#### A2 Physical Chemistry

## Equilibrium Constants and Le Chatelier's Principle

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## Changing concentrations

 $2 SO_2(g) + O_2(g) \Rightarrow 2 SO_3(g)$ 

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$$K_{p} = \frac{(P_{SO_{3(g)}})^{2}}{(P_{SO_{2(g)}})^{2} (P_{O_{2(g)}})}$$

$$2 SO_2(g) + O_2(g) \Rightarrow 2 SO_3(g)$$

a fixed 
$$K_p = \frac{(P_{so_{3(g)}})^2}{(P_{so_{2(g)}})^2 (P_{O_{2(g)}})}$$

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$$K_p = \frac{(5)^2}{(3)^2(4)} = \frac{25}{36} = 0.695 \text{ atm}^{-1}$$

$$2 SO_2(g) + O_2(g) \Rightarrow 2 SO_3(g)$$

$$K_{p} = \frac{(P_{SO_{3(g)}})^{2}}{(P_{SO_{2(g)}})^{2} (P_{O_{2(g)}})} = \frac{(5)^{2}}{(3)^{2} (4)} = 0.695 \text{ atm}^{-1}$$

Changing concentrations and Kc/Kp  

$$2 SO_{2}(g) + O_{2}(g) \Rightarrow 2 SO_{3}(g)$$
Additional  

$$SO_{2(g)} \text{ added} \qquad K_{p} = \frac{(P_{SO_{3(g)}})^{2}}{(P_{SO_{2(g)}})^{2} (P_{O_{2(g)}})} = \frac{(5)^{2}}{(3)^{2} (4)} = 0.695 \text{ atm}^{-1}$$



 $P_{SO_2}$  to 6 atm









The partial pressures of  $SO_2$  and  $O_2$  must decrease and the partial pressure of  $SO_3$  increase i.e. the equilibrium moves to the right.

$$2 \text{ SO}_{2}(g) + \text{ O}_{2}(g) \Rightarrow 2 \text{ SO}_{3}(g)$$
$$K_{p} = \frac{(P_{\text{SO}_{3}(g)})^{2}}{(P_{\text{SO}_{2}(g)})^{2} (P_{\text{O}_{2}(g)})} = \frac{(5)^{2}}{(3)^{2} (4)} = 0.695 \text{ atm}^{-1} \text{ Original}$$
$$(A)^{2}$$

$$= \frac{(A)^{-}}{(B)^{2}(C)} = 0.1736$$

The partial pressures of  $SO_2$  and  $O_2$  must decrease and the partial pressure of  $SO_3$  increase i.e. the equilibrium moves to the right.

$$K_{p} = \frac{(P_{so_{3(g)}})^{2}}{(P_{so_{2(g)}})^{2} (P_{O_{2(g)}})} = \frac{(5)^{2}}{(3)^{2} (4)} = 0.695 \text{ atm}^{-1} \text{ Original}$$
(5)<sup>2</sup>

New conditions - not at equilibrium

 $(6)^{2}(4)$ 

#### Equilibrium re-established

 $= \frac{(A)^2}{(4)^2 (C)}$ 

$$K_{p} = \frac{(P_{so_{3(g)}})^{2}}{(P_{so_{2(g)}})^{2} (P_{O_{2(g)}})} = \frac{(5)^{2}}{(3)^{2} (4)} = 0.695 \text{ atm}^{-1} \text{ Original}$$
New conditions - not at equilibrium  $(5)^{2}$ 

(6)<sup>2</sup> (4)

#### **Equilibrium re-established**

$$= \frac{(A)^2}{(4)^2 (3)}$$

$$K_{p} = \frac{(P_{SO_{3(g)}})^{2}}{(P_{SO_{2(g)}})^{2} (P_{O_{2(g)}})} = \frac{(5)^{2}}{(3)^{2} (4)} = 0.695 \text{ atm}^{-1}$$

