

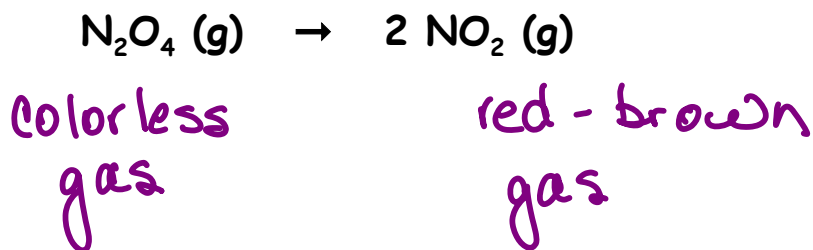
# CHEMICAL EQUILIBRIUM

[MH5; 12.1, 12.2, 12.4, 12.5]

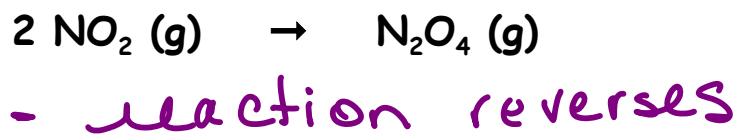
- Recall that at equilibrium, the rate of a reaction is equal to the rate of its reverse reaction.
- So.....it is going nowhere fast; the amounts of the reactants and the products do not change.
- Every equilibrium is governed by a number which we call the **Equilibrium Constant** (denoted by  $K_{eq}$ ).
- The equilibrium constant defines the relationship between the amounts of each reactant and product in the system.

## AN EXPERIMENTAL APPROACH TO EQUILIBRIUM [MH5;12.1]

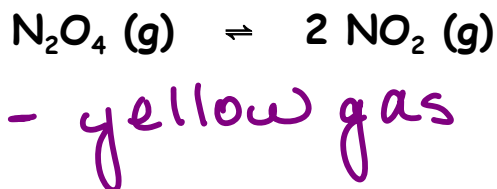
- Consider the following reaction:



- Initially, this is the only reaction taking place. But before long.....



- And soon.....



- equilibrium is established.

- Once the system attains equilibrium, the amounts of the two gases do not change; at 100 ° C, the pressures of each gas can be measured and found to be:

$$P(\text{N}_2\text{O}_4) = 0.22 \text{ atm}$$

$$P(\text{NO}_2) = 1.56 \text{ atm}$$

- The following table (MH5: Table 12.2) outlines three different ways that this equilibrium may be approached.

Experiment	Species	P (initial)	P(equilibrium)
1	$\text{N}_2\text{O}_4$	1.00	0.22
	$\text{NO}_2$	0.00	1.56
2	$\text{N}_2\text{O}_4$	0.00	0.07
	$\text{NO}_2$	1.00	0.86
3	$\text{N}_2\text{O}_4$	1.00	0.42
	$\text{NO}_2$	1.00	2.16

- Do these experiments have anything in common ?
- It turns out that there is a relationship between the equilibrium pressures of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  that is valid for all three experiments.

$$\frac{(P_{\text{NO}_2})^2}{(P_{\text{N}_2\text{O}_4})} \approx 11 \quad \text{-for all 3 experiments}$$

## THE EQUILIBRIUM CONSTANT EXPRESSION [MH5; 12.2]

- For the reaction:  $a A + b B \rightleftharpoons c C + d D$

at equilibrium  $K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$

- [A] represents the concentration of A and  $K_{eq}$  is the **Equilibrium Constant** for the reaction at that temperature.
- Concentration is usually expressed in **Molarity** ( $\text{molL}^{-1}$ ) for solution chemistry; for gases, values may be in  $\text{molL}^{-1}$  ( $K_c$  values) or in partial pressures ( $K_p$  values).

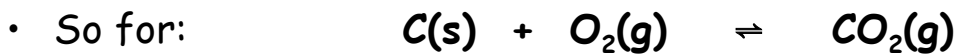
- For the gaseous equilibrium:  $H_2(g) + I_2(g) \rightleftharpoons 2 HI(g)$

$$K_p = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})} = 55 \quad \text{- at some temperature}$$

- For the gaseous equilibrium:  $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$

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

- When all reactants and products are in the same phase (all gas phase in the above examples) we have a **homogeneous** equilibrium.
- In a **heterogeneous** equilibrium, at least one reactant or product is in a different phase: ie; gas + solid, or solid + solution etc.



$$K_p = \frac{P_{CO_2}}{P_{O_2}}$$

SOLID

- The concentration of  $C(s)$ ,  $[C]$ , is a constant, and is always omitted.

