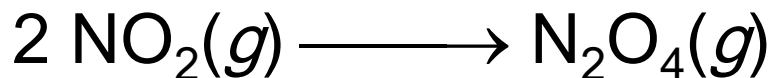- The concentrations of reactants and products no longer change with time.

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C$$
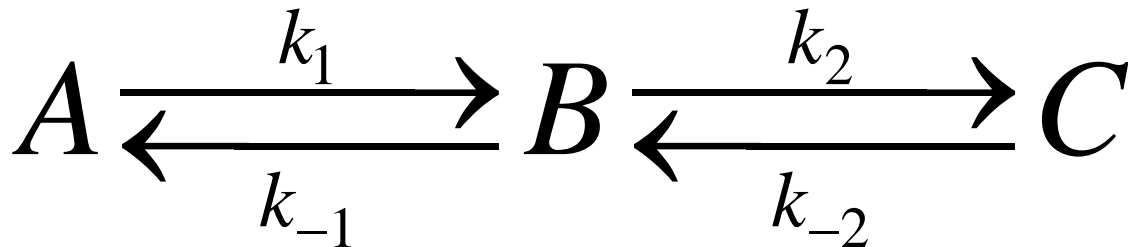
Deriving the equilibrium constant

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

- Forward reaction:

    $$N_2O_4(g) \longrightarrow 2NO_2(g)$$

- Rate law:

    Rate = $k_f[N_2O_4]$

- Reverse reaction:

    $$2\ NO_2(g) \longrightarrow N_2O_4(g)$$

- Rate law:

    Rate = $k_r[NO_2]^2$

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$
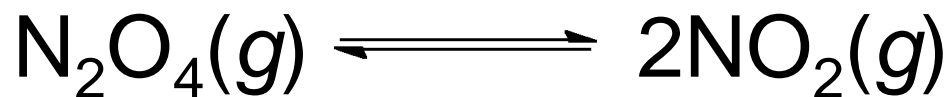
- Therefore, at equilibrium

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

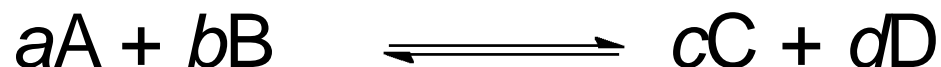$$k_f\,[N_2O_4] = k_r\,[NO_2]^2$$

- Rewriting this, it becomes

$$\frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]}$$

Equilibrium constant

$$K_{eq} = \frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]}$$

The law of mass action

- Consider the generalized reaction

$$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$$

- The equilibrium expression for this reaction would be

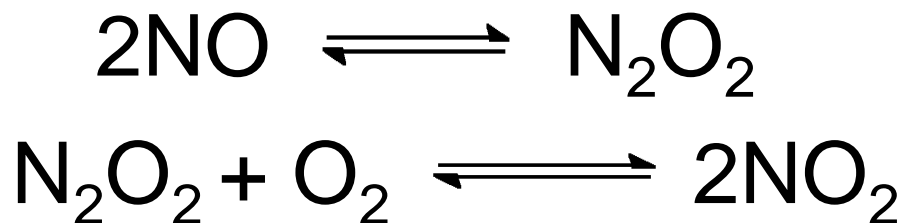$$K_c = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$$

Also valid for non-elementary processes!

- The proof of this law and its historical development can be found in Wikipedia under "Law of mass action"

The law of mass action

$$2NO + O_2 \rightleftharpoons 2NO_2 \qquad \frac{[NO_2]^2}{[NO]^2[O_2]} = K_1K_2$$

Elementary Processes

$$2NO \rightleftharpoons N_2O_2$$
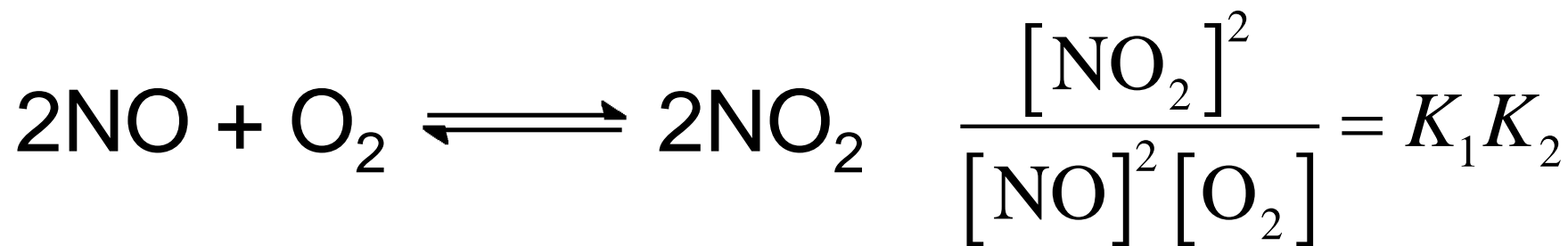
$$N_2O_2 + O_2 \rightleftharpoons 2NO_2$$

Principle of detailed balance

$$\frac{[N_2O_2]}{[NO]^2} = K_1 \qquad \frac{[NO_2]^2}{[N_2O_2][O_2]} = K_2$$

Chemical Equilibrium

At equilibrium

- The concentrations of all reactants and products remain constant with time. (macroscopically static)