New conditions - not at equilibrium

(5)<sup>2</sup> (6)<sup>2</sup> (4) Original

#### Equilibrium re-established

 $= \frac{(5.78)^2}{(4)^2 (3)}$ 

$$K_{p} = \frac{(P_{SO_{3(g)}})^{2}}{(P_{SO_{2(g)}})^{2} (P_{O_{2(g)}})} = \frac{(5)^{2}}{(3)^{2} (4)} = 0.695 \text{ atm}^{-1} \text{ Original}$$
  
New conditions - not at equilibrium 
$$\frac{(5)^{2}}{(6)^{2} (4)}$$

Equilibrium re-established

$$= \frac{(5.78)^2}{(4)^2(3)} = 0.695 \text{ atm}^{-1}$$

## Changing pressure

$$K_{p} = \frac{(P_{SO_{3(g)}})^{2}}{(P_{SO_{2(g)}})^{2} (P_{O_{2(g)}})}$$

$$K_{p} = \frac{(Y_{SO_{3(g)}} \times 4)^{2}}{(Y_{SO_{2(g)}} \times 4)^{2} (Y_{O_{2(g)}} \times 4)}$$

$$K_{p} = \frac{(4Y_{SO_{3(g)}})^{2}}{(4Y_{SO_{2(g)}})^{2} (4Y_{O_{2(g)}})}$$

$$K_{p} = \frac{16(Y_{SO_{3(g)}})^{2}}{16(Y_{SO_{2(g)}})^{2} \times 4(Y_{O_{2(g)}})}$$

$$K_{p} = \frac{16(Y_{SO_{3(g)}})^{2}}{64[(Y_{SO_{2(g)}})^{2} \times (Y_{O_{2(g)}})]}$$





#### Pressure increased to 6 atm

# $2 \text{ SO}_2(g) + \text{ O}_2(g) \Rightarrow 2 \text{ SO}_3(g)$ Total pressure - 4 atm $K_p = \frac{16(Y_{\text{SO}_{3(g)}})^2}{64[(Y_{\text{SO}_{2(g)}})^2 \times (Y_{\text{O}_{2(g)}})]}$

Pressure increased to 6 atm – the system is no longer at equilibrium if the mole fractions remain the same.

$$2 \text{ SO}_2(g) + O_2(g) \Rightarrow 2 \text{ SO}_3(g)$$
  
Total pressure - 4 atm  $K_p = \frac{16(Y_{SO_{3(g)}})^2}{64[(Y_{SO_{2(g)}})^2 \times (Y_{O_{2(g)}})]}$ 

Pressure increased to 6 atm – the system is no longer at equilibrium if the mole fractions remain the same.

 $(Y_{SO_{3(g)}} \times 6)^2$  $(Y_{SO_{2(g)}} \times 6)^2 (Y_{O_{2(g)}} \times 6)$ 

# $2 \text{ SO}_2(g) + \text{ O}_2(g) \Rightarrow 2 \text{ SO}_3(g)$ Total pressure - 4 atm $K_p = \frac{16(Y_{\text{SO}_{3(g)}})^2}{64[(Y_{\text{SO}_{2(g)}})^2 \times (Y_{\text{O}_{2(g)}})]}$

Pressure increased to 6 atm – the system is no longer at equilibrium if the mole fractions remain the same.

 $36(Y_{SO_{3(g)}})^2$ 

 $216[(Y_{so_{2(g)}})^{2}x (Y_{O_{2(g)}})]$ 

$$2 \text{ SO}_{2}(g) + O_{2}(g) \Rightarrow 2 \text{ SO}_{3}(g)$$
  
At equilibrium:  $K_{p} = \frac{16(Y_{SO_{3}(g)})^{2}}{64[(Y_{SO_{2}(g)})^{2}\chi(Y_{O_{2}(g)})]} = 0.25 \times \text{Mole fraction}$   
expression

Pressure increased to 6 atm – the system is no longer at equilibrium if the mole fractions remain the same.