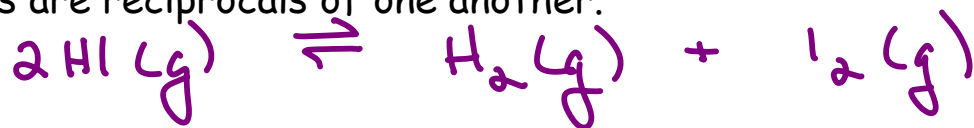
### Points about Equilibrium Constants

- 1) The expression for  $K$  depends upon the chemical equation.



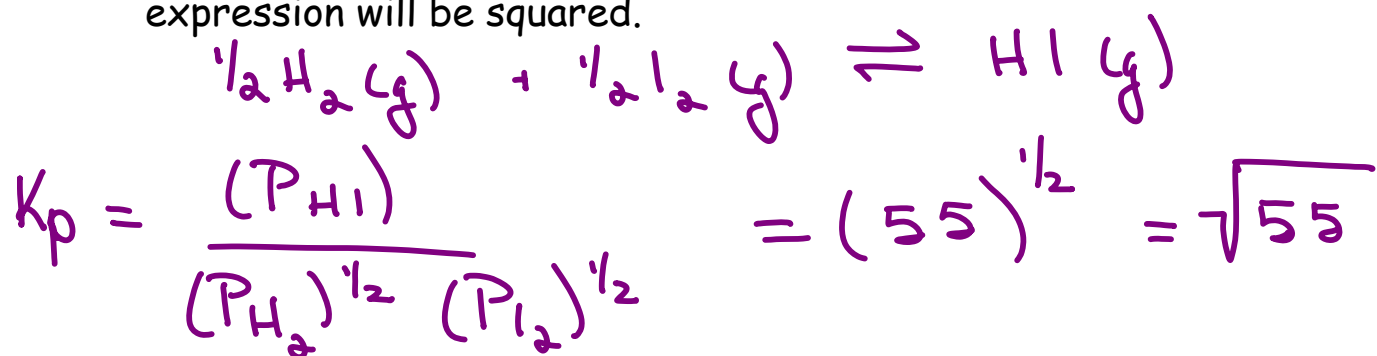
$$K_p = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})} = 55 \text{ at } 426^\circ C$$

- 2) If the equation is reversed, the  $K_{eq}$  expression is inverted - so the  $K$  values are reciprocals of one another.

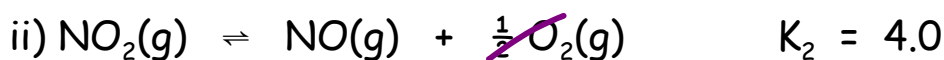
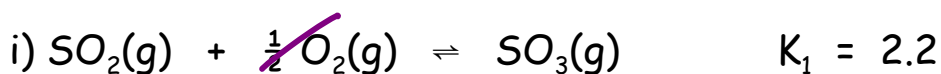


$$K_p = \frac{(P_{H_2})(P_{I_2})}{(P_{HI})^2} = \frac{1}{55}$$

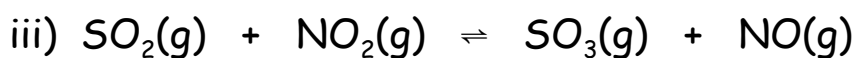
- 3) If the equation is halved, the  $K_{eq}$  expression becomes the square root of the original. Or if the equation is doubled, the  $K_{eq}$  expression will be squared.



- 4) For reactions added together, the  $K_{eq}$  is the product of the  $K_{eq}$  expressions for each step.



add i) and ii) to get . . .



$$K_3 = K_1 \times K_2 = 2.2 \times 4.0 = 8.8$$

Because:  $K_3 = \frac{(P_{SO_3})(P_{NO})}{(P_{SO_2})(P_{NO_2})}$

$$K_1 = \frac{(P_{SO_3})}{(P_{SO_2})(P_{O_2})^{1/2}}$$

$$K_2 = \frac{(P_{NO})(P_{O_2})^{1/2}}{(P_{NO_2})}$$

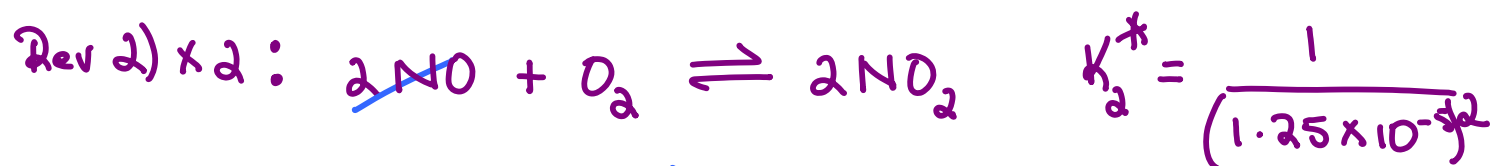
This is sometimes called the "Rule of Multiple Equilibria".