- The forward and reverse reactions continue at equal rates in both directions. (microscopically dynamic)
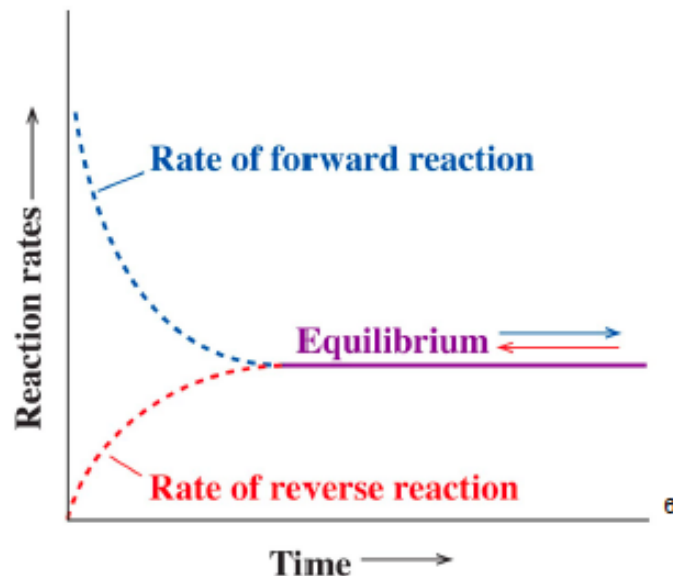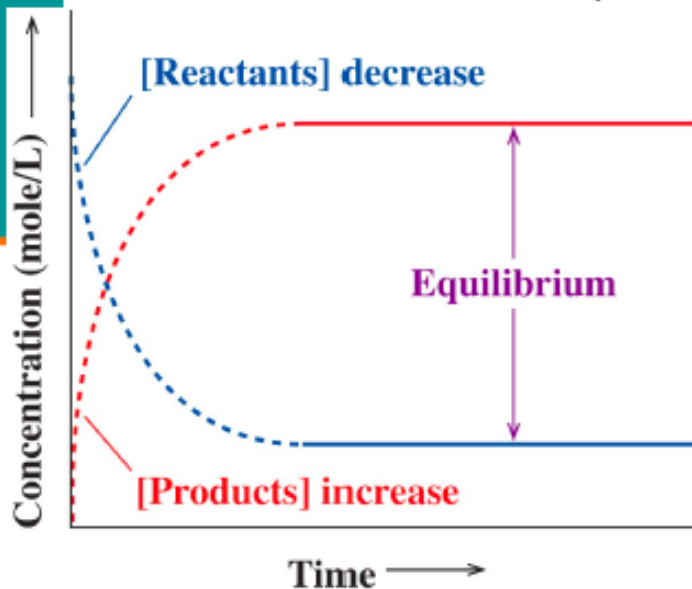
Manipulating Equilibrium Constants

$$A \rightleftharpoons B \qquad K_1 = \frac{[B]}{[A]}$$

$$B + 2C \rightleftharpoons D + E \qquad K_2 = \frac{[D][E]}{[B][C]^2}$$
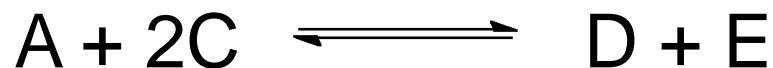
$$A + 2C \rightleftharpoons D + E \qquad K = K_1 K_2 = \frac{[D][E]}{[A][C]^2}$$

For gas-phase reactions

- K_c is K_{eq} based on concentration units
- K_p is K_{eq} based on pressure units

$$aA + bB \rightleftharpoons cC + dD$$
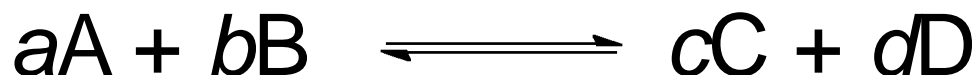
$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad K_p = \frac{(P_C^c)\,(P_D^d)}{(P_A^a)\,(P_B^b)}$$

- K_p and K_c have the same physical meaning (just different units!)

Relationship Between K_c and K_p

- From the ideal-gas law we know that

$$PV = nRT$$

- Rearranging it, we get

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

Relationship Between K_c and K_p

Plugging this into the expression for K_p for each substance, the relationship between K_c and K_p becomes

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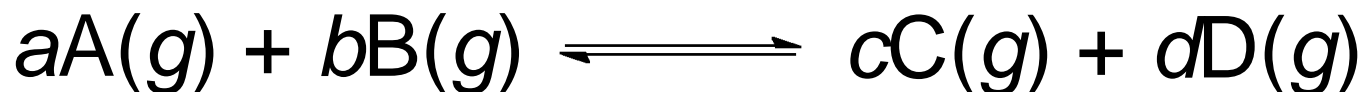
where

Δn = (moles of gaseous product) − (moles of gaseous reactant)

$$a\mathrm{A}(g) + b\mathrm{B}(g) \rightleftharpoons c\mathrm{C}(g) + d\mathrm{D}(g)$$

$$\Delta n = (c + d) - (a + b)$$

Examples

TABLE 15.1 • **Initial and Equilibrium Concentrations of $N_2O_4(g)$ and $NO_2(g)$ at 100 °C**

Experiment	Initial $[N_2O_4]$ (M)	Initial $[NO_2]$ (M)	Equilibrium $[N_2O_4]$ (M)	Equilibrium $[NO_2]$ (M)	K_c
1	0.0	0.0200	0.00140	0.0172	0.211
2	0.0	0.0300	0.00280	0.0243	0.211
3	0.0	0.0400	0.00452	0.0310	0.213
4	0.0200	0.0	0.00452	0.0310	0.213

It doesn't matter what the initial condition is, we always have the same K_c at the same temperature, if the concentration is not too high.

At high concentrations?

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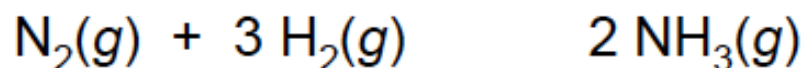
Equilibrium constant

- K always has the same value at a given temperature regardless of the amounts of reactants or products that are present initially.

- For a reaction, at a given temperature, there are many equilibrium *positions* but only *one value* for K.
    - Equilibrium position is a set of equilibrium concentrations.

- K involves concentrations.
- K_p involves pressures.

