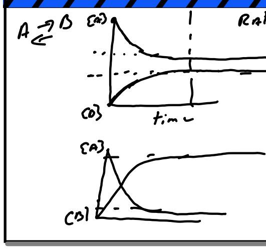
Chemical Equilibrium

Chemical Equilibrium

The state where the concentrations of all reactants and products remain constant with time.

On the molecular level, there is frantic activity. Equilibrium is not static, but is a highly dynamic situation.



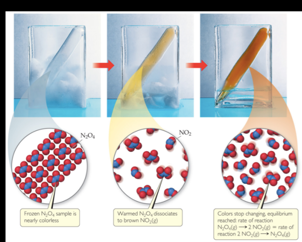
$A \rightleftarrows B$

$Rate = k_f[A]$

$Rate = k_r[B]$

$Rate_f = Rate_r$

The Concept of Equilibrium

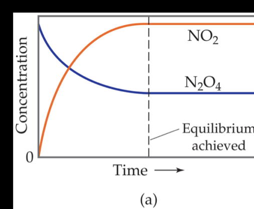


Chemical equilibrium occurs when a reaction and its reverse reaction proceed at the same rate.

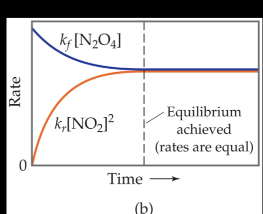
$Rate_f = Rate_r$

A System at Equilibrium

Once equilibrium is achieved, the *amount* of each reactant and product remains constant.



The Concept of Equilibrium



As a system approaches equilibrium, both the forward and reverse reactions are occurring.

At equilibrium, the forward and reverse reactions are proceeding *at the same rate*.

Depicting Equilibrium

Since, in a system at equilibrium, both the forward and reverse reactions are being carried out, we write its equation with a double arrow:

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

$Rate = k[N_2O_4]$

The Equilibrium Constant

Therefore, at equilibrium

$$Rate_f = Rate_r$$

$$k_f[N_2O_4] = k_r[NO_2]^2$$

Rewriting this, it becomes $\frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]}$

$R_f = k_f\{N_2O_4\} = k_r\{NO_2\}^2$

$K = \frac{k_f}{k_r} = \frac{\{NO_2\}^2}{\{N_2O_4\}}$

The Equilibrium Constant

The ratio of the rate constants is a constant at that temperature, and the expression becomes

$$K_{eq} = \frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]}$$

at 270 K

The Equilibrium Constant

Consider the generalized reaction

$$aA + bB \rightleftharpoons cC + dD$$

- The equilibrium expression for this reaction would be

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

$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O$

$K = \frac{\{CO_2\}\{H_2O\}^2}{\{CH_4\}\{O_2\}^2}$

Problem 15.9

Suppose that the gas-phase reactions A → B and B → A are both elementary processes with rate constants of $3.8 \times 10^{-2} s^{-1}$ and $3.1 \times 10^{-1} s^{-1}$, respectively.

(a) What is the value of the equilibrium constant for the equilibrium A ↔ B.

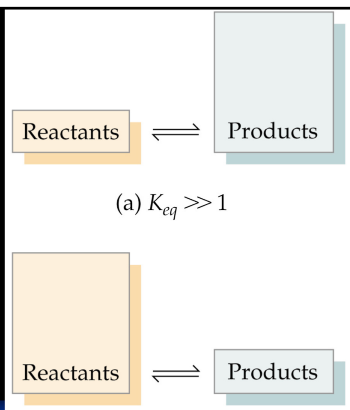
(b) Which is greater at equilibrium, the partial pressure of A or the partial pressure of B? Explain.

$Rate_f = k_f\{A\}$ $\quad Rate_r = k_r\{B\}$

$k_f\{A\} = k_r\{B\}$

$K = \frac{k_f}{k_r} = \frac{\{B\}}{\{A\}}$

$K = \frac{3.8\times10^{-2}}{3.1\times10^{-1}} = 0.123$



(a) $K_{eq} \gg 1$

(b) $K_{eq} \ll 1$

Equilibrium Expression

$$4NH_3(g) + 7O_2(g) \leftrightarrow 4NO_2(g) + 6H_2O(g)$$

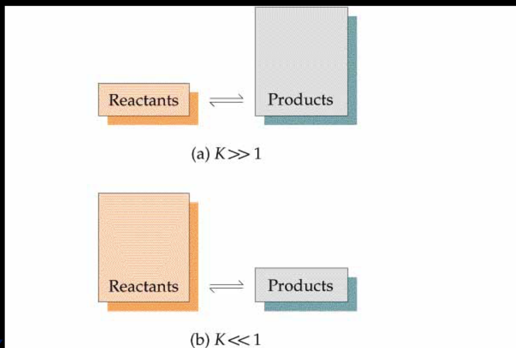
$$K_f = \frac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7} \quad \frac{Prod}{React}$$

$4NO_2 + 6H_2O \rightleftharpoons 4NH_3 + 7O_2$

$K_r = \frac{\{NH_3\}^4\{O_2\}^7}{\{NO_2\}^4\{H_2O\}^6} = \frac{1}{K_f}$

$2\times \quad 8NO_2 + 12H_2O \rightleftharpoons 8NH_3 + 14O_2$

$K = (K_r)^2$



Notes on Equilibrium Expressions (EE)

- The Equilibrium Expression for a reaction is the reciprocal of that for the reaction written in reverse.
- When the equation for a reaction is multiplied by n, $EE_{new} = (EE_{original})^n$
- The units for K depend on the reaction being considered.

