

# **EQUILIBRIUM - 1**

## **INTRODUCTION AND CALCULATING $K_C$ AND $K_P$**

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# INTRODUCTION

- Some reactions go to completion because they occur readily.
- Some reactions progress slowly, so the forward and reverse reactions can be observed.
- Equilibrium occurs when both forward and reverse reactions occur at the same rate,
- Examples: (the  $\rightleftharpoons$  arrow indicates equilibrium.)



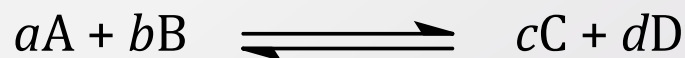
Forward reaction is synthesis of ammonia; while reverse is decomposition of ammonia to give hydrogen and nitrogen.



# EQUILIBRIUM CONSTANT, $K_c$

- The **equilibrium constant expression** for a reaction is obtained by multiplying the concentrations of products, dividing by the concentrations of reactants, and raising each concentration term to a power equal to its **coefficient** in the balanced chemical equation.
- The **equilibrium constant,  $K_c$** , is the value obtained for the  $K_c$  expression when equilibrium concentrations are substituted.

For the reaction



The equilibrium constant expression is

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

# EXAMPLE: $K_c$

Methanol (also called wood alcohol) is made commercially by hydrogenation of carbon monoxide at elevated temperature and pressure in the presence of a catalyst:



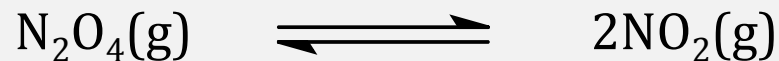
What is the  $K_c$  expression for this reaction?

**Solution:**

$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{H}_2]^2[\text{CO}]}$$

# EQUILIBRIUM CONSTANT

Calculation of equilibrium constant.

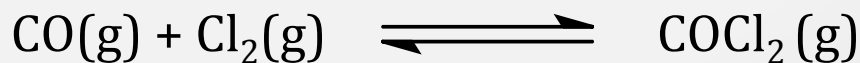


Experiment	Initial Concentrations (M)		Equilibrium Concentrations (M)		
	$[\text{N}_2\text{O}_4]_i$	$[\text{NO}_2]_i$	$[\text{N}_2\text{O}_4]_{\text{eq}}$	$[\text{NO}_2]_{\text{eq}}$	$\frac{[\text{NO}_2]_{\text{eq}}^2}{[\text{N}_2\text{O}_4]_{\text{eq}}}$
1	0.670	0.00	0.643	0.0547	$4.65 \times 10^{-3}$
2	0.446	0.0500	0.448	0.0457	$4.66 \times 10^{-3}$
3	0.500	0.0300	0.491	0.0475	$4.60 \times 10^{-3}$
4	0.600	0.0400	0.594	0.0523	$4.60 \times 10^{-3}$
5	0.000	0.200	0.0898	0.0204	$4.63 \times 10^{-3}$

The  $K_c$  for this reaction is “constant” at  $25^\circ\text{C}$ . The  $K_c$  is the same at the beginning and end of the reaction.

# REACTION QUOTIENT

- **Reaction quotient** =  $Q_c$  = the value of the “equilibrium constant expression” under any conditions. This indicates the progress of reaction.



$$K_c = \frac{[\text{COCl}_2]_{\text{eq}}}{[\text{CO}]_{\text{eq}}[\text{Cl}_2]_{\text{eq}}} \quad Q_c = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]}$$

$Q_c > K_c \Rightarrow$  **reverse reaction favored (reactants favored)**

$Q_c = K_c \Rightarrow$  **equilibrium present (at equilibrium)**

$Q_c < K_c \Rightarrow$  **forward reaction favored (products favored)**

OR one can calculate  $K_c$  and determine which way the equilibrium will proceed.

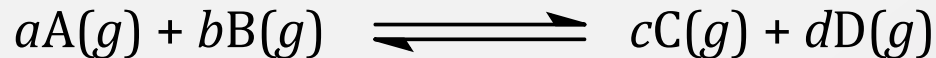
$K_c = \text{very large } (10^2)$

$K_c = \text{small } (10^{-2})$

$K_c = 1$  **equilibrium**

# EQUILIBRIUM CONSTANT FOR GASES $K_p$

- Calculate  $K_p$  instead of  $K_c$ .  $K_p$  will be different from  $K_c$ .



$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

Using gas law  $PV = nRT$  where conc. is mol/L =  $n/V$ ; so  $P_A = \frac{n_A}{V_A} RT$

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b} = \frac{[C]^c (RT)^c [D]^d (RT)^d}{[A]^a (RT)^a [B]^b (RT)^b}$$

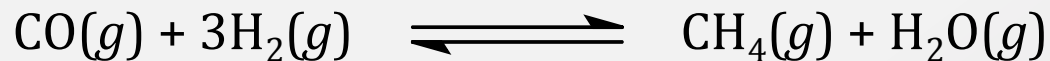
$$K_p = \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{(c+d-a-b)} \quad \text{so} \quad K_p = \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{\Delta n}$$

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

where  $\Delta n$  is (mols of product – reactant); R = gas const.