Equilibrium constant
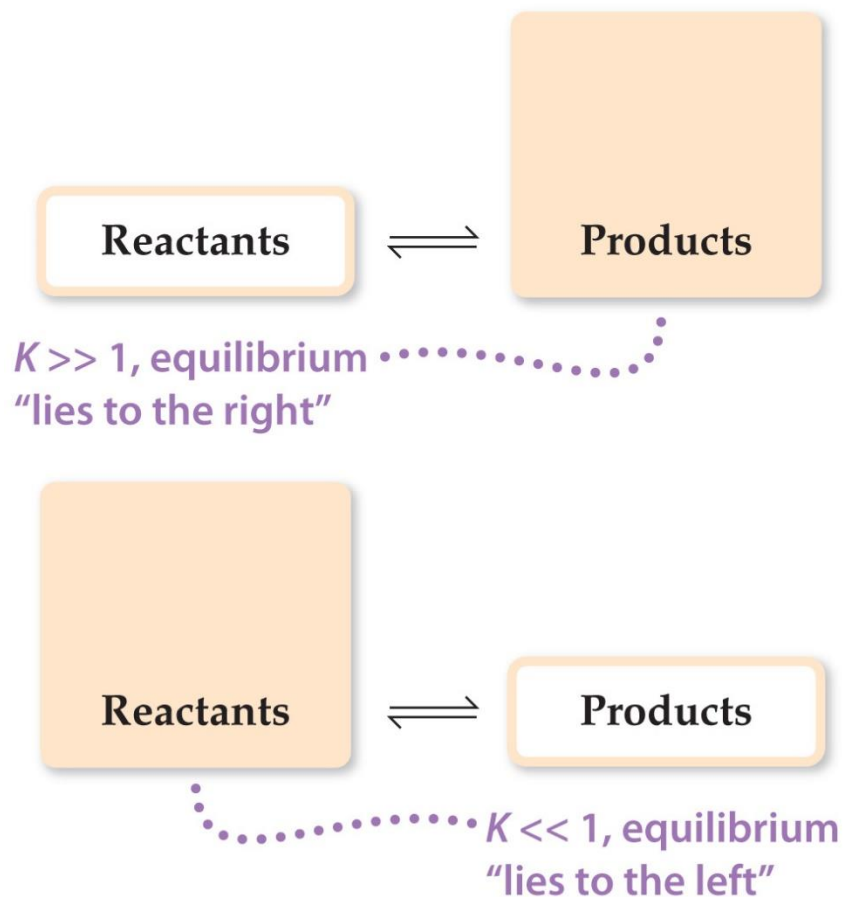
Considering the following reaction:

$$N_2(g) \ + \ 3\,H_2(g) \qquad 2\,NH_3(g)$$

Experiment	Initial concentration	Equilibrium concentration	$K = [NH_3]^2/([N_2][H_2]^3)$
1	$[N_2]_0 = 1.000M$ $[H_2]_0 = 1.000M$ $[NH_3]_0 = 0$	$[N_2] = 0.921\ M$ $[H_2] = 0.763\ M$ $[NH_3] = 0.157M$	$K = 6.02 \times 10^{-2}$
2	$[N_2]_0 = 0$ $[H_2]_0 = 0$ $[NH_3]_0 = 1.000M$	$[N_2] = 0.399M$ $[H_2] = 1.197\ M$ $[NH_3] = 0.203\ M$	$K = 6.02 \times 10^{-2}$
3	$[N_2]_0 = 2.00\ M$ $[H_2]_0 = 1.00\ M$ $[NH_3]_0 = 3.00\ M$	$[N_2] = 2.59\ M$ $[H_2] = 2.77\ M$ $[NH_3] = 1.82\ M$	$K = 6.02 \times 10^{-2}$

Equilibrium position

One _K_ for the system at a particular temperature

What Does the Value of *K* Mean?

Reactants ⇌ Products

K >> 1, equilibrium
"lies to the right"

Reactants ⇌ Products

K << 1, equilibrium
"lies to the left"

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- If *K* >> 1, the reaction is *product-favored*; product predominates at equilibrium.

- If *K* << 1, the reaction is *reactant-favored*; reactant predominates at equilibrium.

Concentrations of Solids and Solvents

Both the concentrations of solids and solvents can be obtained by dividing the density of the substance by its molar mass—and both of these are constants at constant temperature.

→ They do not appear in equilibrium constants

Concentrations of Solids and Solvents

Therefore, the concentrations of solids and solvents do not appear in the equilibrium expression.

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

$$K_c = [Pb^{2+}] [Cl^-]^2$$

$$CaCO_3(s) \rightleftharpoons CO_2(g) + CaO(s)$$
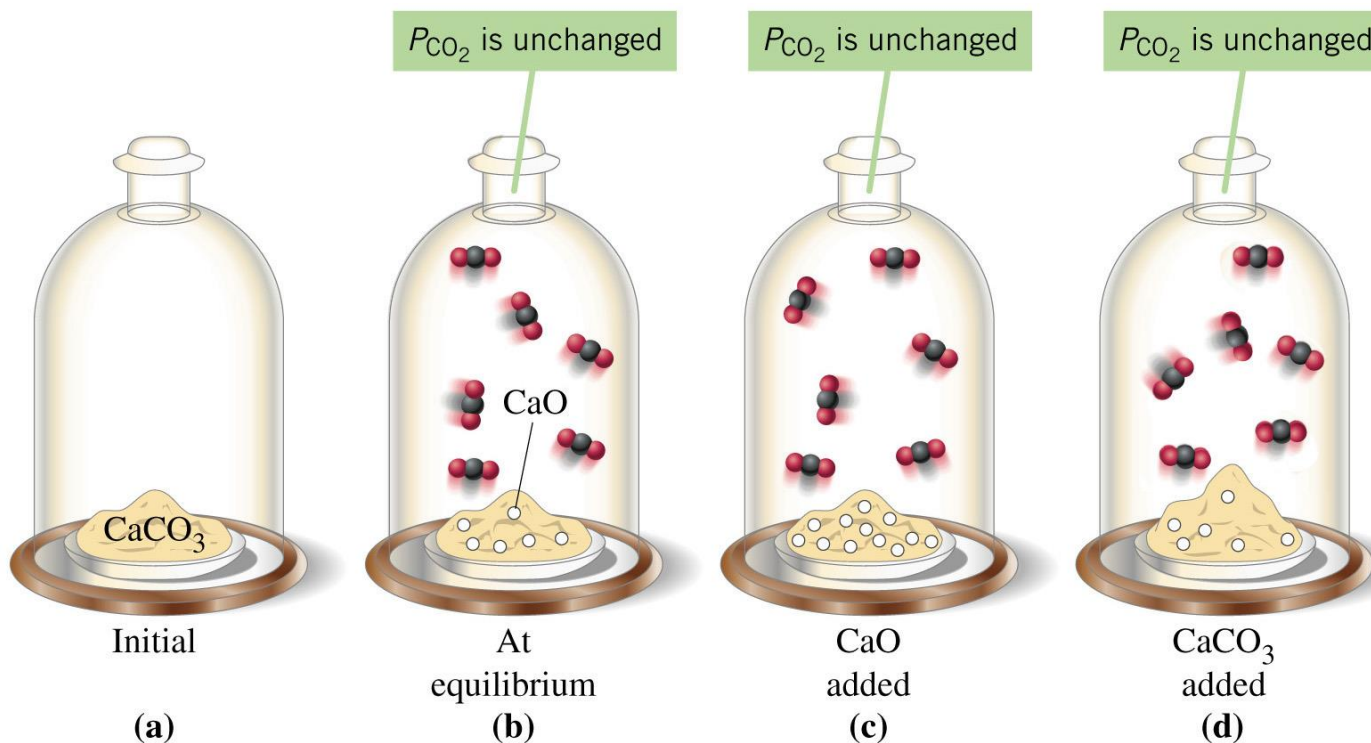
As long as *some* CaCO$_3$ and CaO remain in the system, the amount of CO$_2$ above the solid will remain the same.

