Chapter 14. Chemical Equilibrium

What we will learn:

- Concept equilibrium
- Equilibrium constant
- Writing equilibrium constant expressions
- Chemical kinetics and chemical equilibrium
- Meaning of equilibrium constant
- Factors that affect chemical equilibrium

Chemical equilibrium

A dynamic stage of a chemical reaction where the concentrations of reactants and products are not changing in time

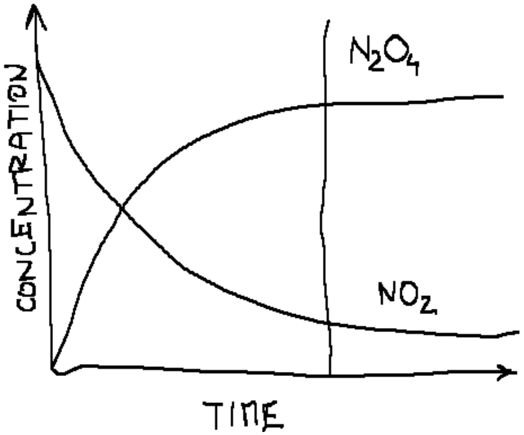
$$A + B \xrightarrow{k_1} C + D \qquad \text{rate} = k_1 [A] [B]$$

$$C + D \xrightarrow{k_{-1}} A + B \qquad \text{rate} = k_{-1} [C] [D]$$

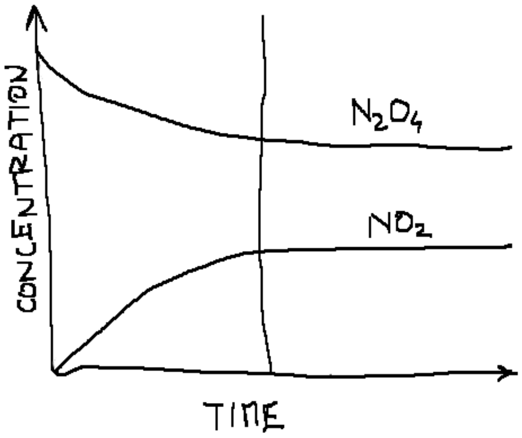
$$A + B \underset{k_1}{\overset{k_{-1}}{\leftrightarrows}} C + D$$

Reaction is proceeding in both directions at the same rate. At the equilibrium there is no net change in concentrations of reactants and products

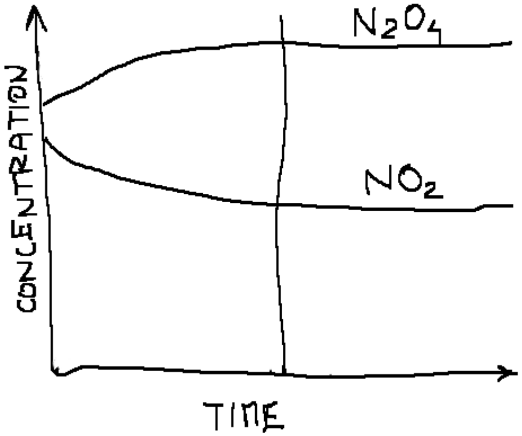
$$N_2O_4 \leftrightarrows 2\,NO_2$$



Initially only NO_2



Initially only N_2O_4



Initially NO_2 and N_2O_4

Equilibrium constant

$$aA + bB \leftrightarrow cC + dD \qquad K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

K = equilibrium constant

[A], [B], [C], [D] = equilibrium concentrations

Magnitude of K

K =~ [products] / [reactants]

$K >> 10$	Have mostly products at equilibrium; “equilibrium lies to the right”; favors products
$K << 0.1$	Have mostly reactants at equilibrium; “ equilibrium lies to the left”; favors reactants
$K = 1$	Roughly equal concentration of reactants and products

Writing equilibrium constant expressions

Homogeneous equilibria (all species are in the same phase)

For gaseous reactions

Since a partial pressure is proportional to a molar concentration, the equilibrium constant can be expressed in terms of partial pressures:

A simple reaction

$$a\,A\,(g) \leftrightarrows b\,B\,(g)$$

$$K_P = \frac{P_B^b}{P_A^a}$$

$K_p = (P_B)^b / (P_A)^a$

$P_A V = n_A RT$

$P_A = n_A RT / V$

$P_B V = n_B RT$

$P_B = n_B RT / V$

$K_P = (n_B RT / V)^b / (n_A RT / V)^a$

$K_P = (n_B / V)^b / (n_A / V)^a \; (RT)^{b-a}$

$[A] = n_A / V$

$[B] = n_B / V$

$K_P = [B]^b / [A]^a \; (RT)^{b-a}$

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

Relationship between K_c and K_p based on ideal gas law

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

Δn = *moles gaseous products - moles gaseous reactants*

or $\Delta n = b - a$

R value = 0.0821 L atm / mole K

Problem

Consider the following reaction

$$N_2\,(g) + O_2\,(g) \leftrightarrows 2\,NO\,(g)$$

If the equilibrium partial pressures of N_2, O_2, and NO are 0.15, atm, 0.33 atm, and 0.05 atm, respectively, at 220 C, what is K_p?

Data

n_{n2} - moles of N_2 = 1	P_{N2} - partial pressure = 0.15 atm
n_{O2} - moles of O_2 = 1	P_{O2} - partial pressure = 0.33 atm
n_{NO} - moles of NO = 2	P_{NO} - partial pressure = 0.05 atm

$$K_p = (P_{NO})^2 / [(P_{N2})^1 (P_{O2})^1]$$

$$= (0.050 \text{ atm})^2 / (0.15\text{atm})(0.33\text{atm})$$

$$= 5.05 \times 10^2$$

Homogenous equilibrium in water

For ionization of acids in water

$$HA\ (aq) + H_2O\ (l) \leftrightarrows A^-\ (aq) + H_3O^+\ (aq)$$

$$K_c{}' = [H_3O^+]\,[A^-] / [HA]\,[H_2O]$$

but in 1 L or 1000 g of water, there are 55.5 mole, therefore the concentration of H_2O = 55.5 mol/L or 55.5 *M* .This quantity is much bigger than concentrations of other compounds therefore it is essentially constant

$$[H_2O] = constant$$

$$K_c = K_c{}'[H_2O] = [H_3O^+]\,[A^-] / [HA]$$

$$K_c = [H_3O^+]\,[A^-] / [HA]$$

Problem

Let us consider the dissociation reaction of acetic acid

$$CH_3COOH(aq) + H_2O(l) \leftrightarrows CH_3COO^-(aq) + H_3O^+(aq)$$

The equilibrium constant is

$$K_c' = [CH3COO^-][H_3O^+] / [CH3COOH][H_2O]$$

Practically, 1 L of water includes 55.5 moles, the concentration of water is 55.5 mol/L. The is a very large amount of concentration (comparing with concentration of the acid) which is not changing during this reaction. Therefore we assume that

$$[H_2O] = constant$$

$$K_c = K_c' [H_2O]$$

$$K_c = [CH3COO^-][H_3O^+] / [CH3COOH]$$

Problem

Let us consider the dissociation reaction of HF

$$HF(aq) \quad + \quad H_2O(l) \quad \leftrightarrows \quad H3O^+(aq) \quad + \quad F^-(aq)$$

The equilibrium constant is

$$K_c' = [F^-][H_3O^+] / [HF][H_2O]$$

$$[H_2O] \quad = \quad constant$$

$$K_c \quad = \quad K_c' [H_2O]$$

$$K_c \quad = [F^-][H_3O^+] / [HF]$$

Problem

Methanol is manufactured according to the reaction

$$CO(g) \quad + \quad 2H_2(g) \quad \leftrightarrows \quad CH_3OH(g)$$

The equilibrium constant (K_c) for the reaction is 10.5 at 220 C. What is the value of K_p at this temperature.

Data

n_{CO} - moles of CO = 1
n_{H2} - moles of H_2 = 2
n_{CH3OH} - moles of CH_3OH = 1
R - constant = 0.0821 L atm / mole K
T - temperature = 220 C = 493 K

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

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

$$= (10.5)(0.0821 \times 493)^{-2} = 6.41 \times 10^{-3}$$

Problem

The equilibrium constant K_p for the decomposition of phosphorus pentachloride (PCl_5) to phosphorus trichloride (PCl_3) and chlorine (Cl_2)

$$PCl_5\,(g) \leftrightarrows PCl_3\,(g) + Cl_2\,(g)$$

is found to be 1.05 at 250 C. The equilibrium partial pressures of PCl_5 and PCl_3 are 0.875 atm and 0.463 atm, respectively. What is the equilibrium partial pressure of Cl_2 at 250 C.