 $\frac{36(Y_{SO_{3(g)}})^2}{216[(Y_{SO_{2(g)}})^2 \chi (Y_{O_{2(g)}})]}$ 

= 0.167 x Mole fraction expression

$$2 \text{ SO}_{2}(g) + \text{O}_{2}(g) \Rightarrow 2 \text{ SO}_{3}(g)$$
At equilibrium:  $K_{p} = \frac{16(Y_{\text{SO}_{3(g)}})^{2}}{64[(Y_{\text{SO}_{2(g)}})^{2}X(Y_{\text{O}_{2(g)}})]} = 0.25 \times \text{Mole fraction expression}$ 
New conditions:  $36(Y_{\text{SO}_{3(g)}})^{2} = 0.167 \times \text{Mole fraction expression}$ 

Consider the change in pressure:

$$2 \text{ SO}_{2}(g) + O_{2}(g) \Rightarrow 2 \text{ SO}_{3}(g)$$
At equilibrium:  $K_{p} = \frac{16(Y_{SO_{3}(g)})^{2}}{64[(Y_{SO_{2}(g)})^{2}\chi(Y_{O_{2}(g)})]} = 0.25 \times \text{Mole fraction expression}$ 
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New conditions:  $36(Y_{SO_{3}(g)})^{2} = 0.167 \times \text{Mole fraction expression}$ 
Consider the change in pressure:

64

$$2 \text{ SO}_{2}(g) + O_{2}(g) \Rightarrow 2 \text{ SO}_{3}(g)$$
At equilibrium:  $K_{p} = \frac{16(Y_{\text{SO}_{3}(g)})^{2}}{64[(Y_{\text{SO}_{2}(g)})^{2}\chi(Y_{\text{O}_{2}(g)})]} = 0.25 \times \text{Mole fraction expression}$ 
New conditions:  $36(Y_{\text{SO}_{3}(g)})^{2}$ 

$$= 0.167 \times \text{Mole fraction expression}$$
Consider the change in pressure:  
16 36

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# $2 \operatorname{SO}_{2}(g) + \operatorname{O}_{2}(g) \Rightarrow 2 \operatorname{SO}_{3}(g)$ $\xrightarrow{x \, 2.25} \qquad 36$ $64 \qquad 216$





The change in pressure has affected the reactants more than the products. Therefore in order to restore Kp and reach equilibrium again, the mole fractions of the reactants must decrease and the mole fraction of the product increase.



The equilibrium shifts to the right i.e. to side with the fewest number of gaseous moles

## Changing temperature

#### 

# Exothermic $2 SO_2(g) + O_2(g) \Rightarrow 2 SO_3(g)$

#### ⊿H -198.2 kJ/mol



⊿H -198.2 kJ/mol



#### ⊿H -198.2 kJ/mol

$$K_{p} = \frac{(P_{SO_{3(g)}})^{2}}{(P_{SO_{2(g)}})^{2} (P_{O_{2(g)}})}$$



$$K_{p} = \frac{(P_{SO_{3(g)}})^{2}}{(P_{SO_{2(g)}})^{2} (P_{O_{2(g)}})}$$



In this reaction the number of moles and partial pressures of SO<sub>2</sub> and O<sub>2</sub> increases





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$$K_{p} = \frac{(P_{SO_{3(g)}})^{2}}{(P_{SO_{2(g)}})^{2} (P_{O_{2(g)}})}$$

**Kp decreases** 



$$K_{p} = \frac{(P_{SO_{3(g)}})^{2}}{(P_{SO_{2(g)}})^{2} (P_{O_{2(g)}})}$$



In this reaction the number of moles and partial pressure of SO<sub>3</sub> increases

$$K_{p} = \frac{(P_{SO_{3(g)}})^{2}}{(P_{SO_{2(g)}})^{2} (P_{O_{2(g)}})}$$



In this reaction the number of moles and partial pressure of SO<sub>3</sub> increases

# $K_{p} = \frac{(P_{SO_{3(g)}})^{2}}{(P_{SO_{2(g)}})^{2} (P_{O_{2(g)}})}$

**Kp increases** 



In this reaction the number of moles and partial pressure of SO<sub>3</sub> increases

# $K_{p} = \frac{(P_{SO_{3(g)}})^{2}}{(P_{SO_{2(g)}})^{2} (P_{O_{2(g)}})}$

**Kp increases** 

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