Gas Solubility

Equilibrium

Pressure is increased.
More CO_2 dissolves

Equilibrium restored

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$$P_{CO_2} = k[CO_2]$$

$$CO_2(g) \rightleftharpoons CO_2(aq)$$
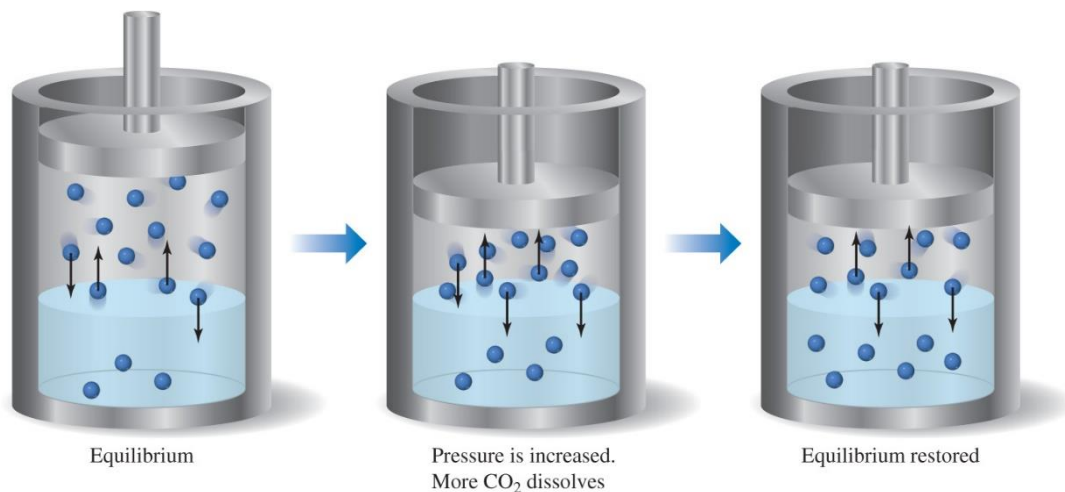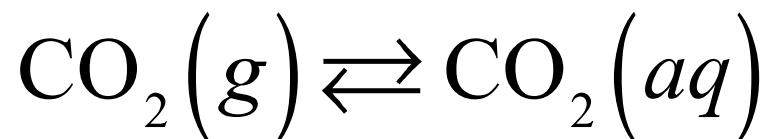
- k is the **Henry's Law** constant of CO_2
- P_{CO_2} is the partial pressure of CO_2

Equilibrium Calculations

A closed system initially containing 1.000×10^{-3} M H_2 and 2.000×10^{-3} M I_2 at 448°C is allowed to reach equilibrium.

Analysis of the equilibrium mixture shows that the concentration of HI is 1.87×10^{-3} M.

Calculate K_c at 448°C for the reaction taking place, which is

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
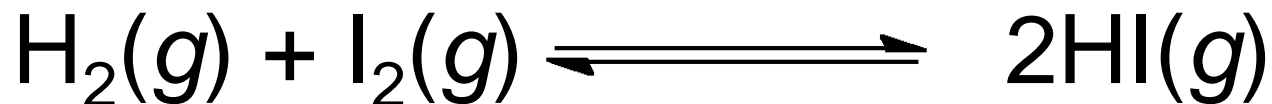
What Do We Know?

	$[H_2]$, M	$[I_2]$, M	$[HI]$, M
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change	-9.35×10^{-4}	-9.35×10^{-4}	$+1.87 \times 10^{-3}$
At equilibrium	6.5×10^{-5}	1.065×10^{-3}	1.87×10^{-3}

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
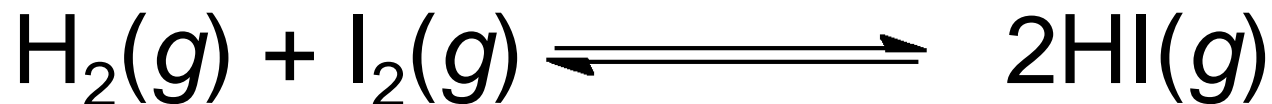
and, therefore, the equilibrium constant:

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]}$$

$$= \frac{(1.87 \times 10^{-3})^2}{(6.5 \times 10^{-5})(1.065 \times 10^{-3})}$$

$$= 51$$

The Reaction Quotient (Q)

- Q gives the same ratio the equilibrium expression gives, but for a system that is *not* at equilibrium.

- To calculate Q, one substitutes the initial concentrations on reactants and products into the equilibrium expression.

- Direction of reaction: Q tends towards K in order to reach equilibrium.

Reaction Quotient, Q

- Apply the law of mass action using initial concentrations instead of equilibrium concentrations.

$$jA + kB \rightleftharpoons lC + mD$$
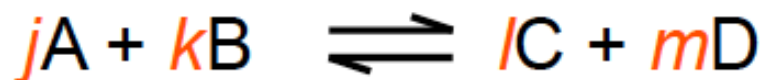
$$Q = \frac{[C]_0^l [D]_0^m}{[A]_0^j [B]_0^k}$$ Initial concentration

