

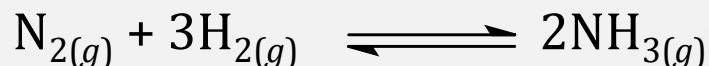
EQUILIBRIUM
1: INTRODUCTION TO
EQUILIBRIUM, CALCULATING K_c
AND K_p

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INTRODUCTION

Some reactions go to completion because they occur readily while 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. It is dynamic, always happening.
- Examples:



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



(the $\rightleftharpoons$ arrow indicates equilibrium.)

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 used for calculation.

For the reaction

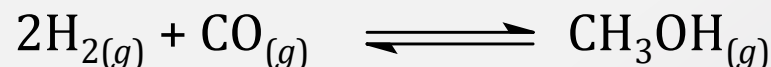


The equilibrium constant expression is

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

EXAMPLE 1: 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:



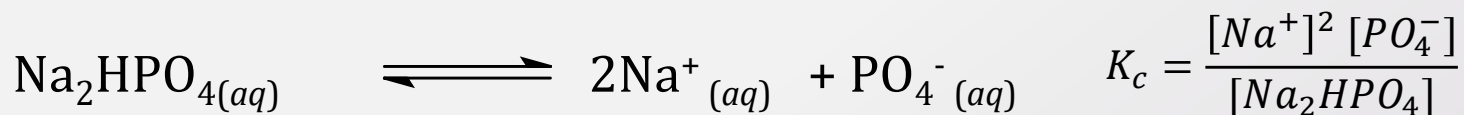
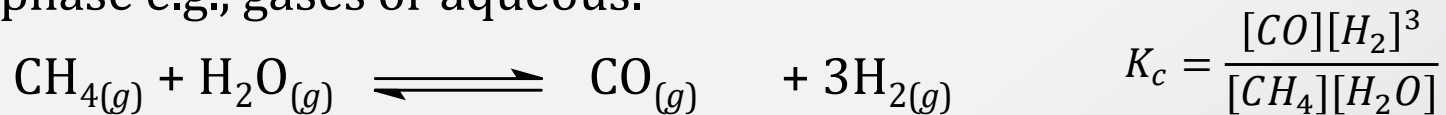
What is the K_c expression for this reaction?

Answer:

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

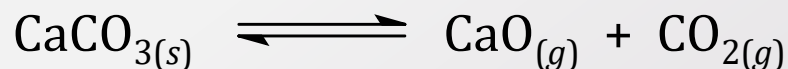
EQUILIBRIUM EXPRESSIONS

- Homogeneous equilibrium – where all reactants and products are in the same phase e.g., gases or aqueous.



- Heterogeneous equilibrium – where not all reactants and products are in the same phase.
- Equilibrium can be between any kind of phase but only gas and aqueous phases are written in K_c expression.

Liquids and solids are **NEVER** part of equilibrium expression. (*WHY?*)

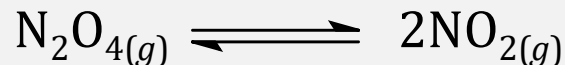


The equilibrium constant expression is, $K = [\text{CO}_2]$

Calcium carbonate and calcium oxide are solids and thus not part of the equilibrium expression.

EQUILIBRIUM CONSTANT

Calculation of equilibrium constant.



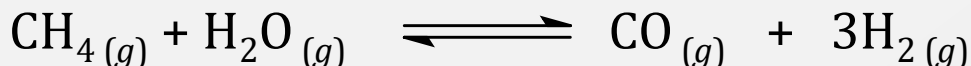
	Initial Concentration (M)		Equilibrium Concentration (M)		Initial Rate
Exp.	[N ₂ O ₄]i	[NO ₂]i	[N ₂ O ₄]eq	[NO ₂]eq	$\frac{[\text{NO}_2]_{\text{eq}}}{[\text{N}_2\text{O}_4]_{\text{eq}}}$
1	0.670	0.00	0.642	0.0546	4.65×10^{-3}
2	0.447	0.0500	0.447	0.0456	4.66×10^{-3}
3	0.500	0.0300	0.490	0.0475	4.60×10^{-3}
4	0.600	0.0400	0.594	0.0522	4.60×10^{-3}
5	0.000	0.200	0.0898	0.0204	4.63×10^{-3}

The K_c for this reaction is “constant” at 25 °C. The K_c is the same at the beginning and end of the reaction.

