

VI) LeChatelier's Principle

If a **stress** is applied to a system at **equil.**, the system will **shift** (if possible) to a **new position** of **equil.** to **minimize** the **stress**.

3 Kinds of Stress

- 1) change **conc.**
- 2) change **pressure**
- 3) change **temp.**

A) Change in Concentration

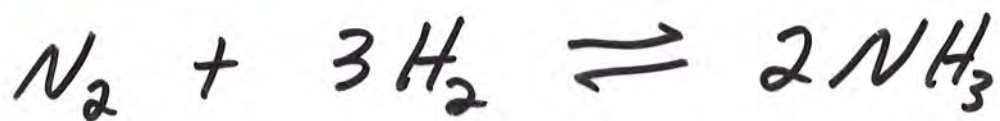
For a system at equilibrium:

Add a substance ("excess stress")
+ rx. shifts + reestablishes
a diff. equil. by consuming
part of the added substance.

Removal of a substance
("deficit stress") causes the
rx. to proceed in direction
that produces more of
the removed substance.

Reduce the excess or deficit

1) Look at Q



$$Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

a) Remove NH₃

numerator dec.,

$$Q_c < K_c$$

Rx. shifts to make $Q_c = K_c$

i.e. create more NH₃

net rx. occurs left to right
(in forward direction)

b) Add H_2

denominator inc.,

$$Q_c < K_c$$

remove excess H_2

net rx. is left to right

i.e. create more NH_3

c) Remove N_2

denominator dec.

