The Equilibrium Constant and the Mass Law Expression

Consider: $1H_2(g) + 1I_2(g) \rightleftharpoons 2HI(g)$ T = 445°C and V = 0.80 Liters

Expt. #	Initial moles ($x10^{-3}$)			Equil. moles ($x10^{-3}$)			Equil. conc. ($x10^{-3}$)M		
	H_2	I_2	HI	H_2	I_2	HI	H_2	I_2	HI
1	1.50	1.50	—	0.330	0.330	2.34	0.412	0.412	2.92
2	—	—	1.50	0.165	0.165	1.17	0.206	0.206	1.46
3	1.50	1.50	1.50	0.495	0.495	3.51	0.619	0.619	4.39

In search of a constant ratio at equilibrium:

Expt. # Try: $\dfrac{[HI]}{[H_2][I_2]}$

1 $\dfrac{(2.92x10^{-3})}{(0.412x10^{-3})^2} = 1.72x10^4$

2 $\dfrac{(1.46x10^{-3})}{(0.206x10^{-3})^2} = 3.44x10^4$

3 $\dfrac{(4.39x10^{-3})}{(0.619x10^{-3})^2} = 1.15x10^4$

Expt. # Try: $\dfrac{2\,[HI]}{[H_2][I_2]}$

1 $\dfrac{2\,(2.92x10^{-3})}{(0.412x10^{-3})^2} = 3.44x10^4$

2 $\dfrac{2\,(1.46x10^{-3})}{(0.206x10^{-3})^2} = 6.88x10^4$

3 $\dfrac{2\,(4.39x10^{-3})}{(0.619x10^{-3})^2} = 2.30x10^4$

Expt. # Try: $\dfrac{[HI]^2}{[H_2][I_2]}$

1 $\dfrac{(2.92x10^{-3})^2}{(0.412x10^{-3})^2} = 50.2$

2 $\dfrac{(1.46x10^{-3})^2}{(0.206x10^{-3})^2} = 50.2$

3 $\dfrac{(4.39x10^{-3})^2}{(0.619x10^{-3})^2} = 50.3$

K_p/K_c Relationship

Consider: $aA + bB \rightleftharpoons cC + dD$ (all species gaseous)

$$K_p = \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b} \quad \text{and} \quad K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

But: $PV = nRT$ $\quad [X] = \dfrac{n_x}{V} = \dfrac{p_x}{RT}$ $\quad p_x = [X]RT$

Therefore: $$K_p = \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b} = \frac{[C]^c (RT)^c [D]^d (RT)^d}{[A]^a (RT)^a [B]^b (RT)^b}$$

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

where $\Delta n_g = \Sigma$ mols product gas - Σ mols reactant gas

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

Hess' Law for K_{eq}

Find K_{eq} for: $1E + 0.5D \rightleftharpoons 0.5A$

Given:	Equ. 1)	$1B \rightleftharpoons 1A$	$K_1 = 2x10^3$
	Equ. 2)	$1B \rightleftharpoons 1C$	$K_2 = 4x10^{-2}$
	Equ. 3)	$1C \rightleftharpoons 1D + 2E$	$K_3 = 3x10^{-1}$

Questions: What must be done with the given equations to obtain the desired overall equation?

What must be done with the given equilibrium constants to obtain the desired K_{eq}?

Hess' Law for K_{eq}

Find K_{eq} for: $1E + 0.5D \rightleftharpoons 0.5A$

Given: Equ. 1)	$1B \rightleftharpoons 1A$	$K_1 = 2x10^3$
Equ. 2)	$1B \rightleftharpoons 1C$	$K_2 = 4x10^{-2}$
Equ. 3)	$1C \rightleftharpoons 1D + 2E$	$K_3 = 3x10^{-1}$

Strategy:

Reverse Equ. 3) and divide by 2: $1E + 0.5D \rightleftharpoons 0.5C$ $\quad K_3' = \dfrac{1}{\sqrt{3x10^{-1}}}$