# GAS EQUILIBRIUM CONSTANT $K_p$

For catalytic methanation,



the equilibrium expression in terms of partial pressures becomes

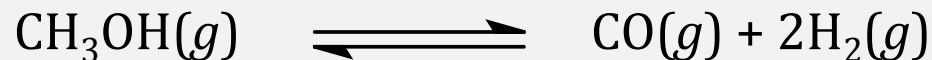
$$K_p = \frac{P_{\text{CH}_4} P_{\text{H}_2\text{O}}}{P_{\text{CO}} P_{\text{H}_2}^3}$$

$$K_p = K_c (RT)^{-2} = \frac{K_c}{(RT)^2}$$



# EXAMPLE: $K_p$ CALCULATION

The value of  $K_c$  at  $227^\circ\text{C}$  is 0.0952 for the following reaction:



What is  $K_p$  at this temperature?

**Solution:**

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

$$K_p = 0.0952(RT)^{\Delta n}$$

Where

$$T = 227 + 273 = 500. \text{ K}$$

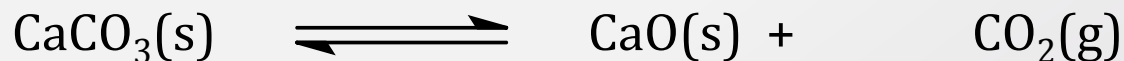
$$R = 0.08206 \text{ L} \cdot \text{atm}/(\text{mol} \cdot \text{K})$$

$$\Delta n = 3 - 1 = 2$$

$$K_p = 1.60 \times 10^2$$

# EQUILIBRIUM EXPRESSIONS

- Homogeneous equilibrium – where all reactants and products are in the same phase.
- Heterogeneous equilibrium – where not all reactants and products are in the same phase.



The equilibrium constant expression is,  $K = [\text{CO}_2]$

- Calcium carbonate and calcium oxide are solids. Liquids and solids are **NOT** part of equilibrium expression.

# EXAMPLES: EQUILIBRIUM EXPRESSIONS

Write the  $K_p$  for the following reactions.



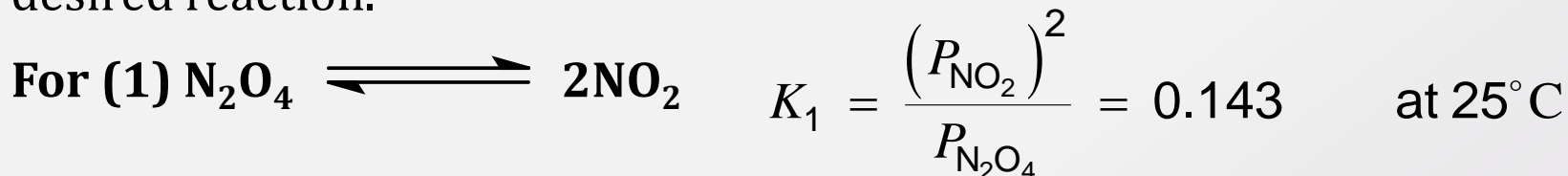
Solution:

$$(a) K_P = P_{\text{N}_2\text{O}} \cdot (P_{\text{H}_2\text{O}})^2$$

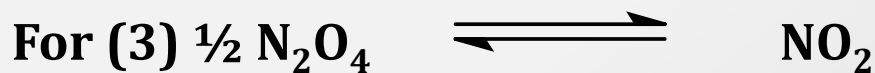
$$(b) K_P = \frac{1}{P_{\text{Cl}_2}}$$

# EQUILIBRIUM EXPRESSIONS

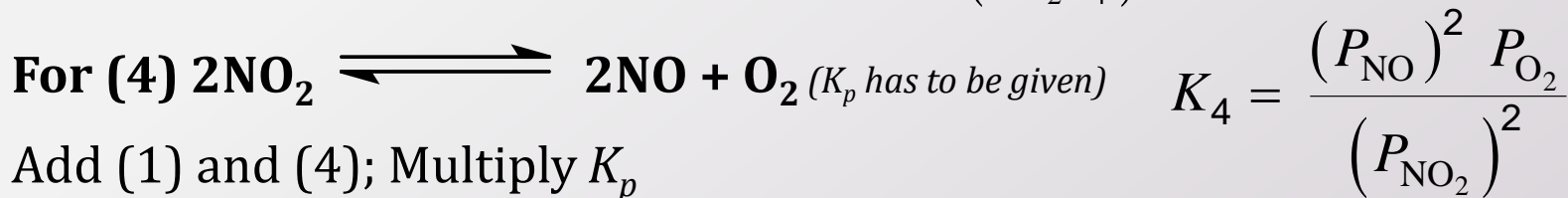
Equilibrium ( $K_c$  or  $K_p$ ) can be manipulated (like Hess's Law) to give  $K_c$  for desired reaction.