$$Q_c > K_c$$

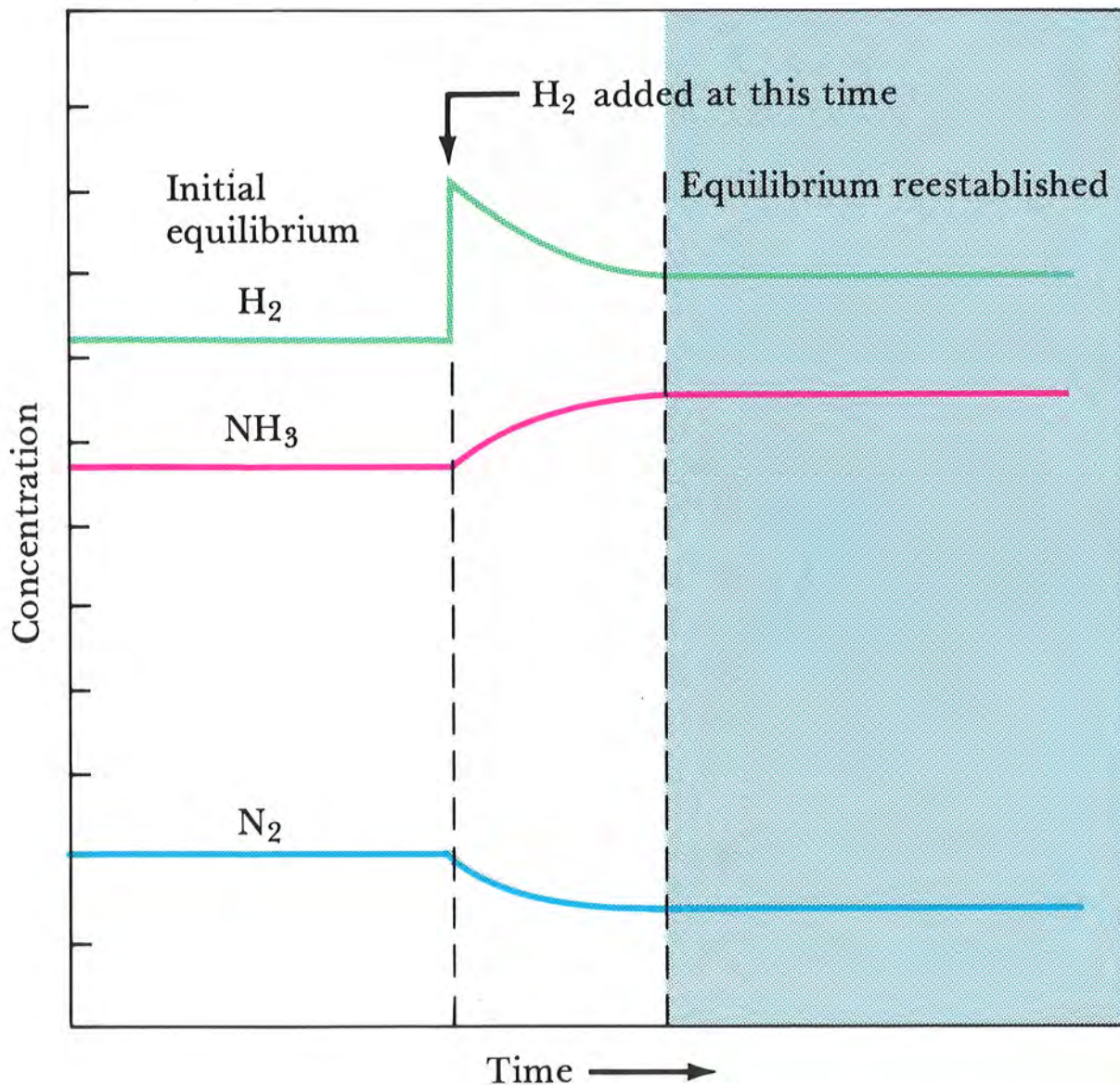
Rx. shifts to create more N_2

net rx. occurs right to left

(in reverse direction)

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Figure 15.8 Le Châtelier, disruption and re-establishment of equilibrium



2) Summary

a) Add reactant or Remove product

net rx. occurs \longrightarrow

- More PRODUCTS produced

b) Add product or Remove reactant

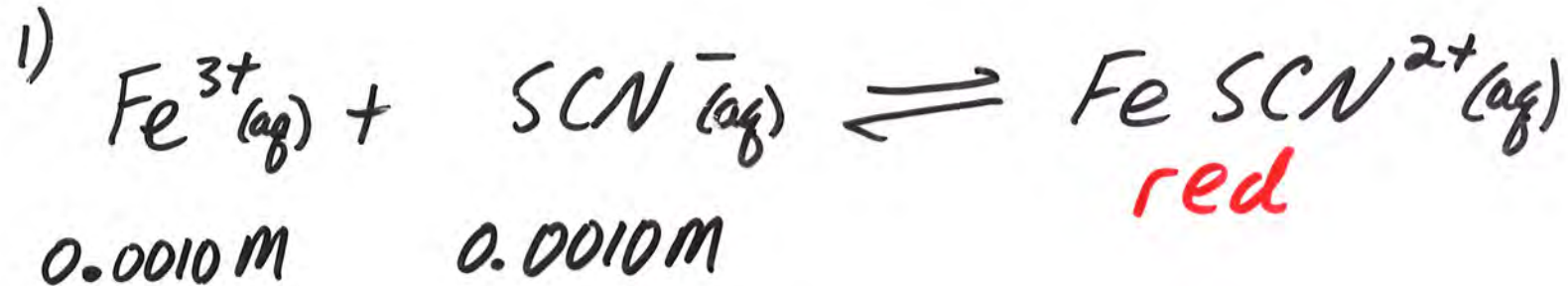
net rx. occurs \longleftarrow

- More REACTANTS produced

c) Change amt. of solid or liquid

Nothing happens as long as some is present

- Don't appear in K (Q)

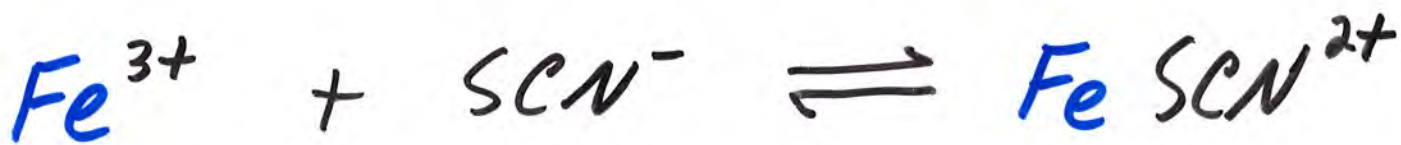


Beaker 1

$K_c = \text{—————}$

2) Beaker 2

Add 0.1 M $Fe(NO_3)_3$



3) Beaker 3

Add 0.1 M KSCN



4) Beaker 4

Add 0.1 M AgNO_3



5) Beaker 5

Add NaF



B) Change Pressure & Volume

Inc. total pressure by application of external pressure (dec. volume), system responds by shifting in the direction that reduces pressure.