$$K = \frac{[C]^l [D]^m}{[A]^j [B]^k}$$ eqilibrium concentration

At equilibrium

$Q < K$ — Reaction forms products

$Q = K$ — Equilibrium

$Q > K$ — Reaction forms reactants
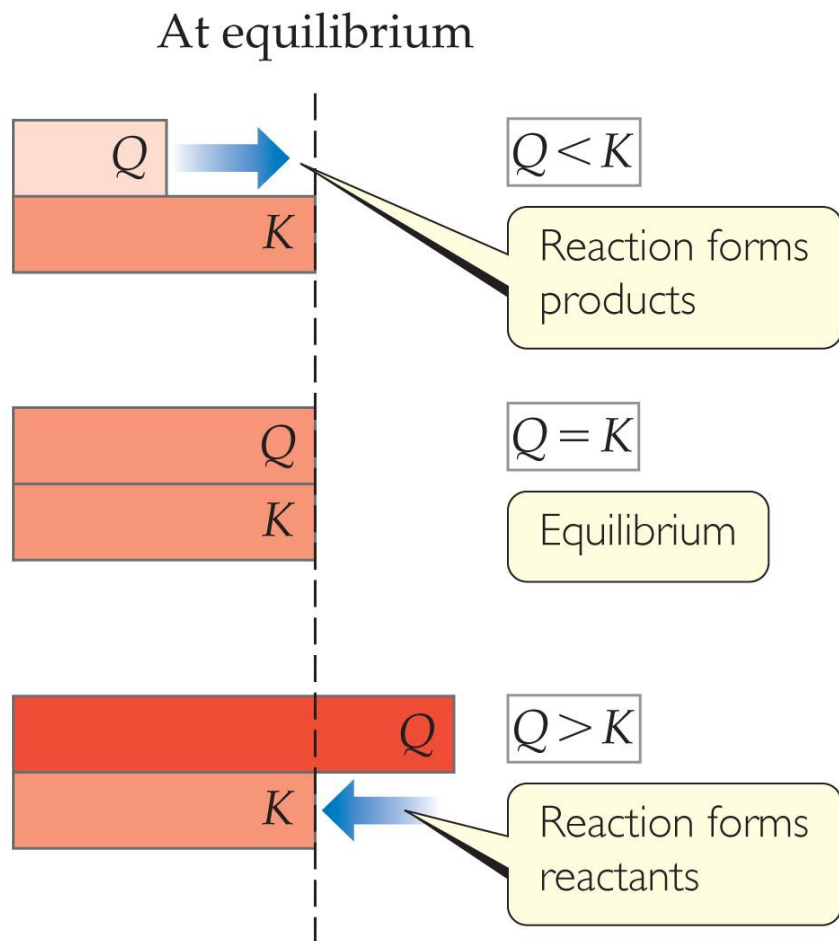
If $Q = K$, the system is at equilibrium.

If $Q > K$, there is too much product, and the equilibrium shifts to the left.

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Le Châtelier's Principle

"If a system at equilibrium is disturbed by a change in temperature, pressure, or the concentration of one of the components, the system will shift its equilibrium position so as to counteract the effect of the disturbance."

1850−1936

15 – Chemical equilibrium

Le Châtelier's Principle

$$CH_3COOH + R\text{-}OH = CH_3COOR + H_2O$$

Acetic acid

1-Octanol

Octyl acetate

Water

Addition of acetic acid

$R_f > R_r$ $R_f = R_r$ $R_f > R_r$ $R_f = R_r$
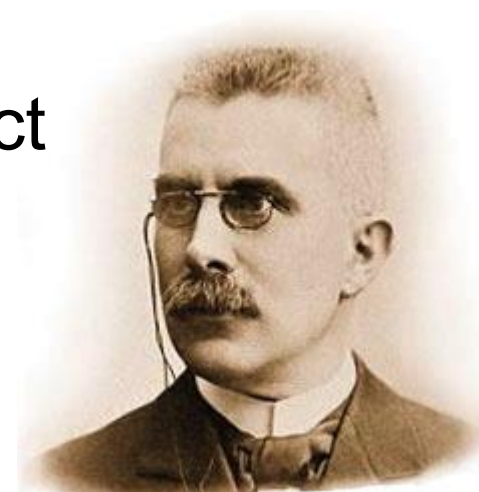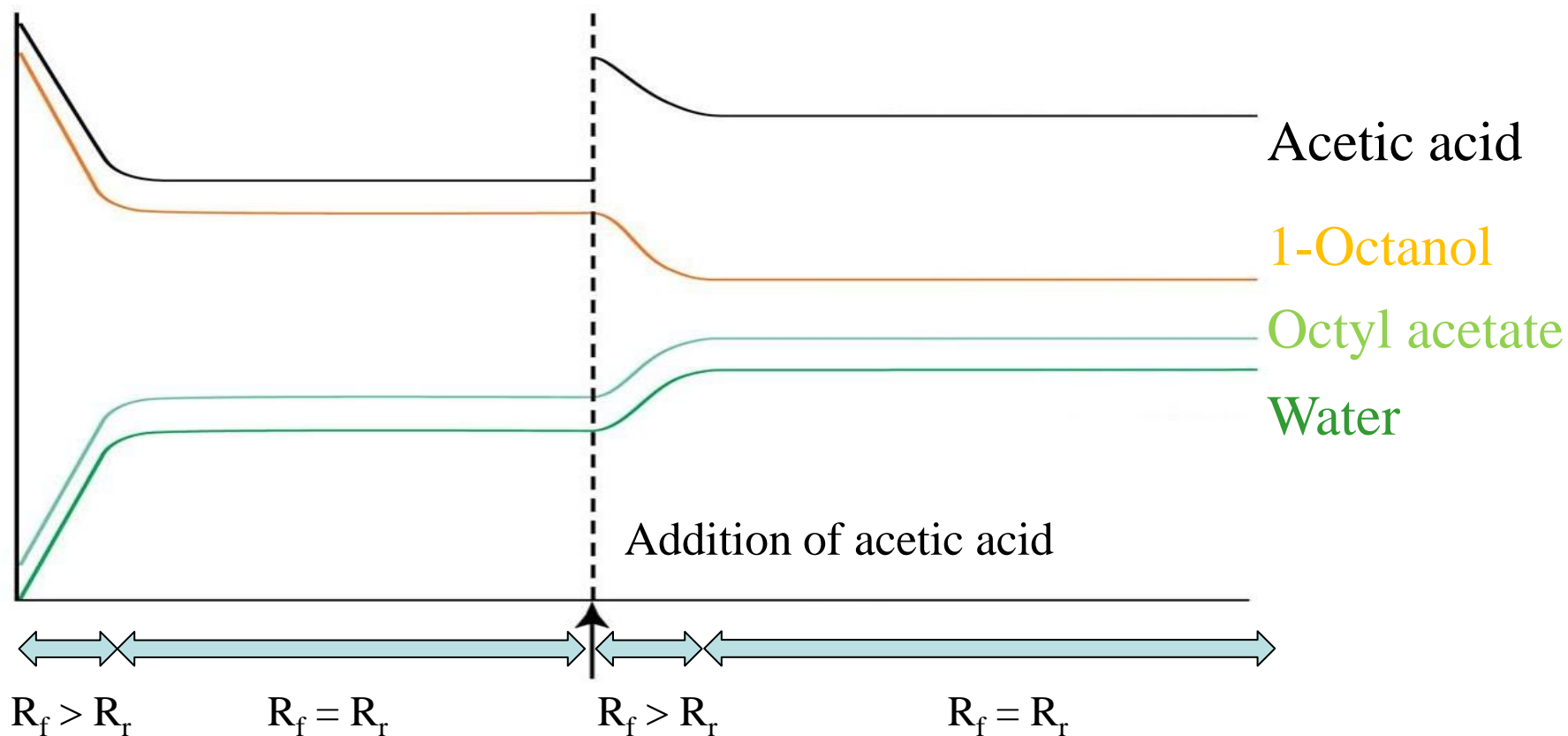
Effects of changing temperature