Data

P_{PCL5} - partial pressure = 0.875 atm
P_{PCL3} - partial pressure = 0.463 atm
K_p - equilibrium constant = 1.05

$$K_p = P_{PCL3}\, P_{Cl2} / P_{PCL5}$$

$$1.05 = (0.463)P_{Cl2} / (0.875)$$

$$P_{Cl2} = (1.05)\,(0.875) / (0.463) = 1.98 \text{ atm}$$

Heterogeneous equilibria

Some reactants or products are in different phases

Concentrations of pure liquids and solids are effectively constants, therefore they do not appear in K expressions

Example

Let us consider the reaction

$$CaO(s) + SO_2(g) \leftrightarrows CaSO_3(s)$$

the equilibrium constant

$$K_c' = [CaSO_3] / [CaO] [SO_2]$$

The concentrations of solid compounds are practically constant

$$[CaO] = constant$$

$$[CaSO_3] = constant$$

$$K_c = K_c' [CaO] / [CaSO_3]$$

$$K_c = 1 / [SO_2]$$

The value of K_c does not depend on how much $CaSO_3$ and CaO are present at the equilibrium, therefore

$$K_c = 1 / [SO_2]$$

The equilibrium constant depends practically only on the concentration of the gas substance

Example

Heating calcium carbonate has a particular equilibrium constant

$$CaCO_3(s) \quad \leftrightarrows \quad CaO(s) + CO_2(g)$$

$$K_c' = [CaO][CO_2] / [CaCO_3]$$

The concentrations of solid compounds ($CaCO_3$ and CaO) are practically constant

$$[CaO] = constant$$

$$[CaCO_3] = constant$$

$$K_c = K_c'[CaO] / [CaCO_3]$$

$$K_c = [CO_2]$$

The value of K_c does not depend on how much $CaCO_3$ and CaO are present at the equilibrium, and the equilibrium constant depends practically only on the concentration CO_2

Problem

Consider the following heterogenous equilibrium

$$CaCO_3(s) \leftrightarrows CaO(s) + CO_2(g)$$

At 800 C the pressure of CO_2 is 0.236 atm. Calculate K_p and K_c for the reation

Data

P_{CO2} - partial pressure = 0.236 atm
T - temperature = 800 C = 1073 K
R - constant = 0.0821 L atm / mole K

$$K_p = K_c(RT)^{\Delta n} \qquad \Delta n = 1$$

$$K_p = P_{CO2} = 0.236$$

$$0.236 = K_c(0.0821)\ (1073)$$

$$K_c = 2.68 \times 10^{-3}$$

Problem

Consider the following equilibrium at 295 K:

$$NH_4HS\ (s) \quad \leftrightarrows \quad NH_3\ (g) + H_2S\ (g)$$

The partial pressure of each gas is 0.265 atm. Calculate K_p and K_c for the reaction

Data

P_{NH3} - partial pressure = 0.265 atm
P_{H2S} - partial pressure = 0.265 atm
T - temperature = 295 C = 568 K
R - constant = 0.0821 L atm / mole K

$$K_p \quad = \quad K_c(RT)^{\Delta n} \qquad \Delta n = 2$$

$$K_p \quad = P_{NH3}\ P_{H2S} = (0.265\ )\ (\ 0.265) = 0.0702$$

$$0.0702 = K_c\ [\ (0.0821)\ (568)\ ]\ ^2$$

$$K_c \quad = \quad (0.0702)\ /\ (2174.61) \quad = 3.2 \times 10^{-6}$$

Multiple equilibria

Two chemical reactions where products of the first reaction are reactants of the second one

$$A + B \leftrightarrows C + D \qquad K'_c$$
$$C + D \leftrightarrows E + F \qquad K''_c$$

$$A + B \leftrightarrows E + F \qquad K_c$$

First reaction

$$K_c' = [C]\,[D] / [A]\,[B]$$

Seond reaction

$$K_c'' = [E]\,[F] / [C]\,[D]$$

$$K_c = [E]\,[F] / [A]\,[B]$$

$$K_c' K_c'' = [C]\,[D] / [A]\,[B] \;\; \mathrm{x} \;\; [E]\,[F] / [C]\,[D] = K_c$$