Inverse the  $K_p$ .  $K_2 = \frac{1}{K_1}$   $K_2 = \frac{P_{\text{N}_2\text{O}_4}}{(P_{\text{NO}_2})^2} = \frac{1}{0.143} = 6.99$  at  $25^\circ\text{C}$



Square root of  $K_p$   $K_3 = \sqrt{K_1}$   $K_3 = \frac{P_{\text{NO}_2}}{(P_{\text{N}_2\text{O}_4})^{1/2}} = \sqrt{0.143} = 0.378$  at  $25^\circ\text{C}$



Add (1) and (4); Multiply  $K_p$

$$K_5 = \frac{(P_{\text{NO}})^2 P_{\text{O}_2}}{P_{\text{N}_2\text{O}_4}} = K_1 \times K_4$$

# EQUILIBRIUM EXPRESSIONS - SUMMARY

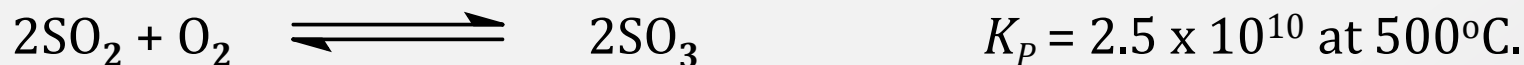
- In  $K_c$  manipulations
  - Twice the mol value in equation and  $K_c$  is squared
  - Half of mol value in equation – take the square root of  $K_c$
  - Reverse reaction is inverse of  $K_c$
  - Addition of equations is multiplying the  $K_c$

**TABLE 15.2** Manipulation of Equilibrium Constant Expressions

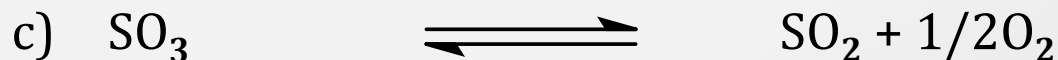
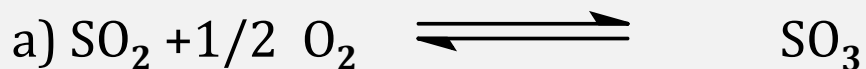
	$A(g) + B(g) \rightleftharpoons 2C(g)$	$K_{c_1} = 4.39 \times 10^{-3}$	
	$2C(g) \rightleftharpoons D(g) + E(g)$	$K_{c_2} = 1.15 \times 10^4$	
Equation	Equilibrium Expression	Relationship to Original $K_c$	Equilibrium Constant
$2C(g) \rightleftharpoons A(g) + B(g)$ Original equation is reversed.	$K'_{c_1} = \frac{[A]_{eq}[B]_{eq}}{[C]_{eq}^2}$	$\frac{1}{K_{c_1}}$	$2.28 \times 10^2$ New constant is the reciprocal of the original.
$2A(g) + 2B(g) \rightleftharpoons 4C(g)$ Original equation is multiplied by a number.	$K''_{c_1} = \frac{[C]_{eq}^4}{[A]_{eq}^2[B]_{eq}^2}$	$(K_{c_1})^2$	$1.93 \times 10^{-5}$ New constant is the original raised to the same number.
$\frac{1}{2}A(g) + \frac{1}{2}B(g) \rightleftharpoons C(g)$ Original equation is divided by 2.	$K'''_{c_1} = \frac{[C]_{eq}}{[A]_{eq}^{1/2}[B]_{eq}^{1/2}}$	$\sqrt{K_{c_1}}$	$6.63 \times 10^{-2}$ New constant is the square root of the original.
$A(g) + B(g) \rightleftharpoons D(g) + E(g)$ Two equations are added.	$K_{c_3} = \frac{[D]_{eq}[E]_{eq}}{[A]_{eq}[B]_{eq}}$	$K_{c_1} \times K_{c_2}$	50.5 New constant is the product of the two original constants.

\*Temperature is the same for both reactions.

# EXAMPLE: $K_C / K_P$ EXPRESSIONS



Compute  $K_p$  for the following reactions:



For

a) half the original equation so take square root of  $K_p$ ,  $(K_p)^{1/2}$

b) Equation is multiplied by 3/2, so  $(K_p)^{3/2}$

c) Equation is reversed and halved – so  $K_p$  is inversed and square rooted.

$$(1 / (K_p)^{1/2})$$

# KEY CONCEPTS

- Write  $K_c$  for equilibrium
- Reaction quotient
- Calculating  $K_p$  for gas reactions
- Stoichiometric manipulation of  $K_c$