- Reduces total # moles
- Only works if rx. involves a change in total moles of gas

$P_{inc.}$ ($V_{dec.}$), dec. moles gas

$P_{dec.}$ ($V_{inc.}$), inc. moles gas



Inc. P (dec. V) : lightens

- shifted to right

(establishes new equil.)

Why?

K remains constant

How can N_2O_4 inc. & NO_2 dec.
w/o changing K ?

$$K = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{n_{\text{N}_2\text{O}_4}/V}{(n_{\text{NO}_2}/V)^2} = \frac{n_{\text{N}_2\text{O}_4}}{n_{\text{NO}_2}^2} \cdot V$$

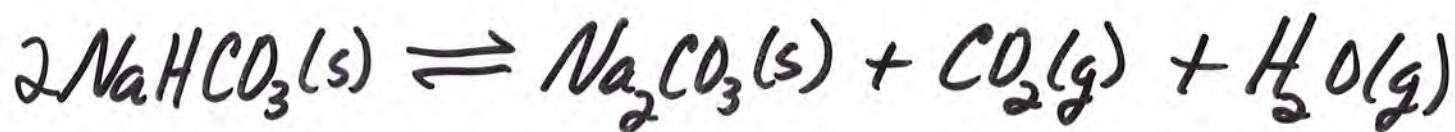
V dec. - mole ratio must inc.
to maintain K

- shift to right

1) Systems involving only solids/liquids
- effect of pressure
is negligible

2) Heterogeneous Equil.

Consider only change in
moles of gas.



Inc. P, shift

c) Change Temperature

Affects the value of K

Think of heat as a reactant or product

1) Endothermic, $\Delta H > 0$

rx. absorbs heat

reactants + heat \rightleftharpoons products

inc. T (add heat), \longrightarrow

\therefore inc. products, dec. reactants

K Inc.

2) Exothermic, $\Delta H < 0$

rx. releases heat

reactants \rightleftharpoons products + heat

inc. T (add heat), \leftarrow

\therefore inc. reactants, dec. products

K Dec.

3) Summary

$\Delta H > 0$: T \uparrow , K \uparrow , shifts right

$\Delta H < 0$: T \uparrow , K \downarrow , shifts left

4) Ex:

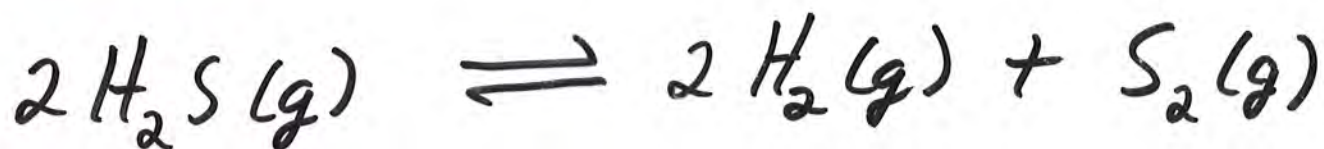


exothermic, $\Delta H < 0$

Inc. T ,

Dec. T ,

5) Ex:



<u>T (°C)</u>	<u>K_p</u>
750	0.000091
850	0.00038
1065	0.0118
1132	0.0260

Inc. T, K_p inc.

$$K_p = \frac{P_{\text{H}_2} \cdot P_{\text{S}_2}}{P_{\text{H}_2\text{S}}^2}$$

Inc. K_p ⇒ rx. shifted right
shift minimized stress of
added heat – used heat

Forward rx. is endothermic,
ΔH > 0

D) Ex:



$$\Delta H = +173 \text{ kJ}$$

What happens to the amount of CO & K when:

Shift CO K

Add CO₂

Add C(s)

P ↑ (V ↓)

T ↑

E) Effects of Catalyst

Catalyst dec. E_a



$$K_c = \frac{[B]}{[A]} = \frac{k_f}{k_r}$$

E_a dec. for both forward
& reverse rx's.