If a reaction can be expressed as sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions

$$K_c = K'_c\, K''_c$$

Example

The equilibrium constants for carbonic acid (H_2CO_3) dissociation at 25 C

$$H_2CO_3(aq) \leftrightarrows H^+(aq) + HCO_3^-(aq)$$

$$K_c' = [H^+]\,[HCO_3^-]\,/\,[H_2CO_3] = 4.2 \times 10^{-7}$$

$$HCO_3^-(aq) \leftrightarrows H^+(aq) + CO_3^{2-}(aq)$$

$$K_c'' = [H^+]\,[CO_3^{2-}]\,/\,[HCO_3^-] = 4.8 \times 10^{-11}$$

The overall reaction is the sum of these two reactions

$$H_2CO_3(aq) \leftrightarrows 2H^+(aq) + CO_3^{2-}(aq)$$

and the corresponding equilibrium constant is given by

$$K_c = [H^+]^2 [CO_3^{2-}] / [H_2CO_3]$$

and the value is

$$K_c = K_c' K_c''$$

$$K_c = (4.2 \times 10^{-7}) (4.8 \times 10^{-11}) = 2.0 \times 10^{-17}$$

Form of K and the equilibrium equation

Two rules of writing equilibrium constants

1. When the equation for a reversible reaction is written in the opposite direction, the equilibrium constant becomes the reciprocal of the original equilibrium constant

$$N_2O_4\,(g) \quad \leftrightarrows \quad 2\,NO_2\,(g)$$

$$K_c \quad = \quad [NO_2]^2 / [N_2O_4] \quad = \quad 4.63 \times 10^{-3}$$

However the reverse reaction

$$2\,NO_2\,(g) \quad \leftrightarrows \quad N_2O_4\,(g)$$

$$K_c' \quad = \quad [N_2O_4] / [NO_2]^2 \quad = \quad 216$$

$$K_c \quad = \quad 1 / K_c'$$

2. The value of K depends on how the equilibrium equation is balanced

$1/2\ N_2O_4\ (g) \leftrightarrows NO_2\ (g)$

$K_c = [NO_2] / [N_2O_4]^{1/2} = 0.068$

$N_2O_4\ (g) \leftrightarrows 2\ NO_2\ (g)$

$K_c' = [NO_2]^2 / [N_2O_4] = 4.63 \times 10^{-3}$

and

$K_c' = (K_c)^2$

If we multiply the first reaction by 2 then the equilibrium constant will be $(K_c)^2$

Problem

Write the equilibrium constant (K_c) for each of the following reactions and show how they are related to each other:

a) $N_2\ (g) + 3H_2\ (g) \leftrightarrows 2\ NH_3\ (g)$

b) $1/2\ N_2\ (g) + 3/2 H_2(g) \leftrightarrows NH_3\ (g)$

c) $1/3\ N_2\ (g) + H_2(g) \leftrightarrows 2/3\ NH_3\ (g)$

$$K_a = [NH_3]^2 / [N_2]\,[H_2]^3$$

$$K_b = [NH_3] / [N_2]^{1/2}\,[H_2]^{3/2}$$

$$K_c = [NH_3]^{2/3} / [N_2]^{1/3}\,[H_2]$$

$$K_a = K_b^{\ 2}$$

$$K_a = K_c^{\ 3}$$

Problem

Write the equilibrium constant (K_c) for each of the following reactions and show how they are related to each other:

$$3\,O_2\,(g) \leftrightarrows 2\,O_3\,(g)$$

$$K_c = [O_3]^2 / [O_2]^3$$

$$O_2\,(g) \leftrightarrows 2/3\,O_3\,(g)$$

$$K_c' = [O_3]^{2/3} / [O_2]$$

The final relation is

$$K_c = (K_c')^3$$

Summary
Writing equilibrium constant expressions

- Concentrations of products and reactants are in mol/L; for gases either mol/L or pressure in atm may be used; K_c is related to K_p
- Concentrations of pure solids and liquids are not used
- The equilibrium constant does not have units
- The equilibrium constant is specified for a balanced equation at a particular temperature
- The equilibrium constant of a reverse reaction is 1/ K
- The equilibrium constant of a reaction which is multiplied by a coefficient “n” is $(K)^n$
- For overall processes of more than one step, the equilibrium constant of the overall reaction is a product of K_s for the individual steps