Reverse Equ. 2) and divide by 2: $0.5C \rightleftharpoons 0.5B$ $\quad K_2' = \dfrac{1}{\sqrt{4x10^{-2}}}$

Divide Equ. 1) by 2: $0.5B \rightleftharpoons 0.5A$ $\quad K_1' = \sqrt{2x10^3}$

Add modified Equations 3), 2), and 1) to obtain the desired overall equation, but **multiply** the modified K_{eq} values for Equations 3), 2), and 1) to obtain the desired K_{eq} for the overall equation.

K_{eq} for $1E + 0.5D \rightleftharpoons 0.5A$ equals $K_3'K_2'K_1' = \dfrac{\sqrt{2x10^3}}{\sqrt{3x10^{-1}}\sqrt{4x10^{-2}}}$

Illustrated Mass Law Problem #1

Consider the following equilibrium:

$SbCl_5(g) \rightleftharpoons SbCl_3(g) + Cl_2(g)$ T = 247°C and V = 2.5 Liters

Initially present: 0.280 mols $SbCl_3(g)$, 0.160 mols $Cl_2(g)$, and no $SbCl_5(g)$

At equilibrium: 0.116 mols $SbCl_5(g)$ have formed

Based on the above data, determine K_p for the above reaction.

Question: What strategies should one employ to address the problem being posed?

Illustrated Mass Law Problem #1 continued

Consider the following equilibrium:

$SbCl_5(g) \rightleftharpoons SbCl_3(g) + Cl_2(g)$ T = 247°C and V = 2.5 Liters

Initially present: 0.280 mols $SbCl_3(g)$, 0.160 mols $Cl_2(g)$, and no $SbCl_5(g)$

At equilibrium: 0.116 mols $SbCl_5(g)$ have formed

Based on the above data, determine K_p for the above reaction.

Strategies to apply:

Note that although the goal of the question is to find the numerical value of K_p, based on given mole and volume data for the species in the equilibrium reaction, it would be advantageous to determine K_c instead.

Also note that in order to write the mass law expression for Kc, the equilibrium concentrations of all species in the equilibrium equation must be known.

Questions: Are the equilibrium concentrations for all the species in the equilibrium reaction known at this point? If not, which must still be determined? How?

Illustrated Mass Law Problem #1 continued

Consider the following equilibrium:

$$SbCl_5(g) \rightleftharpoons SbCl_3(g) + Cl_2(g) \qquad T = 247°C \text{ and } V = 2.5 \text{ Liters}$$

Initially present: 0.280 mols $SbCl_3(g)$, 0.160 mols $Cl_2(g)$, and no $SbCl_5(g)$

At equilibrium: 0.116 mols $SbCl_5(g)$ have formed

Based on the above data, determine K_p for the above reaction.

Approach to take:

The problem stipulates that 0.116 mols $SbCl_5(g)$ have formed at equilibrium. Therefore, the equilibrium concentration of $SbCl_5(g)$ is:

$$[SbCl_5] = \frac{(0 + 0.116)\text{mols}}{2.5 \text{ Liters}} = 0.0464\text{M}$$

To determine the equilibrium concentrations of the reaction products, utilize the 1:1 mole ratio that exists between reactant and products in the balanced equilibrium equation.
Therefore, the equilibrium concentration of $SbCl_3(g)$ is:

$$[SbCl_3] = \frac{(0.280\text{-}0.116)\text{mols}}{2.5 \text{ Liters}} = 0.0656\text{M}$$

Likewise, the equilibrium concentration of $Cl_2(g)$ is:

$$[Cl_2] = \frac{(0.160\text{-}0.116)\text{mols}}{2.5 \text{ Liters}} = 0.0176\text{M}$$

Illustrated Mass Law Problem #1 concluded

Consider the following equilibrium:

$$SbCl_5(g) \rightleftharpoons SbCl_3(g) + Cl_2(g) \qquad T = 247°C \text{ and } V = 2.5 \text{ Liters}$$

Initially present: 0.280 mols $SbCl_3(g)$, 0.160 mols $Cl_2(g)$, and no $SbCl_5(g)$

At equilibrium: 0.116 mols $SbCl_5(g)$ have formed

Based on the above data, determine K_p for the above reaction.