Magnitude of K_c : Large K_c values (10^5 or 10^7) indicate reaction is more forward favored. Small K_c number (10^{-20}) show reversed is favored.

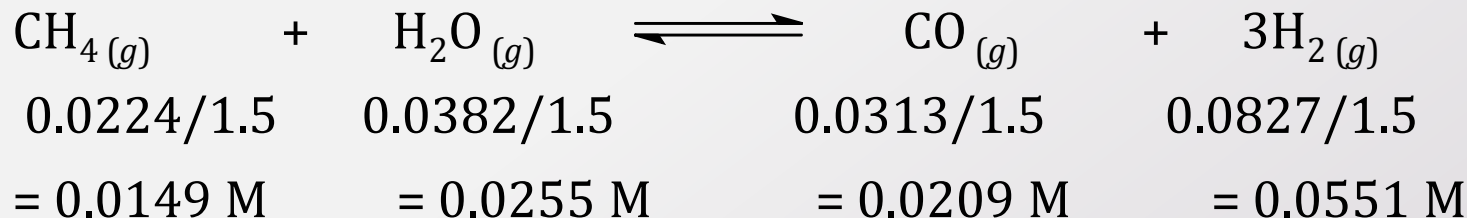
EXAMPLE 2: CALCULATING K_c

What is the value of K_c when 0.0224 mol of methane reacts with 0.0382 mol water to give 0.0313 mol carbon monoxide and 0.0827 mol hydrogen in a 1.5 L reaction vessel.



Answer:

Calculate concentrations (mol/L) of all and use K_c expression to calc. K_c .

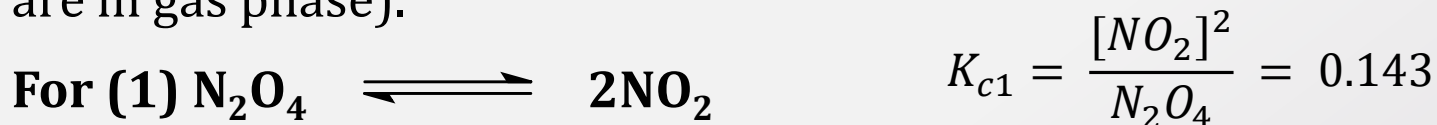


$$K_c = \frac{[\text{CO}][\text{H}_2]^3}{[\text{CH}_4][\text{H}_2\text{O}]} = \frac{0.0209 \times (0.0551)^3}{0.0149 \times 0.0255} = 9.20 \times 10^{-3}$$

Note: There are no units for K_c

MANIPULATION OF EQUILIBRIUM EXPRESSION

Equilibrium constants (K_c) can be manipulated (like Hess's Law) to give K_c for desired reaction. K_c for the reaction below at 25 °C is 0.143. The equations below show some examples of these manipulations. (All chemicals are in gas phase).



K_c , 0.143, is set up as shown with the K_1 equation.



Inverse the K_c . $K_2 = \frac{1}{K_1}$ $K_{c2} = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{1}{0.143} = 6.99$



Square root of K_c $K_3 = \sqrt{K_1}$ $K_{c3} = \frac{[\text{NO}_2]}{[\text{N}_2\text{O}_4]^{1/2}} = \sqrt{0.143} = 0.378$

EQUILIBRIUM MANIPULATIONS - SUMMARY

In K_c manipulations

- If twice the mol value in equation then K_c is squared.
- Half of mol value in equation then take the square root of K_c .
- Reverse reaction is inverse of K_c
- Addition of equations is multiplying the K_c