Relationship between chemical kinetics and equilibrium

A. One step reversible reaction

$$A + 2B \quad \leftrightarrows \quad AB_2$$

The forward reaction rate is given

$$rate(f) \quad = \quad k_{forward} [A] [B]^2$$

The reverse reaction rate is given

$$rate(r) \quad = \quad k_{reverse} [AB_2]$$

At the equilibrium two reaction rates are the same

$$rate(f) \quad = \quad rate(r)$$

$$k_{forward} [A] [B]^2 = k_{reverse} [AB_2]$$

$$K_c \quad = \quad k_{forward} / k_{reverse} = \quad [AB_2] / [A] [B]^2$$

B. Two step reversible reaction

$$
\begin{array}{llllll}
\text{Step 1} & & & 2B & \underset{k'_{forward}}{\overset{k'_{reverse}}{\leftrightarrows}} & B_2 \\
\text{Step 2} & A & + & B_2 & \underset{k''_{forward}}{\overset{k''_{reverse}}{\leftrightarrows}} & AB_2 \\
\hline
\text{Overall} & A & + & 2B & \leftrightarrows & AB_2
\end{array}
$$

The expressions for the equilibrium constants

$$K' = [B_2] / [B]^2 = k'_{forward} / k'_{reverse}$$

$$K'' = [AB_2] / [A]\,[B_2] = k''_{forward} / k''_{reverse}$$

$$K'K'' = ([B_2] / [B]^2) ([AB_2] / [A][B_2])$$

$$= [AB_2] / [A] [B]^2$$

$$K'K'' = (k'_{forward} / k'_{reverse}) (k''_{forward} / k''_{reverse})$$

$$= (k'_{forward} \, k''_{forward}) / (k'_{reverse} \, k''_{reverse})$$

Generally

$$aA + bB \leftrightarrows cC + dD$$

$$K_c = [C]^c [D]^d / [A]^a [B]^b$$

The requilibrium constant of a reaction can be expressed as a ratio of the rate constant of the forward and reverse reactions. Because a rate constant is a constant and depends on temperature, therefore the equilibrium constant is also a constant and its value also changes with temperature

Predicting the direction of a reaction

Let us consider a reaction of hydrogen iodide formation

$$H_2\,(g) \quad + \quad I_2\,(g) \quad \leftrightarrows \quad 2HI\,(g)$$

The equilibrium constant of this reaction at 430 C is 54.3. Let us assume that we have an experiment where we place 0.243 mole of H_2, 0.146 mole of I_2 and 1.98 mole of HI in a 1 L container at 430 C. Let us calculate the ratio of the initial concentrations Q_c

$$Q_c = [HI]_0^2 / [H_2]_0\,[I_2]_0$$

$$= (1.98\,)^2 / (0.243\,)\,(\,0.146)$$

$$= 111$$

$$Q_c > K_c$$

The system is not at the equilibrium because Q_c is different than K_c.

To predict the direction in which the net reaction will proceed we compare the Q_c value with K_c.

- $Q_c > K_c$ too many products; the reaction must convert some prodcuts to reactants; the reaction proceeds from right to left (←)

- $Q_c < K_c$ too many reactants; the reaction must convert some reactants to products; the reaction proceeds from left to right (→)

- $Q_c = K_c$ systems is at equilibrium (⇆)

Reaction quotient (Q_c)