Solution to the problem:

$$K_c = \frac{[SbCl_3]^1[Cl_2]^1}{[SbCl_5]^1} = \frac{(0.0656)(0.0176)}{(0.0464)} = 0.0249$$

But: $K_p = K_c(RT)^{\Delta n_g} = 0.0249[(0.082)(247+273)]^{2-1}$

$$K_p = 1.06$$

Illustrated Mass Law Problem #2

Consider the following equilibrium:

$2A_3B(g) \rightleftharpoons 3A_2(g) + 1B_2(g)$ T = 27°C and V = 3.0 Liters

Initially present: 0.300 mols $A_3B(g)$, 0.200 mols $A_2(g)$, and 0.150 mols $B_2(g)$

At equilibrium: 0.100 mols $B_2(g)$ are present

Based on the above data, determine K_c and K_p for the above reaction.

Question: Which K_{eq} should be determined first?

Illustrated Mass Law Problem #2 continued

Consider the following equilibrium:

$2A_3B(g) \rightleftharpoons 3A_2(g) + 1B_2(g)$ T = 27°C and V = 3.0 Liters

Initially present: 0.300 mols $A_3B(g)$, 0.200 mols $A_2(g)$, and 0.150 mols $B_2(g)$

At equilibrium: 0.100 mols $B_2(g)$ are present

Based on the above data, determine K_c and K_p for the above reaction.

Strategy to apply to the problem:

Determine K_c first. Why?

Write the mass law expression for K_c taking careful note of the coefficients in the balanced equilibrium equation.

Given that all three species are present initially, how does one assess the change in the number of moles of each for the system to achieve equilibrium?

Hint: Compare the moles of $B_2(g)$ present initially and at equilibrium.

Solution to Problem #2:

$2A_3B(g) \rightleftharpoons 3A_2(g) + 1B_2(g)$ T = 27°C and V = 3.0 Liters

Initially present: 0.300 mols $A_3B(g)$, 0.200 mols $A_2(g)$, and 0.150 mols $B_2(g)$

At equilibrium: 0.100 mols $B_2(g)$ are present

Write the mass law expression for K_c: $K_c = \dfrac{[A_2]^3[B_2]^1}{[A_3B]^2}$

Then determine the equilibrium concentrations of the reactant and products. Based on the given data, the concentration of $B_2(g)$ is:

$$[B_2] = \frac{0.100 \text{ mols}}{3.0 \text{ Liters}} = 0.033\text{M}$$

Note that 0.050 mols, (0.150-0.100)mols, of $B_2(g)$ have been consumed. From the balanced equation, for every mole of $B_2(g)$ that reacts, **three times** that number of moles of $A_2(g)$ react. Therefore, 0.150 moles of $A_2(g)$, of the 0.200 moles initially present, are consumed as well leading to an equilibrium concentration for $A_2(g)$ of:

$$[A_2] = \frac{(0.200\text{-}0.150)\text{mols}}{3.0 \text{ Liters}} = 0.017\text{M}$$

Likewise, for every mole of $B_2(g)$ that reacts, **twice** that number of moles of $A_3B(g)$ are formed. Therefore, the equilibrium reaction creates 2x0.050moles, 0.100 mols, of $A_3B(g)$ in addition to the 0.300 moles initially present leading to an equilibrium concentration for $A_3B(g)$ of:

$$[A_3B] = \frac{(0.300+0.100)\text{mols}}{3.0 \text{ Liters}} = 0.133\text{M}$$

Solve for K_c: $K_c = \dfrac{[A_2]^3[B_2]^1}{[A_3B]^2} = \dfrac{(0.017)^3(0.033)^1}{(0.133)^2} = 9.1\text{x}10^{-6}$