EXAMPLE of 4:

Given the following equilibria:



Calculate the value of  $K_c$  for  $\text{N}_2 (\text{g}) + 2 \text{O}_2 (\text{g}) \rightleftharpoons 2 \text{NO}_2 (\text{g})$



$$K_3 = K_1 \times K_2^* = 4.3 \times 10^{-25} \times \frac{1}{(1.25 \times 10^{-5})^2}$$

$$= \underline{\underline{2.752 \times 10^{-15}}}$$

- 5) The magnitude of the equilibrium constant is indicative of the position of the equilibrium.....

If "K" is large (greater than 1), the equilibrium lies towards the right, or the product side.

If "K" is small (less than 1), the equilibrium lies towards the left, or the reactant side.

**The Reaction Quotient, Q [MH5; 12.4]**

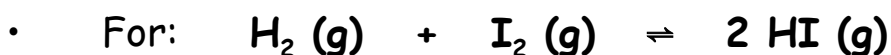
- For any equilibrium:  $aA + bB \rightleftharpoons cC + dD$

we may write a Reaction Quotient, "Q":

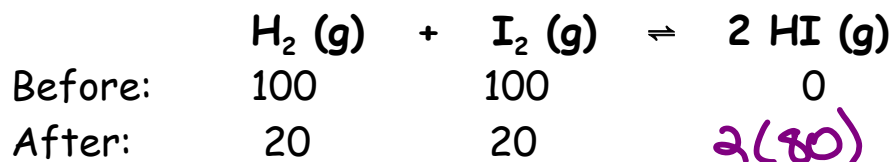
$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- looks just like the eq CONSTANT

- If the concentrations (or pressures of gaseous species) of the reactants and products are known, a numerical value for Q can be calculated.
- Comparison of this numerical value for Q to the equilibrium constant,  $K_{eq}$  gives us information about the direction of the reaction and the position of the equilibrium.



$$K_{eq} = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})} = \underline{55} \quad (\text{at } 426^\circ C)$$



kPa  
If 20 is left then 80 reacted

Before:  $Q = \frac{(0)^2}{(100)(100)} = 0$

Since  $Q < K$ , reaction goes forward.

After:  $Q = \frac{(160)^2}{(20)(20)} = 64$

If  $Q > K$ , reaction goes in reverse direction.

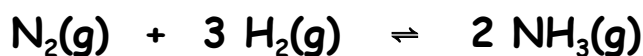
$64 > 55 \quad \therefore$  reaction reverse

If  $Q = K$ , the system is at equilibrium.

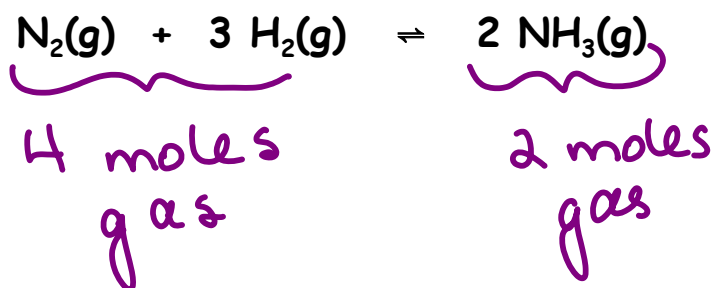
### LE CHATELIER'S PRINCIPLE [MH5; 12.5]

- "If a chemical system at equilibrium is disturbed by addition or removal of a reactant or product, the equilibrium will shift in a way to minimize the disturbance".  $K_p = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}$

- Consider the equilibrium:



- Addition of  $H_2(g)$  causes:
  - increase in amt of  $NH_3$
  - decrease the amt of  $N_2$
 } system tries to use extra  $H_2$
- Removal of  $NH_3(g)$  causes:
  - decrease in  $H_2$  and  $N_2$
  - they react to form more  $NH_3$
- Not only can addition or removal of a reagent affect the position of equilibrium, but also a change in pressure.....





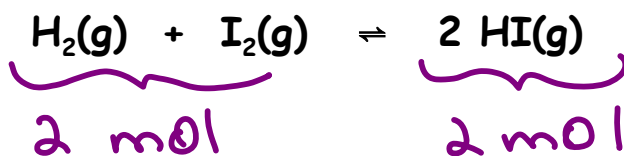
- If the system is compressed: (smaller volume)
  - pressure increases
  - system shift to offset inc. pressure

⇒ TO RIGHT; smaller # moles, ∴ P decreases

- If the system is expanded: (volume increases)
  - pressure decreases
  - system shifts to increase pressure

⇒ TO LEFT; greater # moles, ∴ P increases

- What about:



- position of equilibrium not affected by pressure changes

- A **temperature change** also affects the position of an equilibrium....
- The change will affect the magnitude of the equilibrium constant.
- If a reaction produces heat as it proceeds, K will decrease as the temperature increases.
- If a reaction requires heat to proceed, K will increase as the temperature increases.