$\Delta H > 0$, endothermic reaction

$$\boxed{\text{Heat}} + Co(H_2O)_6^{2+}(aq) + 4\,Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6\,H_2O(l)$$

Pink   Blue
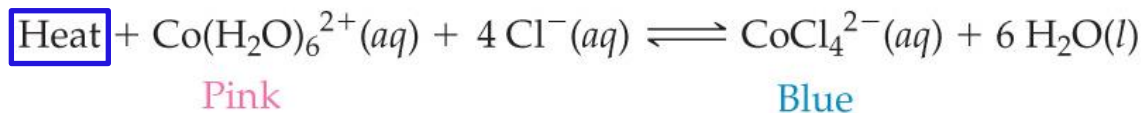
Heat

Cool

At equilibrium, significant amounts of both pink $Co(H_2O)_6^{2+}$ and blue $CoCl_4^{2-}$ are present; solution appears violet
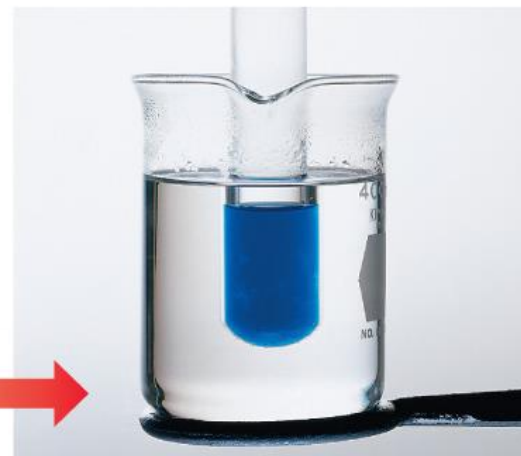
Add heat: reaction shifts right to increase blue $CoCl_4^{2-}$ concentration and decrease pink $Co(H_2O)_6^{2+}$ concentration
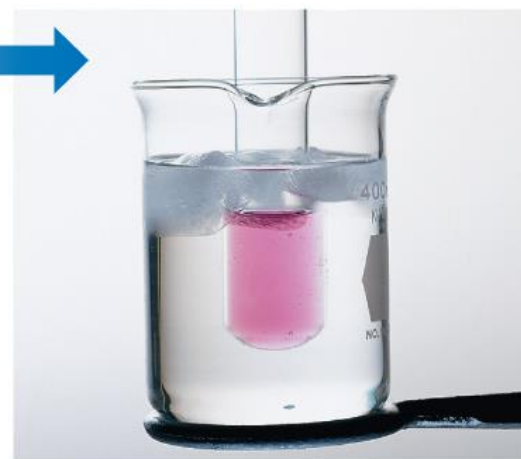
Remove heat: reaction shifts left to decrease blue $CoCl_4^{2-}$ concentration and increase pink $Co(H_2O)_6^{2+}$ concentration

15 – Chemical equilibrium

Effects of changing pressure

$$N_2O_4 \leftrightarrow 2NO_2 + \boxed{work}$$

= N₂O₄

= NO₂

(a) P = 1 atm

(b) P = 2 atm

(c) P = 2 atm
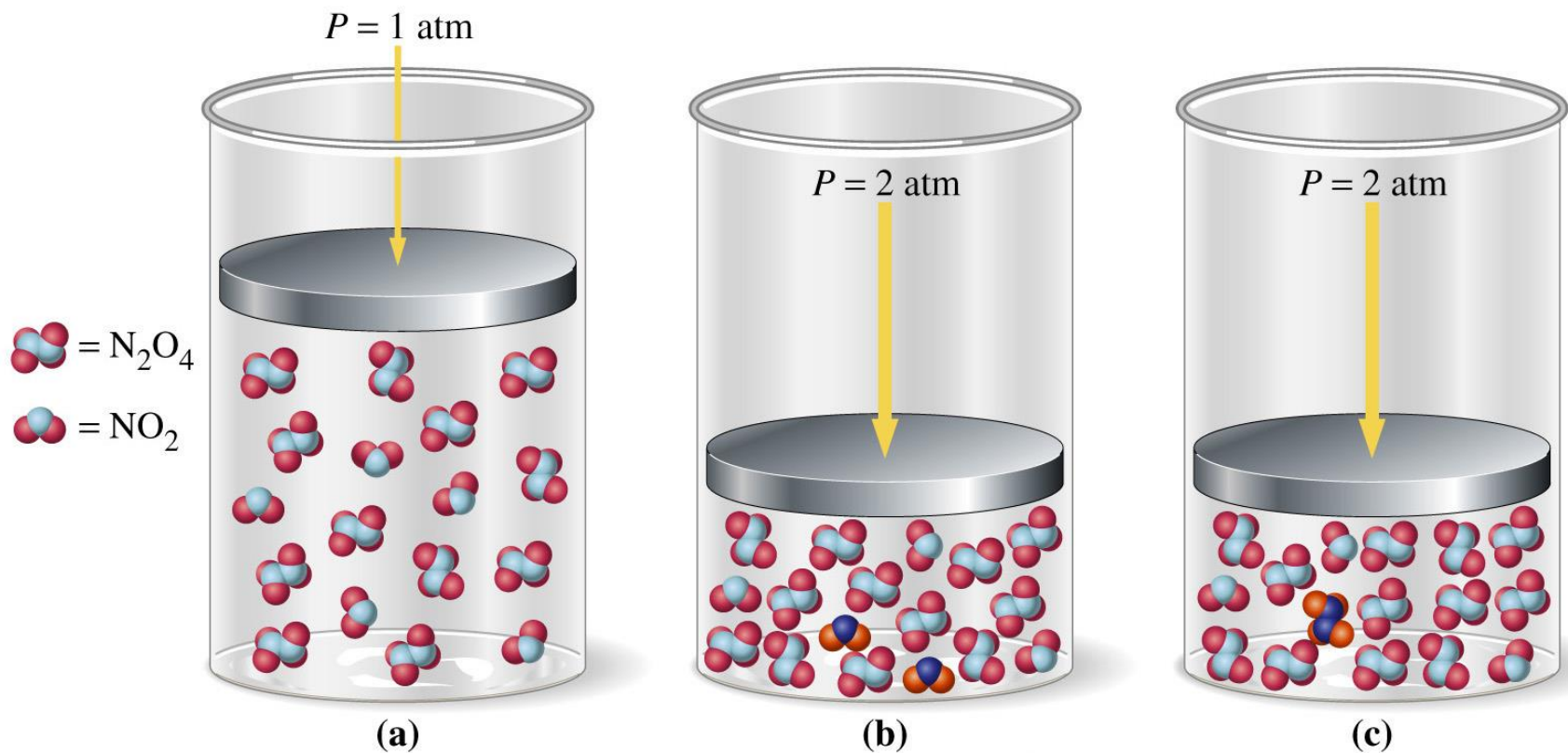
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Catalysts