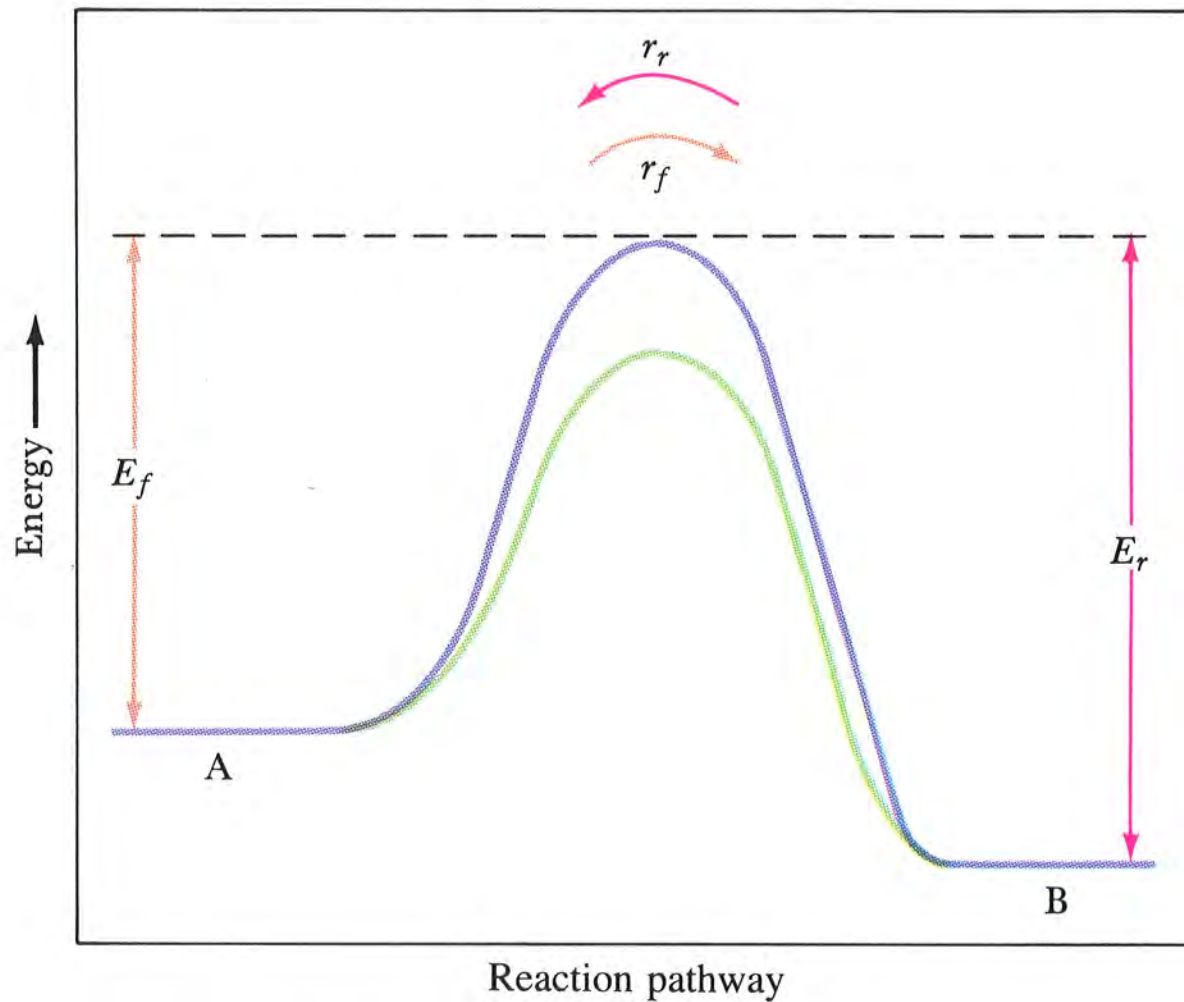
\therefore rates of both rx's inc.

