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:

  $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

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

  $CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$

  (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

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$$

The equilibrium constant expression is

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

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:

$$2H_{2(g)} + CO_{(g)} \rightleftharpoons CH_3OH_{(g)}$$

What is the K_c expression for this reaction?

Answer:

$$K_c = \frac{[CH_3OH]}{[H_2]^2[CO]}$$

EQUILIBRIUM EXPRESSIONS

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

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)} \qquad K_c = \frac{[CO][H_2]^3}{[CH_4][H_2O]}$$

$$Na_2HPO_{4(aq)} \rightleftharpoons 2Na^+_{(aq)} + PO_4^-{}_{(aq)} \qquad K_c = \frac{[Na^+]^2\,[PO_4^-]}{[Na_2HPO_4]}$$

- 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 Kc expression.

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

$$CaCO_{3(s)} \rightleftharpoons CaO_{(g)} + CO_{2(g)}$$

The equilibrium constant expression is, $K = [CO_2]$
Calcium carbonate and calcium oxide are solids and thus not part of the equilibrium expression.

EQUILIBRIUM CONSTANT

Calculation of equilibrium constant.

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

	Initial Concentration (M)		Equilibrium Concentration (M)		Initial Rate
Exp.	$[N_2O_4]i$	$[NO_2]i$	$[N_2O_4]eq$	$[NO_2]eq$	$\frac{[NO_2]eq}{[N_2O_4]eq}$
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.

$$CH_{4\,(g)} + H_2O_{\,(g)} \rightleftharpoons CO_{\,(g)} + 3H_{2\,(g)}$$

Answer:

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

$CH_{4\,(g)}$	+	$H_2O_{\,(g)}$	$\rightleftharpoons$	$CO_{\,(g)}$	+	$3H_{2\,(g)}$
0.0224/1.5		0.0382/1.5		0.0313/1.5		0.0827/1.5
= 0.0149 M		= 0.0255 M		= 0.0209 M		= 0.0551 M

$$K_c = \frac{[CO][H_2]^3}{[CH_4][H_2O]} = \frac{0.0209 \times (0.0551)^3}{0.0149 \times\ 0.0255} = \boxed{9.20 \times 10^{-3}}$$

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 ^{o}C is 0.143. The equations below show some examples of these manipulations. (All chemicals are in gas phase).

For (1) $\mathbf{N_2O_4 \rightleftharpoons 2NO_2}$ $\qquad K_{c1} = \dfrac{[NO_2]^2}{N_2O_4} = 0.143$

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

For (2) $\mathbf{2NO_2 \rightleftharpoons N_2O_4}$ ***(equation is reversed)***

Inverse the K_c . $\boldsymbol{K_2} = \dfrac{1}{K_1}$ $\qquad K_{c2} = \dfrac{[N_2O_4]}{[NO_2]^2} = \dfrac{1}{0.143} = 6.99$

For (3) $\mathbf{\frac{1}{2}\ N_2O_4 \rightleftharpoons NO_2}$ ***(equation is halved)***

Square root of K_c $\quad \boldsymbol{K_3} = \sqrt{K_1}$ $\qquad K_{c3} = \dfrac{[NO_2]}{[N_2O_4]^{1/2}} = \sqrt{0.143} = 0.378$

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.

$2A_{(g)} + 2B_{(g)} \rightleftharpoons 4C_{(g)}$ $\quad Kc_1 = 4.39 \times 10^{-5}$ $\quad Kc_1 = \dfrac{[C]^4}{[A]^2\,[B]^2}$

$4C_{(g)} \rightleftharpoons D_{(g)} + E_{(g)}$ $\quad Kc_2 = 1.15 \times 10^{4}$

Equation	Manipulation on Original Equation	Equilibrium Expression	Relationship to Kc	Equilibrium Constant
$4C\,(g) \rightleftharpoons 2A(g) + 2B\,(g)$	Reversed/ Inversed	$K'c_1 = \dfrac{[A]^2\,[B]^2}{[C]^4}$	$\dfrac{1}{Kc_1}$	2.28×10^{4}
$4A\,(g) + 4B\,(g) \rightleftharpoons 8C\,(g)$	Multiplied by 2/ squared	$K''c_1 = \dfrac{[C]^8}{[A]^4\,[B]^4}$	$(Kc_1)^2$	1.93×10^{-9}
$A\,(g) + B\,(g) \rightleftharpoons 2C\,(g)$	Divided by 2/square root	$K''c_1 = \dfrac{[C]^2}{[A]\,[B]}$	$\sqrt{Kc_1}$	6.63×10^{-3}
$2A\,(g) + 2B\,(g) \rightleftharpoons D\,(g) + E\,(g)$	Addition of 2 equations	$Kc_3 = \dfrac{[D]\,[E]}{[A]^2\,[B]^2}$	$Kc_1 \times Kc_2$	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.

