The production of ammonia is an exothermic process –
$$N_2(g) + 3 H_2(g) \Leftrightarrow 2 NH_3(g) \qquad Kc = 3.5 \times 10^8 \text{ @ } 25^\circ C$$
To **maximize the [NH$_3$] at equilibrium it is best to**

a) Heat the reaction
b) Cool the reaction ✓
c) Leave it as is

$$N_2(g) + 3 H_2(g) \Longleftrightarrow 2 NH_3(g) + \text{'heat'}$$

To maximize NH$_3$(g), Remove a product ...
Remove heat by cooling the reaction.

15.4   Disturbing a Chemical Equilibrium: Le Chatelier's Principle
Change in Temperature – van't Hoff Equation

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

$$N_2\,(g) + 3\,H_2(g) \Leftrightarrow 2\,NH_3\,(g)$$
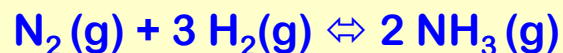
At 25°C, ΔH° = -91.8 kJ.mol^{-1}, K = 3.5x10^8 – however at this temperature the reaction is extremely slow.

With the help of a catalyst, the optimum temperature for the reaction is 450°C.
ΔH° = -111.3kJ.mol^{-1} at this temperature. What is the **value for K** at this temperature?

$K_1 = 3.5 \times 10^8$ $T_1 = 298\,K$

$K_2 = ?$ $T_2 = 723\,K$

$\Delta H^\circ = -111,300\,J.mol^{-1}$

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

$$\ln \frac{K_2}{K_1} = -\left(\frac{-111,300}{8.314}\right)\left(\frac{1}{723} - \frac{1}{298}\right)$$

$\ln K_2 - \ln(3.5 \times 10^8) = 13387(-1.9726 \times 10^{-3})$

$\ln K_2 - 19.6734 = -26.4072$
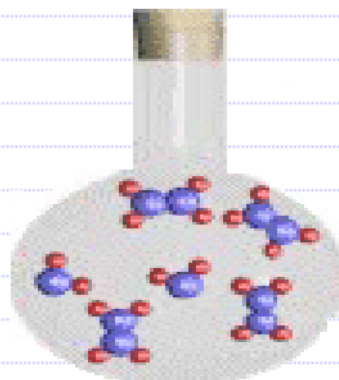
$\ln K_2 = -26.4072 + 19.6734$

$\ln K_2 = -6.7338$

$K_2 = 1.19 \times 10^{-3}$ @ 723K

↳ Ouch ... a ~ 10¹¹ drop.
While the decrease in K was
expected since the process
involved heating an Exothermic
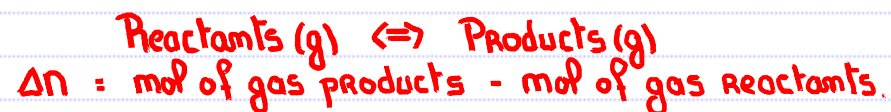equilibrium, this decrease is
dramatic.

15.4   Disturbing a Chemical Equilibrium: Le Chatelier's Principle
Change in the Volume of the System

Chemistry Interactive: Effect of Changing Volume on the NO_2/N_2O_4 Equilibrium

$$2\ NO_2(g) \rightleftharpoons N_2O_4(g) \qquad K = 171$$

See Closs Web Site.

Reactants (g) <=> Products (g)

Δn = mol of gas products - mol of gas reactants.

Δn :   = 0,   > 0,   or   < 0

ACTION:

EQUILIBRIUM SHIFT

a) Volume ↑, ie Pressure ↓

Toward the side with the greater number of gas molecules ... trying to increase the pressure ... if it can.*

b) Volume ↓, ie Pressure ↑

Toward the side with the fewest number of gas molecules ... trying to decrease the pressure ... if it can.*

* $\Delta n = 0$: Nothing the equilibrium can do to counter any pressure changes.
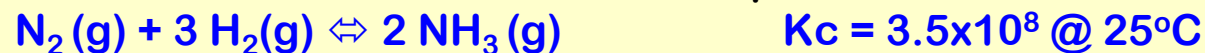
15.4   Disturbing a Chemical Equilibrium: Le Chatelier's Principle
Change in the Volume of the System – A Summary