Solve for K_p: $K_p = K_c(RT)^{\Delta n_g} = (9.1\text{x}10^{-6})[(0.082)(27+273)]^{4-2} = \mathbf{5.5x10^{-3}}$

Illustrated Mass Law Problem #3

Consider the following equilibrium reaction at a given temperature:

$$1H_2(g) + 1CO_2(g) \rightleftharpoons 1CO(g) + 1H_2O(g) \qquad K_c = 0.771$$

Given: One mole of $H_2(g)$ and one mole of $CO_2(g)$ are introduced into an empty 5.0 liter vessel.

Problem: Find the molar concentration of each species when equilibrium is achieved.

Illustrated Mass Law Problem #3 concluded

Consider the following equilibrium reaction at a given temperature:

$$1H_2(g) + 1CO_2(g) \rightleftharpoons 1CO(g) + 1H_2O(g) \qquad K_c = 0.771$$

Given: One mole of $H_2(g)$ and one mole of $CO_2(g)$ are introduced into an empty 5.0 liter vessel.

Solution:

Write the mass law expression for K_c: $$0.771 = \frac{[CO]^1[H_2O]^1}{[H_2]^1[CO_2]^1}$$

To establish equilibrium, an unknown number of moles of product must form. Because the mole ratio between all species in the balanced overall equation is 1:1, the moles of each product species obtained will be the same and will also be identical to the number of moles of each reactant that is consumed, x. K_c can now be written as follows:

$$0.771 = \frac{[\frac{0+x}{5}][\frac{0+x}{5}]}{[\frac{1-x}{5}][\frac{1-x}{5}]} = \frac{x^2}{(1-x)^2}; \quad \sqrt{0.771} = \frac{x}{1-x}; \quad x = 0.47 \text{ mols}$$

At equilibrium: $[CO] = [H_2O] = 0.094M$; $[H_2] = [CO_2] = 0.11M$

Illustrated Mass Law Problem #4

Consider the following equilibrium reaction at a given temperature:

$$2NaHCO_3(s) \rightleftharpoons 1Na_2CO_3(s) + 1CO_2(g) + 1H_2O(g) \quad K_p = 0.25$$

An unspecified amount of $NaHCO_3(s)$ is placed in an empty vessel at a given temperature and is allowed to decompose.

Find $\mathbf{P_{total}}$ when equilibrium is achieved.

Hint: What species will appear in the mass law expression?

Illustrated Mass Law Problem #4 concluded

Consider the following equilibrium reaction at a given temperature:

$$2NaHCO_3(s) \rightleftharpoons 1Na_2CO_3(s) + 1CO_2(g) + 1H_2O(g) \quad K_p = 0.25$$

An unspecified amount of $NaHCO_3(s)$ is placed in an empty vessel at a given temperature and is allowed to decompose.

Find P_{total} when equilibrium is achieved.

Solution:

$$K_p = 0.25 = (P_{CO_2})^1(P_{H_2O})^1 \quad 0.25 = (x)(x) \quad x = 0.50 \text{ atm}$$

Whereas $CO_2(g)$ and $H_2O(g)$ are produced in a 1:1 ratio, both will have partial pressures of 0.50 atm. According to Dalton's law:

$$P_{total} = P_{CO_2} + P_{H_2O} = 0.50 + 0.50 = 1.00 \text{ atm}$$

Illustrated Mass Law Problem #5

Consider the following equilibrium reaction at a given temperature:

$$1H_2(g) + 1I_2(g) \rightleftharpoons 2HI(g)$$

At equilibrium, 0.10 moles of $H_2(g)$, 0.10 moles of $I_2(g)$, and 0.74 moles of $HI(g)$ are present in a 10 liter vessel. The existing equilibrium is disturbed by adding an additional 0.50 moles of $HI(g)$ to the mixture. Find the molar concentration of each species when equilibrium is reestablished.