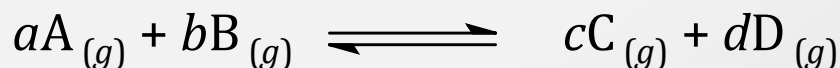
$$K_{c1} = \frac{[C]^4}{[A]^2 [B]^2}$$



Equation	Manipulation on Original Equation	Equilibrium Expression	Relationship to K_c	Equilibrium Constant
$4C_{(g)} \rightleftharpoons 2A_{(g)} + 2B_{(g)}$	Reversed/ Inversed	$K'_{c1} = \frac{[A]^2 [B]^2}{[C]^4}$	$\frac{1}{K_{c1}}$	2.28×10^4
$4A_{(g)} + 4B_{(g)} \rightleftharpoons 8C_{(g)}$	Multiplied by 2/ squared	$K''_{c1} = \frac{[C]^8}{[A]^4 [B]^4}$	$(K_{c1})^2$	1.93×10^{-9}
$A_{(g)} + B_{(g)} \rightleftharpoons 2C_{(g)}$	Divided by 2/square root	$K''_{c1} = \frac{[C]^2}{[A][B]}$	$\sqrt{K_{c1}}$	6.63×10^{-3}
$2A_{(g)} + 2B_{(g)} \rightleftharpoons D_{(g)} + E_{(g)}$	Addition of 2 equations	$K_{c3} = \frac{[D][E]}{[A]^2 [B]^2}$	$K_{c1} \times K_{c2}$	0.505

EQUILIBRIUM CONSTANT FOR GASES K_p

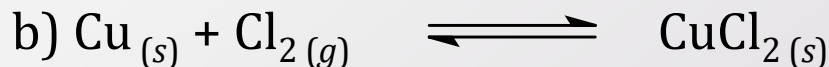
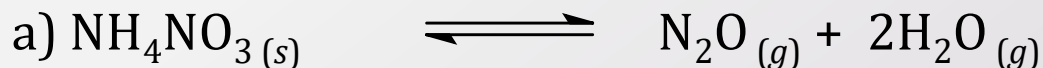
When an equilibrium has chemicals all in gas phases, then K_p can be calculated instead of K_c . K_p will numerically be different from K_c , however it is set up the same way as K_c . Pressure values are used instead of concentrations as all chemicals are in gas phase.



$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

EXAMPLE 3: WRITING EQUILIBRIUM CONSTANT FOR GASES

Write the K_p for the following reactions.



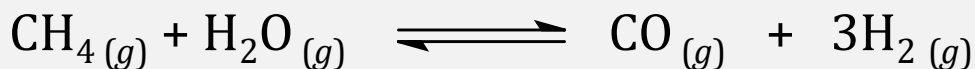
Answer:

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

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

EXAMPLE 4: CALCULATING K_p

What is the value of K_p when P_{CH_4} is 0.245 atm, $P_{\text{H}_2\text{O}}$ is 2.90 atm, P_{CO} is 1.27 atm and P_{H_2} is 1.038 atm. in a 1.5 L reaction vessel at 500 °C.

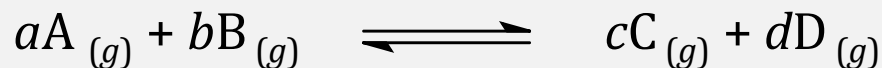


Answer:

$$K_p = \frac{P_{\text{CO}} P_{\text{H}_2}^3}{P_{\text{CH}_4} P_{\text{H}_2\text{O}}} = \frac{0.0245 \times (2.90)^3}{1.27 \times 1.038} = 0.453$$

RELATIONSHIP BETWEEN K_c AND K_p

K_p can be converted to K_c so K_c values across reactions can be compared for research purposes.



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

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

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

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

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

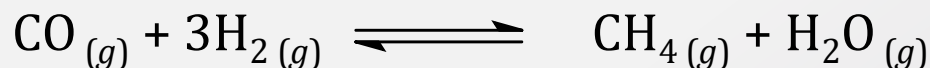
$$K_p = \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{\Delta n}$$

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

where Δn is (mols of product – reactant); R = gas const.