Catalysts increase the rate of both the forward *and* reverse reactions.

When one uses a catalyst, equilibrium is achieved faster, but the equilibrium composition remains unaltered.

Transition states

Uncatalyzed reaction is slower

Catalyzed reaction has lower activation energy

Catalyzed reaction proceeds more rapidly

$K = [B]_{eq}/[A]_{eq}$ = same for uncatalyzed and catalyzed reactions

Energy

$[B]_{eq}$

[B]

Time

A

B

Reaction pathway

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15 – Chemical equilibrium
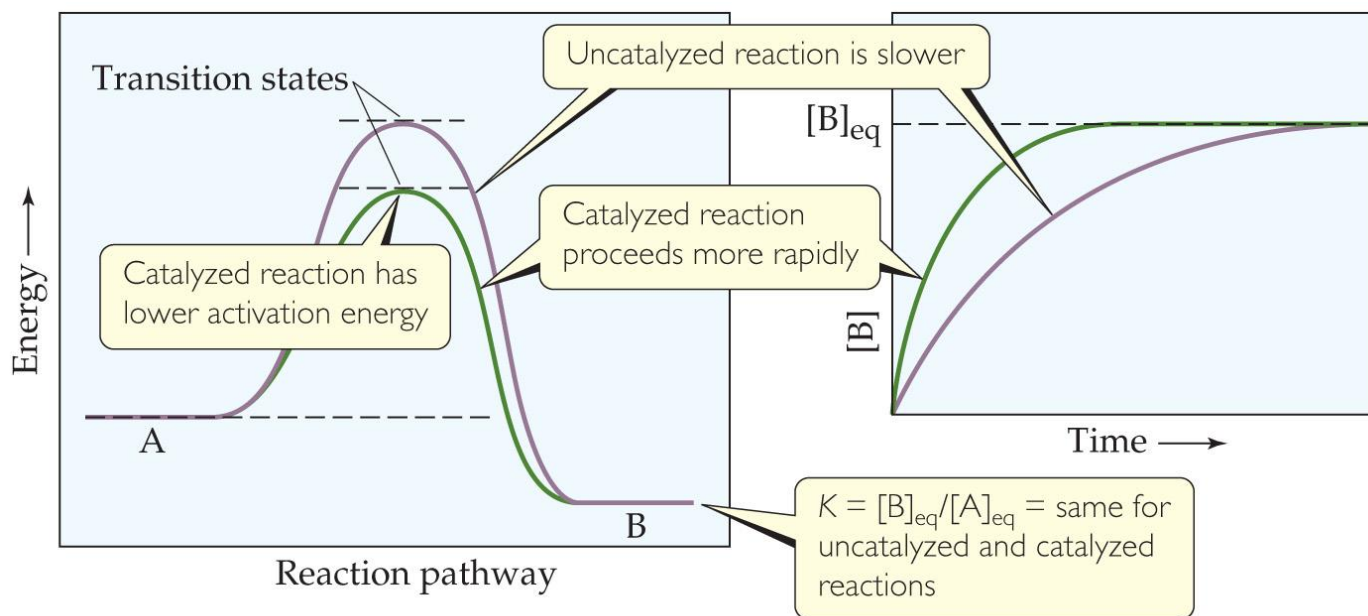
Importance of Haber Process

- Without nitrogen, plants cannot make proteins (polymers of amino acids)
- Without plants fixing nitrogen, animals cannot make proteins
- Nitrogen fertilizer is important for global agriculture
- Without Haber process, world population would be 50% less

The Haber Process

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2\ NH_3\ (g) \qquad \Delta H = -92\ kJ$$

The Haber Process

"P" + N_2 (g) + $3H_2$ (g) $\rightleftharpoons$ 2 NH_3 (g) +heat $\Delta H = -92$ kJ

Overall yield per run ≈ 15%

1. Temperature   450−500 °C
2. Pressure   200 atm
3. Catalyst   Fe

Percent of NH_3 increases with increasing pressure

Percent of NH_3 decreases with increasing temperature

Percent NH_3 produced

8.8% 12.9% 16.9% 20.8%
18.9% 26.0% 32.2% 37.8%
27.4% 35.9% 42.9% 48.8%
38.7% 47.8% 54.9% 60.6%