Consider a reaction which is not at the equilibrium

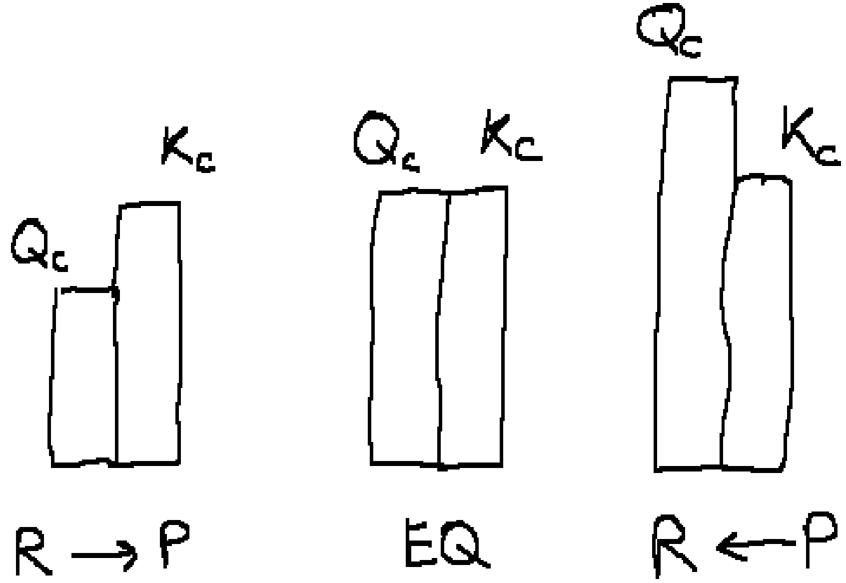
$$aA + bB \leftrightarrows cC + dD$$

Let us calculate a reaction quotient (Q_c)

$$Q_c = [C]^c [D]^d / [A]^a [B]^b$$

[A], [B], [C], [D] non equilibrium concentrations

by substituting the initial concentrations into the equilibrium constant expression. By comparing Q_c witk K_c we can determine the direction in which the net reaction will proceed



- Q > K too many products, therefore the reaction converts some products to reactants; the reaction proceeds from right to left (←)
- Q < K too many reactants, therefore the reaction converts some reactants to products; the reaction proceeds from left to right (→)
- Q = K the reacting system is at equilibrium (⇆)

Problem

The initial concentrations of the reaction below are 0.249 mol N_2, 3.21 x 10^{-2} mol H_2, and 6.42 x 10^{-4} mol NH_3 in a 3.5 L container at 375 C.

$$N_2\,(g) \quad + \quad 3\,H_2\,(g) \quad \leftrightarrows \quad 2\,NH_3\,(g)$$

The equilibrium constant K_c of this reaction is 1.2 at this temperature. Predict in which way the reaction will proceed to reach the equilibrium

Data

$[N_2]_0$ = 0.249 mol / 3.5 L = 0.0711 *M*
$[H_2]_0$ = 3.21 x 10^{-2} mol / 3.5 L = 9.17 x 10^{-3} *M*
$[NH_3]_0$ = 6.24 x 10^{-4} mol / 3.5 L = 1.83 x 10^{-4} *M*
K_c = 1.2

$$Q_c = [NH_3]_0^2 / [N_2]_0\,[H_2]_0^3 = 0.611$$

$$Q_c < K_c$$

The reaction will proceed to increase the concentration of NH_3 and decrease the concentrations of N_2 and H_2 (from left to right)

Problem

The equilibrium constant K_c for the formation of nitrosyl chloride from nitric oxide and molecular chlorine

$$2\ NO\ (g) \quad + \quad Cl_2\ (g) \quad \leftrightarrows \quad 2\ NOCl\ (g)$$

is 6.5×10^4 at 35 C. The initial concentrations in a 2 L container are: 2.0×10^{-2} mole of NO, 8.3×10^{-3} mole of Cl_2, and 6.8 mole of NOCl. In which direction the reaction will proceed

Data

$[NO]_0 = 2.0 \times 10^{-2}\ \text{mol} / 2\ \text{L} = 0.01\ M$

$[Cl_2]_0 = 8.3 \times 10^{-3}\ \text{mol} / 2\ \text{L} = 0.0083\ M$

$[NOCl]_0 = 6.8\ \text{mol} / 2\ \text{L} = 3.4\ M$

$K_c = 6.5 \times 10^4$

$$Q_c = [NOCl]_0^2 / [NO]_0^2\ [Cl_2]_0 = (3.4)^2 / (0.01)^2\ (0.0083)$$

$$= 13.9 \times 10^6$$

$Q_c > K_c$ (the reaction will proceed from right to left)

Calculating equilibrium concentrations

Given K_c and one or more initial concentrations, determine the equilibrium concentrations

General Method:

- Set up a “concentration table” based on an unknown “x” - usually one of the equilibrium concentrations or a change in a concentration
- Express all equilibrium concentrations in terms of “x” and initial values. Insert these equilibrium values (in terms of “x”) into the proper equation for K, and
- Solve directly for “x” or, make a chemically reasonable assumption