ACTION	EQUILIBRIUM SHIFT	WHY ?
a) V↑, P↓		
b) V↓, P↑		

1. $O_3(g) + NO(g) \rightleftharpoons O_2(g) + NO_2(g)$

● + ● ⇌ ● + ●

a)   No shift

b)   No shift   } $\Delta n = 0$, Q Remains unchanged

2. $2\ NOCl(g) \rightleftharpoons 2\ NO(g) + Cl_2(g)$

● + ● ⇌ ● + ● + ●

a)   Towards products $\Delta n > 0$,   Q > K

b)   Towards Reactants $\Delta n > 0$,   Q < K

3. $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$

● + ● + ● + ● ⇌ ● + ●

a)   Towards Reactants $\Delta n < 0$,   Q < K

b)   Towards products $\Delta n < 0$,   Q > K

The production of ammonia is an exothermic process –
          $N_2(g) + 3 H_2(g) \Leftrightarrow 2 NH_3(g)$ $Kc = 3.5 \times 10^8$ @ 25°C
To **maximize the [NH$_3$] at equilibrium it is best to**

     a)   Increase the volume
     b)   Decrease the volume ✓ .. Increases the pressure
     c)   Leave it as is

$N_2(g)$ +   3 $H_2(g)$ $\Leftleftarrows$ 2 $NH_3(g)$

→ less gas molecules on NH$_3$ side.
$\Delta n < 0$
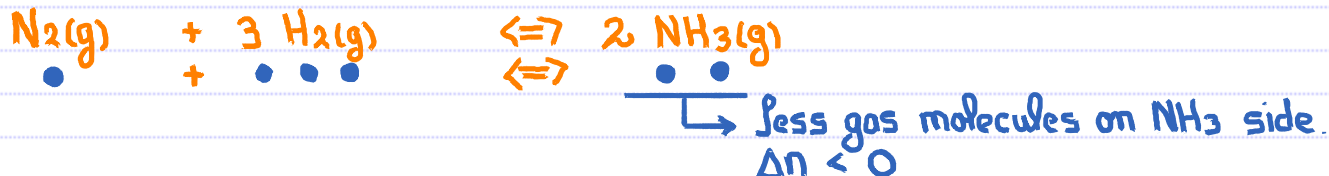
15.4   Disturbing a Chemical Equilibrium: Le Chatelier's Principle
Production of ammonia – an equilibrium dilemma!
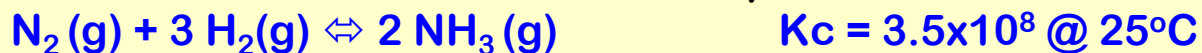
The production of ammonia is an exothermic process –
$$N_2 (g) + 3 H_2(g) \Leftrightarrow 2 NH_3 (g) \qquad Kc = 3.5 \times 10^8 \text{ @ } 25^oC$$
How can we maximize the production of $[NH_3]$.

a) At Room temperature, Kc is product favored
   However at Room temperature this Reaction is extremely slow. Very high Activation Energy.
   To speed it up ... heat it ... and /or use a catalyst to lower the Activation Energy

b) However the Reaction is exothermic ... thus heating it will Result in Kc decreasing
   As we calculated previously .. even with a catalyst the process is done at ~ 450°C ...
   at 450°C, Kc = 1.19 x 10⁻³. Thus while Reaching equilibrium in a Reasonable
   time, the equilibrium is now very Reactant favored.

c) Not daunted as this gaseous Reaction has Δn < 0
   Therefore if P is increased, then Q becomes > Kc, thereby causing a shift
   towards products ... increasing the [NH₃].

16.1   Introduction to Acids and Bases
Acid and Base Definitions

ARRHENIUS:

ACID :- A substance containing hydrogen that, when dissolved in water, increases the concentration of H^+ ions.

BASE :- A substance containing the hydroxide group that, when dissolved in water, increases the concentration of OH^- ions.

BRONSTED-LOWRY:

ACID :- A substance that can donate a proton (H^+ ion).

BASE :- A substance that can accept a proton.

As the Bronsted-Lowry definition is more inclusive, this is the definition that we will focus on. For example NH_3 is a base, which would not be obvious under the Arrhenius definition.

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+ + OH^-$$

Proton acceptor.
Base

OH^- ion concentration increase, thus it now obviously fits the Arrhenius definition