Total pressure (atm): 200 300 400 500

Temperature (°C): 550 500 450 400
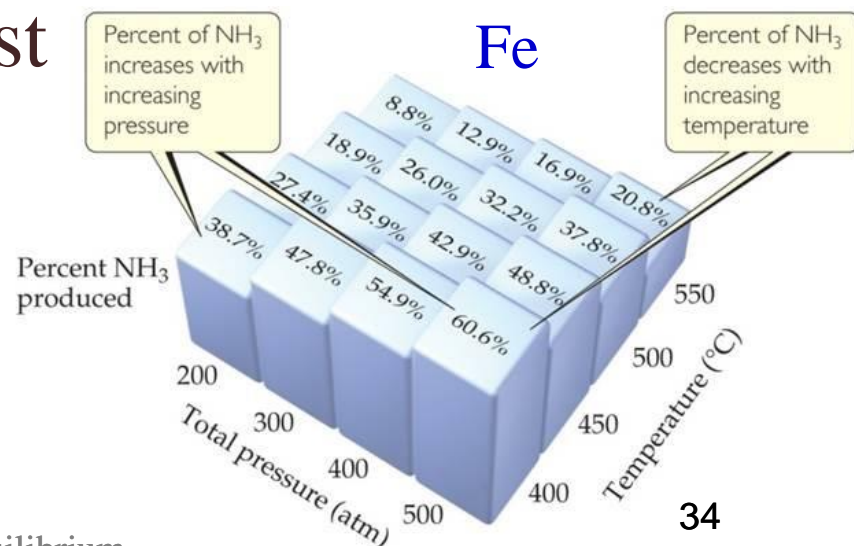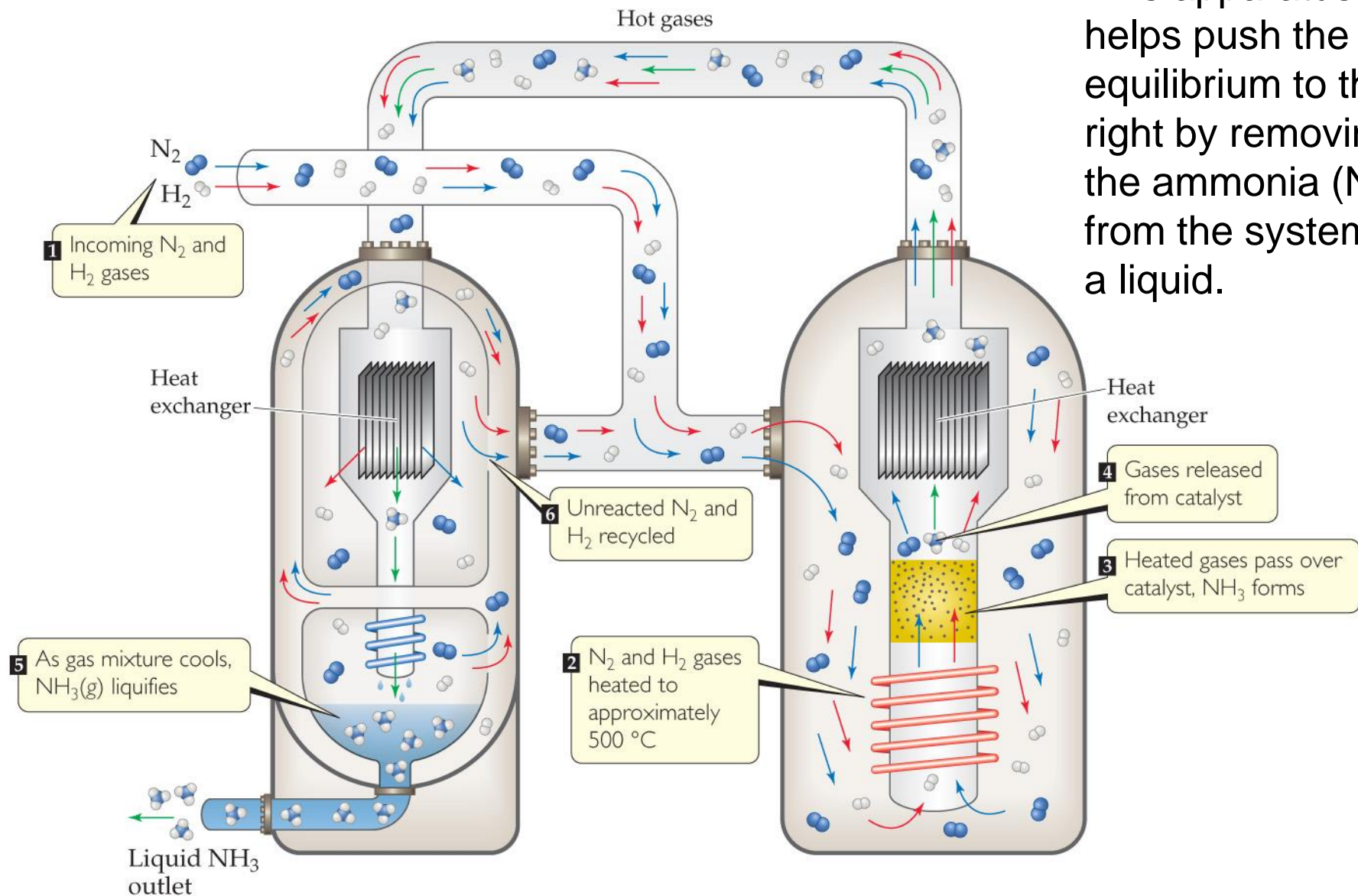
This apparatus helps push the equilibrium to the right by removing the ammonia (NH_3) from the system as a liquid.

Hot gases

N_2

H_2

1 Incoming N_2 and H_2 gases

Heat exchanger

Heat exchanger

6 Unreacted N_2 and H_2 recycled

4 Gases released from catalyst

3 Heated gases pass over catalyst, NH_3 forms

5 As gas mixture cools, $NH_3(g)$ liquifies

2 N_2 and H_2 gases heated to approximately 500 °C

Liquid NH_3 outlet

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Changes and Equilibrium

Effects of Condition Changes on Equilibrium

Condition	Change (Stress)	Reaction to Remove Stress
Concentration	Add reactant	Forward
	Remove reactant	Reverse
	Add product	Reverse
	Remove product	Forward
Volume (container)	Decrease	Toward fewer moles in the gas phase
	Increase	Toward more moles in the gas phase
Temperature	**Endothermic reaction**	
	Raise T	Forward, new value for K_c
	Lower T	Reverse, new value for K_c
	Exothermic reaction	
	Raise T	Reverse, new value for K_c
	Lower T	Forward, new value for K_c
Catalyst	Increases rates equally	No effect