$$a\mathrm{A}_{(g)} + b\mathrm{B}_{(g)} \rightleftharpoons c\mathrm{C}_{(g)} + d\mathrm{D}_{(g)}$$

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

EXAMPLE 3: WRITING EQUILIBRIUM CONSANT FOR GASES

Write the K_p for the following reactions.

a) $\mathrm{NH_4NO_{3\,(s)}} \rightleftharpoons \mathrm{N_2O_{(g)}} + 2\mathrm{H_2O_{(g)}}$

b) $\mathrm{Cu_{(s)}} + \mathrm{Cl_{2\,(g)}} \rightleftharpoons \mathrm{CuCl_{2\,(s)}}$

Answer:

(a) $K_P = P_{\mathrm{N_2O}} \cdot \left(P_{\mathrm{H_2O}}\right)^2$

(b) $K_P = \dfrac{1}{P_{\mathrm{Cl_2}}}$

EXAMPLE 4: CALCULATING K_P

What is the value of K_p when P_{CH4} is 0.245 atm, P_{H2O} is 2.90 atm, P_{CO} is 1.27 atm and P_{H2} is 1.038 atm. in a 1.5 L reaction vessel at 500 °C.

$$CH_{4\,(g)} + H_2O_{\,(g)} \rightleftharpoons CO_{\,(g)} + 3H_{2\,(g)}$$

Answer:

$$K_p = \frac{P_{CO}\,P_{H2}^3}{P_{CH4}\,P_{H2O}} = \frac{0.0245 \times (2.90)^3}{1.27 \times 1.038} = \boxed{0.453}$$

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.

$$aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$$

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

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

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

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

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

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.

$$CO_{(g)} + 3H_{2\,(g)} \rightleftharpoons CH_{4\,(g)} + H_2O_{(g)}$$

Answer:

The equilibrium expression in terms of partial pressures is: $K_p = \frac{P_{CH_4} P_{H_2O}}{P_{CO}\, P_{H_2}^3}$

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

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

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

500 + 273 = 773 K

$$\mathrm{K}_c = \frac{K_P}{(\mathrm{RT})^{-2}} = \frac{0.453}{(0.0821 \times 773)^{-2}} = 1.12\ x\ 10^{-4}$$

EXAMPLE 6: K_P FROM K_C CALCULATION

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

$$CH_3OH_{(g)} \rightleftharpoons CO_{(g)} + 2H_{2(g)}$$

What is K_p at this temperature?

Answer:

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

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

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

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

$\Delta n = 3\text{-}1 = 2$

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

EXAMPLE 7: K_P MANIPULATIONS

Given the equation below with all chemicals in gas phase:

$2SO_2 + O_2 \rightleftharpoons 2SO_3$ $\qquad K_P = 2.5 \times 10^{10}$ at 500°C.

Compute K_P for the following reactions:

a) $SO_2 + 1/2\ O_2 \rightleftharpoons SO_3$

b) $3SO_2 + 3/2\ O_2 \rightleftharpoons 3SO_3$

c) $SO_3 \rightleftharpoons SO_2 + 1/2O_2$

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 = $\boldsymbol{Q_c}$ = the value of the "equilibrium constant expression" under <u>any</u> conditions. This indicates the progress of reaction.

$$CO_{(g)} + Cl_{2\,(g)} \rightleftharpoons COCl_{2\,(g)}$$

$$K_c = \frac{[COCl_2]_{eq}}{[CO]_{eq}[Cl_2]_{eq}} \qquad Q_c = \frac{[COCl_2]}{[CO][Cl_2]}$$

$Q_c > K_c \Rightarrow$ 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 = very large (10^2) **K_c = 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.

$$2ICl_{(g)} \rightleftharpoons Cl_{2\,(g)} + I_{2\,(g)} \qquad K_c = 8.33 \times 10^{-4}$$

0.15 M 0.00125 M 0.0075 M

Answer:

The Q_c expression is:

$$Q_c = \frac{[Cl_2][I_2]}{[ICl]^2}$$

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.