rate constants inc. by
the same factor

$\therefore K_c$ is unchanged

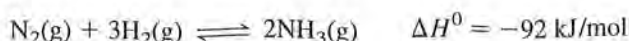
A catalyst **only** changes rate
at which equil. is reached, &
NOT value of K

Transparency 112 **Figure 15.12 Energy profile of an equilibrium reaction, with and without catalyst**



The Haber Process

Nitrogen, N_2 , is very unreactive. The Haber process is the economically important industrial process by which atmospheric N_2 is converted to ammonia, NH_3 , a soluble, reactive compound. Innumerable dyes, plastics, explosives, fertilizers, and synthetic fibers are made from ammonia. The Haber process provides insight into kinetic and thermodynamic factors that influence reaction rates and the positions of equilibria. In this process the reaction between N_2 and H_2 to produce NH_3 is never allowed to reach equilibrium, but moves toward it.



$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = 3.6 \times 10^8 \quad (\text{at } 25^\circ\text{C})$$

The process is diagrammed in Figure 17-3. The reaction is run at about 450°C under pressures ranging from 200 to 1000 atmospheres. Hydrogen is obtained from coal gas or petroleum refining and nitrogen from liquefied air.

The value of K_c is 3.6×10^8 at 25°C . This very large value of K_c indicates that *at equilibrium* virtually all of the N_2 and H_2 (mixed in a 1:3 mole ratio) would be converted

into NH_3 . However, at 25°C the reaction occurs so slowly that no measurable amount of NH_3 is produced within a reasonable time. Thus, the large equilibrium constant (a thermodynamic factor) indicates that the reaction proceeds toward the right almost completely. However, it tells us *nothing* about how fast the reaction occurs (a kinetic factor).

There are four moles of gases on the left side of the equation and only two moles of gas on the right, so increasing the pressure favors the production of NH_3 . Therefore, the Haber process is carried out at very high pressures, as high as the equipment will safely stand.

The reaction is exothermic (ΔH_{rxn}^0 is negative), so increasing the temperature favors the *decomposition* of NH_3 (the reverse reaction). But, the rates of both forward and reverse reactions increase as temperature increases.

The addition of a catalyst of finely divided iron and small amounts of selected oxides also speeds up both the forward and reverse reactions. This allows NH_3 to be produced not only faster but at a lower temperature, which increases the yield of NH_3 and extends the life of the equipment.

Table 17-1 shows the effects of increases in temperature and pressure on the equilibrium yield of NH_3 , starting with 1:3 mole ratios of $N_2:H_2$. K_c decreases by more than ten orders of magnitude, from 3.6×10^8 at 25°C to only 1.4×10^{-2} at 758°C . This tells us that the reaction proceeds *very far to the left* at high temperatures. Casual examination of the data might suggest that the reaction should be run at lower temperatures, because a higher percentage of the N_2 and H_2 is converted into NH_3 . However, the reaction occurs so slowly, even in the presence of a catalyst, that it cannot be run economically at temperatures below about 450°C .

The emerging reaction mixture is cooled down, and NH_3 (bp = -33.43°C) is removed as a liquid. This favors the forward reaction. The unreacted N_2 and H_2 are recycled. Excess N_2 is used to favor the reaction to the right.

Approximately 135 pounds of NH_3 are required for each person per year in the United States. Haber developed the process to provide a cheaper and more reliable source of explosives as Germany prepared for World War I. (Britain controlled the seas and access to the natural nitrates in India and Chile.) The current use of the process is more humanitarian; most NH_3 is used to produce fertilizers.

In practice the mixed reactants are compressed by special pumps and injected into the heated reaction vessel.

Ten orders of magnitude is 10^{10} , i.e., 10 billion.

$$1 \times 10^{10} = 10,000,000,000$$

Table 17-1 Effect of T and P on Yield of Ammonia

°C	K_c	Mole % NH_3 in Equilibrium Mixture		
		10 atm	100 atm	1000 atm
209	650	51	82	98
467	0.5	4	25	80
758	0.014	0.5	5	13