Hint: In order to do this problem, one must invoke Le Chatelier's principle.

Illustrated Mass Law Problem #5 concluded

First, write the mass law expression for K_c, and determine its numerical value:

$$K_c = \frac{[HI]^2}{[H_2]^1[I_2]^1} = \frac{[\frac{0.74}{10}]^2}{[\frac{0.10}{10}]^1[\frac{0.10}{10}]^1} = 54.76$$

As a consequence of adding additional HI(g) to the pre-existing equilibrium, $Q_c > K_c$. To restore the ratio of product to reactants to 54.76, some unknown amount of HI(g) must decompose to generate more $H_2(g)$ and $I_2(g)$. Let 2x represent the # of moles of HI(g) that decompose, and x will represent the moles (each) of $H_2(g)$ and $I_2(g)$ that will form. Why is this so? Use the mass law expression to solve for x:

$$54.76 = \frac{[HI]^2}{[H_2]^1[I_2]^1} = \frac{[\frac{0.74+0.50-2x}{10}]^2}{[\frac{0.10+x}{10}]^1[\frac{0.10+x}{10}]^1} = \frac{(1.24-2x)^2}{(0.10+x)^2}$$

$$7.4 = \frac{1.24-2x}{0.10+x}\ ; \quad x = 0.053 \text{ mols}$$

The new equilibrium concentrations are: $[H_2] = [I_2] = 0.0153M$
$[HI] = 0.113M$

Illustrated Mass Law Problem #6

Consider the following equilibrium reaction at a given temperature:

$$1SO_2(g) + 1NO_2(g) \rightleftharpoons 1NO(g) + 1SO_3(g) \qquad K_c = 85.0 \text{ at } 460°C$$

0.050 moles of each species in the above equilibrium reaction are introduced into an empty 1.0 liter vessel. Find the molar concentration of each species when equilibrium is established.

Questions to consider:

Is the system already at equilibrium initially?

If not, what must the system do to establish equilibrium? How?

What crucial concept is involved in this problem?

Illustrated Mass Law Problem #6 concluded

Write the mass law expression: $K_c = 85.0 = \dfrac{[NO]^1[SO_3]^1}{[SO_2]^1[NO_2]^1}$

Note: In a **one liter** vessel, moles and molarity are identical.

Also note: $Q_c = \dfrac{[NO]^1[SO_3]^1}{[SO_2]^1[NO_2]^1} = \dfrac{[0.050]^1[0.050]^1}{[0.050]^1[0.050]^1} = 1.0$

In order for the mass law ratio to increase numerically from 1.0 to 85.0, the numerator must increase as the denominator decreases. To do so, Le Chatelier's principle requires that reactants be consumed to create more product. Why?

How much more product will there be at equilibrium than there was initially? How much less reactant will there be at equilibrium than there was initially? In each instance, the answer is x moles (Don't forget that each species in the equilibrium equation is related to any other species by a 1:1 mole ratio).

Therefore, $K_c = 85.0 = \dfrac{[0.050+x]^1[0.050+x]^1}{[0.050-x]^1[0.050-x]^1} = \dfrac{[0.050+x]^2}{[0.050-x]^2}$

$9.22 = \dfrac{0.050+x}{0.050-x}$; $0.461-9.22x = 0.050+x$; $10.22x = 0.411$; $x = 0.040$ mols

At Equilibrium: $[NO] = [SO_3] = (0.050+0.040)\text{mols}/1.0\text{ liter} = 0.090M$

$[SO_2] = [NO_2] = (0.050-0.040)\text{mols}/1.0\text{ liter} = 0.010M$

Illustrated Mass Law Problem #7

Consider the following equilibrium reaction at a given temperature:

$$1CO(g) + 1Cl_2(g) \rightleftharpoons 1COCl_2(g) \qquad K_c = 4.6x10^9$$

Initially, 0.200 moles of $COCl_2(g)$ are introduced into an empty 10.0 liter vessel. Find the molar concentration of each species when equilibrium is established.