Problem

Let us consider the reaction in which cis-stilbene is in equilibrium with trans-stilbene in a nonpolar solvent:

cis-stilbene $\leftrightarrows$ *trans-stilbene*

The equilibrium constant K_c for this system is 24 at 200 C. Assume that initially only cis-stilbene is present at a concentration 0.850 mol/L. According to the reaction, from 1 mole of cis-stilbene the reaction forms 1 mole of trans-stilbene

	cis-stilbene $\leftrightarrows$	*trans-stilbene*
Initial (*M*)	0.850	0
Change (*M*)	-x	+x
Equilibrium (*M*)	(0.850 - x)	x

A negative sign indicates a decrease of the concentration, and a positive sign indicates an incease of the concentration

K_c = *[trans-stilbene] / [cis-stilbene]*

24 = (x) / (0.850 - x)

x = 0.816 *M*

[cis-stilbene] = (0.850 - 0.816) *M* = 0.034 *M*

[trans-stilbene] = 0.816 *M*

Problem

At 430 C the equilibrium constant (K_c) for the reaction

$$H_2\,(g) \quad + \quad I_2(g) \quad \leftrightarrows \quad 2\,HI\,(g)$$

is 54.3 at this temperature. If the initial concentrations are $[H_2] = 0.5\ M$ and $[I_2] = 0.5\ M$, calculate the concentrations of these species at equilibrium

Data

	$H_2\,(g)$	+	$I_2(g)$	$\leftrightarrows$	$2\,HI\,(g)$
Initial (*M*)	0.5		0.5		0.0
Change (*M*)	-x		-x		+2x
Equilibrium (*M*)	(0.5 - x)		(0.5 - x)		2x

At equilibrium

$$K_c = [HI]^2 / [H_2][I_2]$$

$$= (2x)^2 / (0.5 - x)(0.5 - x)$$

$$(K_c)^{1/2} = (2x) / (0.5 - x)$$

$$7.37(0.5 - x) = 2x$$

$$3.685 - 7.37x = 2x$$

$$x = 3.685/(7.37 + 2)$$

$$x = 0.393\ M$$

$$[H_2] = (0.5 - 0.393)M = 0.107\ M$$

$$[I_2] = (0.5 - 0.393)M = 0.107\ M$$

$$[HI] = 2(0.393)\ M = 0.786\ M$$

Problem

At 1280 C the equilibrium constant (K_c) for the reaction

$$Br_2\,(g) \quad \leftrightarrows \quad 2\,Br\,(g)$$

is 1.1×10^{-3}. If the initial concentrations are $[Br_2] = 0.2\ M$ and $[Br] = 0\ M$, calculate the concentrations of these species at equilibrium

Data

	$Br_2\,(g)$	$\leftrightarrows$	$2\,Br\,(g)$
Initial (*M*)	0.2		0
Change (*M*)	-x		+2x
Equilibrium (*M*)	(0.2 - x)		2x

$K_c = [Br]^2 / [Br_2]$

$1.1 \times 10^{-3} = (2x)^2 / (0.2 - x)$

$0.0011\,(0.2 - x) = (2x)^2$

$0.00022 - 0.0011x = 4x^2$

$4x^2 + 0.0011x - 0.00022 = 0$

$$\boxed{\begin{array}{ll} ax^2 + bx + c = 0 & x_1 = (-b - \Delta^{1/2}) / (2a) \\ \Delta = b^2 - 4ac & x_2 = (-b + \Delta^{1/2}) / (2a) \end{array}}$$

a = 4

b = 0.0011

c = -0.00022

$\Delta = 0.00352$

$x_1 = (-b - \Delta^{1/2}) / (2a)$

$x_2 = (-b + \Delta^{1/2}) / (2a)$

$x_1 = -0.00755$ (a negative concentration is not accepted)

$x_2 = +0.00727$

At equilibrium we have

$[Br_2] = (0.2 - 0.00727) = 0.1927$

$[Br] = 2 (0.00727) = 0.0145$

Factors that Affect Chemical Equilibrium

Le Châtelier's Principle

When a system at equilibrium is subjected to an external stress, the system will shift in a direction to counteract (to eliminate) the stress and achieve a new equilibrium state.