EXAMPLE 5: RELATIONSHIP BETWEEN K_c AND K_p

Find the K_p and K_c expression for catalytic reaction of carbon monoxide with hydrogen to product methane. Using the data from slide 10 on calculating K_p for this equation, calculate the K_c .



Answer:

The equilibrium expression in terms of partial pressures is:

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

To express that in terms of K_c , use: $K_p = K_c (RT)^{\Delta n}$

Δn is stoichiometric coefficients (products – reactants) = 2 - 4 = -2

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

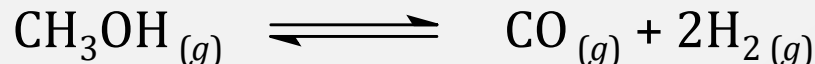
$$K_c = \frac{K_p}{(RT)^{-2}}$$

$$500 + 273 = 773 \text{ K}$$

$$K_c = \frac{K_p}{(RT)^{-2}} = \frac{0.453}{(0.0821 \times 773)^{-2}} = 1.12 \times 10^{-4}$$

EXAMPLE 6: K_p FROM K_c CALCULATION

The value of K_c at 227°C is 0.0952 for the following reaction:



What is K_p at this temperature?

Answer:

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

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

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

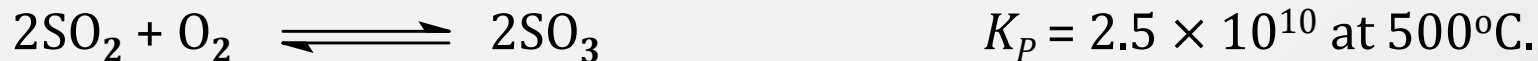
$$R = 0.08206 \text{ L} \cdot \text{atm}/(\text{mol} \cdot \text{K})$$

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

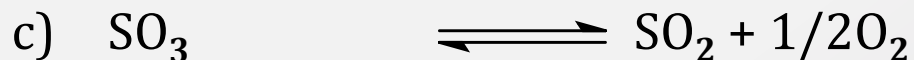
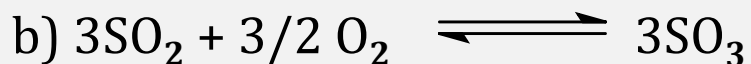
$$K_p = 0.0952(0.08206 \times 500)^2 = 1.60 \times 10^2$$

EXAMPLE 7: K_p MANIPULATIONS

Given the equation below with all chemicals in gas phase:



Compute K_p for the following reactions:



Answer:

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.

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

REACTION QUOTIENT

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



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

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

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

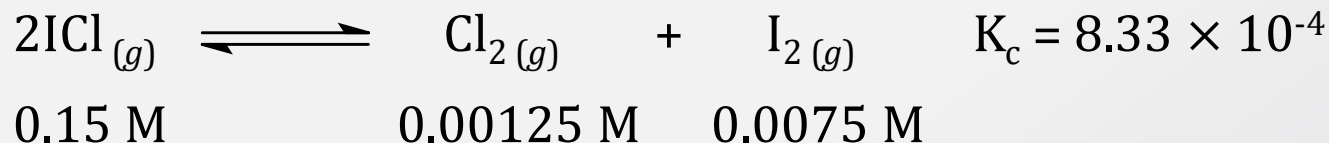
$Q_c < K_c \Rightarrow$ **forward reaction favored (products favored)**

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**

EXAMPLE 8: CALCULATING Q_c

Determine the direction of equilibrium of the reaction below when the concentrations are in the equation.



Answer:

The Q_c expression is:

$$Q_c = \frac{[\text{Cl}_2][\text{I}_2]}{[\text{ICl}]^2}$$

And calculating Q_c is:

$$Q_c = \frac{[0.00125][0.0075]}{[0.15]^2} = 4.17 \times 10^{-4}$$

$Q_c < K_c$; equilibrium is going forward.

Note: Q_p is calculated the same way as Q_c except using pressure of gases.

KEY CONCEPTS

- Write K_c for equilibrium.
- Stoichiometric manipulation of K_c .
- Calculating K_p for gas reactions.
- Relationship between K_p and K_c .
- Reaction quotient.