Question: Is the system at equilibrium initially? If not, what must happen for equilibrium to be established?

Strategy: Write the mass law expression for the above equilibrium equation. Note the mole ratio of products and reactants in the above equation.

Illustrated Mass Law Problem #7 concluded

$$K_c = \frac{[COCl_2]^1}{[CO]^1[Cl_2]^1} = \frac{[\frac{0.200-x}{10.0}]^1}{[\frac{0+x}{10.0}]^1[\frac{0+x}{10.0}]^1} = \frac{[0.200-x]^1}{[\frac{x^2}{10.0}]^1} = 4.6x10^9$$

$(4.6x10^8)x^2 = 0.200\text{-}x$; $(4.6x10^8)x^2+1x-0.200 = 0$ is a quadratic equation that can be solved using the quadratic formula (a tedious process subject to careless error).

Simplified Solution:

In order to establish equilibrium, x moles of $COCl_2(g)$ must decompose to generate x moles of CO(g) and x moles of $Cl_2(g)$. The numerical value of the equilibrium constant for the $COCl_2(g)$ decomposition (the reverse of the equilibrium equation shown above) is the inverse of $4.6x10^9$ or $2.17x10^{-10}$ (a very small number indeed). This means that **very little** $COCl_2(g)$ decomposes and that, for all intents and purposes, x moles is **insignificant** compared to 0.200 moles!

$$K_c = \frac{[COCl_2]^1}{[CO]^1[Cl_2]^1} = \frac{[\frac{0.200-x}{10.0}]^1}{[\frac{0+x}{10.0}]^1[\frac{0+x}{10.0}]^1} \cong \frac{[0.200]^1}{[\frac{x^2}{10.0}]^1} = 4.6x10^9$$

$$\frac{0.200}{4.6x10^9} = \frac{x^2}{10.0} \; ; \quad x = 2.1x10^{-5} \text{ mols}$$

At Equilibrium: $[CO] = [Cl_2] = \dfrac{2.1x10^{-5} \text{ mols}}{10.0 \text{ liters}} = 2.1x10^{-6}$ M

$$[COCl_2] = \frac{(2.00x10^{-1} - 2.1x10^{-5}) \text{ mols}}{10.0 \text{ liters}} \cong 0.0200 \text{ M}$$

Equilibrium Exercise #1

Consider the following equilibrium reaction at a given temperature:

$$1H_2(g) + 1Br_2(g) \rightleftharpoons 2HBr(g) \qquad K_c = 5.5x10^8 \text{ at } 700°K$$

Initially, 0.34 moles of $H_2(g)$ and 0.22 moles of $Br_2(g)$ are introduced into an empty 10.0 liter vessel. Find the molar concentration of each species when equilibrium is established.

Question: Is the system at equilibrium initially? If not, what must happen for equilibrium to be established?

Strategy: Write the mass law expression for the above equilibrium equation. Note the mole ratio of products and reactants in the above equation.

Equilibrium Exercise #2

Consider the following equilibrium reaction at a given temperature:

$1SO_2(g) + 1NO_2(g) \rightleftharpoons 1SO_3(g) + 1NO(g)$ $K_c = 85.0$ at 460°C

Initially, $[SO_2] = 0.010$ M, $[NO_2] = 0.020$ M, $[SO_3] = 0.015$ M, and $[NO] = 0.010$ M. Find the molar concentration of each species when equilibrium is established.

Question: Is the system at equilibrium initially? If not, what must happen for equilibrium to be established?

Strategy: Write the mass law expression for the above equilibrium equation. Note the mole ratio of products and reactants in the above equation.