Common factors ("external stresses") to consider:

- Addition or removal of some reactant or product (change in concentration)
- Change in volume (pressure)
- Change in temperature
- Effect of a catalyst

Example of changing concentration

At 720 C the equilibrium constant for the reaction

$$N_2\,(g) \quad + \quad 3\,H_2\,(g) \;\leftrightarrows\; 2\,NH_3\,(g)$$

is 2.37×10^{-3} . The equilibrium concentrations are $[N_2] = 0.683\ M$, $[H_2] = 8.8\ M$ and $[NH_3] = 1.05\ M$. Some NH_3 is added to the mixture so its concentration is increased to 3.65 *M*. (a) Predict the shift in the direction of the reaction based on Le Châtelier's principle. (b) Predict the shift in the direction of the reaction based on the reaction quotient Q_c.

a) The stress is applied to the system by increasing the concentration of NH_3. To eliminate this stress, the equilibrium is shifted to form N_2 and H_2

$$N_2\,(g) \quad + \quad 3\,H_2\,(g) \;\leftarrow\; 2\,NH_3\,(g)$$

b) When NH_3 is added the system is no longer at the equilibrium. Therefore

$$Q_c \quad = \quad [NH_3]_0^2 \,/\, [N_2]_0\,[H_2]_0^3$$

$Q_c = (3.65)^2 / (0.683)(8.8)^3$

$= 2.86 \times 10^{-2}$

Because $Q_c > K_c$ then the shift of the equilibrium is from right to left

$N_2(g) + 3H_2(g) \leftarrow 2NH_3(g)$

Example of changing volume (pressure)

Let us consider a reaction in the gas phase

$$N_2O_4\,(g) \leftrightarrows 2\,NO_2\,(g)$$

What happens if we increase a pressure (by changing a volume of the container) at constant temperature. Because the volume decreases, the concentration (n/V) of both NO_2 and N_2O_4 increases.

The system is not longer at the equilibrium therefore we use the reaction quotient which is

$$Q_c = [NO_2]^2_0 / [N_2O_4]_0$$

Note that in the numerator the concentration of NO_2 is squared, therefore the bigger pressure increases more in the numerator than in the denominator and

$$Q_c > K_c$$

and the equilibrium is shift to the left until $Q_c = K_c$

Example of changing temperature

Let us consider a reaction in the gas phase

$$N_2O_4\,(g) \leftrightarrows 2\,NO_2\,(g)$$

The forward reaction is endothermic (absorbs heat, $\Delta H^0 > 0$)

$$\text{heat} + N_2O_4\,(g) \rightarrow 2\,NO_2\,(g) \qquad \Delta H^0 = 58\ \text{kJ/mol}$$

The reverse reaction is exothermic (releases heat, $\Delta H^0 < 0$)

$$2\,NO_2\,(g) \rightarrow N_2O_4\,(g) + heat \qquad \Delta H^0 = -58\ \text{kJ/mol}$$

At equilibrium the heat effect is zero. If we increase the temperature (increasing the heat in the reaction) the system shifts to reduce the heat effect. Therefore at bigger temperature the system shifts the equilibrium by decreasing the concentration of N_2O_4 and increasing the concentration of NO_2

Problem

Consider a series of possible changes to the following equilibrium reaction:

$$PCl_3\,(g) + Cl_2\,(g) \leftrightarrows PCl_5\,(g) + 88\text{ kJ}$$

this reaction is exothermic: $\Delta H° = -88$ kJ

What happens to [Cl_2] if

(a) Some PCl_3 is added

- The “stress” is more PCl_3
- System needs to remove PCl_3
- Thus, reaction shifts forward and [Cl_2] decreases

(b) Some PCl_5 is added

- The “stress” is more PCl_5
- System needs to remove PCl_5
- Thus, reaction shifts in reverse and $[Cl_2]$ increases

(c) The temperature is increased (this requires knowing a ΔH° value)

- The “stress” is added heat
- The system needs to remove heat
- Since the reaction is exothermic, heat is a “product”
- Adding a “product” causes reaction to shift in reverse
- Thus, $[Cl_2]$ increases

(d) The volume is increased (or pressure is decreased)

- The "stress" is more space for gas molecules
- System tries to produce more gas to fill the space
- Reaction shifts in direction of more moles of gas
- In this case, it shifts in reverse
- (2 mol gaseous reactants vs. 1 mol gaseous product)
- Thus, [Cl_2] increases

(e) A catalyst is added

Addition of a catalyst does not affect the position of equilibrium. There is no change in any of the equilibrium concentrations. The catalyst is changing only the rate (speed) of the reaction