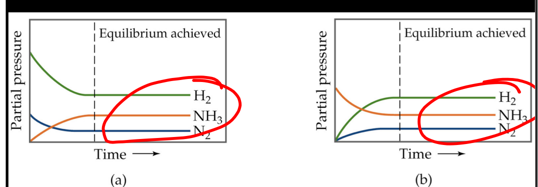
Manipulating Equilibrium Constants

The equilibrium constant of a reaction in the reverse reaction is the reciprocal of the equilibrium constant of the forward reaction:

$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.212$ at 100 °C

$2NO_2(g) \rightleftharpoons N_2O_4(g) \quad K_c = \frac{[N_2O_4]}{[NO_2]^2} = 4.72$ at 100 °C

$K_f = 0.212 \qquad K_r = \frac{1}{0.212} = 4.72$



$3H_2 + N_2 \rightarrow 2NH_3$

$K_f = \frac{[NH_3]^2}{[H_2]^3[N_2]}$

$2NH_3 \rightleftharpoons 3H_2 + N_2$

$K_r = \frac{[H_2]^3[N_2]}{[NH_3]^2}$

Manipulating Equilibrium Constants

The equilibrium constant of a reaction that has been multiplied by a number is the equilibrium constant raised to a power that is equal to that number:

$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.212$ at 100 °C

$2N_2O_4(g) \rightleftharpoons 4NO_2(g) \quad K_c = \frac{[NO_2]^4}{[N_2O_4]^2} = (0.212)^2$ at 100 °C

Manipulating Equilibrium Constants

The equilibrium constant for a net reaction made up of two or more steps is the product of the equilibrium constants for the individual steps.

$O_3 + Cl \rightarrow ClO + O_2 \qquad K_1$

$ClO + O \rightarrow Cl + O_2 \qquad K_2$

$O_3 + O \rightarrow 2O_2$

$K_{overall} = \frac{[O_2]^2}{[O_3][O]}$

$K_{overall} = K_1 K_2$

17.16 At a particular temperature, $K_c = 1.6\times10^{-2}$ for

$$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$$

Calculate K_c for each of the following reactions:

(a) $\frac{1}{2}S_2(g) + H_2(g) \rightleftharpoons H_2S(g)$

(b) $5H_2S(g) \rightleftharpoons 5H_2(g) + \frac{5}{2}S_2(g)$

$$K_c = \frac{[H_2]^2[S_2]}{[H_2S]^2} = 1.6\times10^{-2}$$

a) $K = \left(\frac{1}{K_c}\right)^{1/2} = \left(\frac{1}{1.6\times10^{-2}}\right)^{1/2} = 7.91$

b) $K = (K_c)^{5/2} = 3.24\times10^{-5}$

Heterogeneous Equilibria

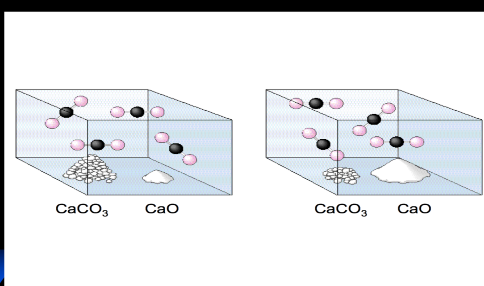
. . . are equilibria that involve more than one phase.

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

$$K = [CO_2]$$

The position of a heterogeneous equilibrium does not depend on the amounts of pure solids or liquids present.

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



The Concentrations of Solids and Liquids Are Essentially Constant

Therefore, the concentrations of solids and liquids do not appear in the equilibrium expression.

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

$$K_c = [Pb^{2+}][Cl^-]^2$$

17.18 Balance each of the following examples of heterogeneous equilibria and write each reaction quotient, Q_c:

(a) $Na_2O_2(s) + CO_2(g) \rightleftharpoons Na_2CO_3(s) + O_2(g)$

(b) $H_2O(l) \rightleftharpoons H_2O(g)$

(c) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$

a) $2Na_2O_{2(s)} + 2CO_{2(g)} = 2Na_2CO_{3(s)} + O_{2(g)}$

$$Q_c = \frac{[O_2]}{[CO_2]^2}$$

c.) $NH_4Cl_{(s)} = NH_{3(g)} + HCl_{(g)}$

$$Q_c = [NH_3][HCl]$$

K_c v. K_p

For

$$jA + kB \leftrightarrow lC + mD$$

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

Δn = sum of coefficients of gaseous products minus sum of coefficients of gaseous reactants.

The Equilibrium Constant

Since pressure is proportional to concentration for gases in a closed system, the equilibrium expression can also be written

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

Relationship Between K_c and K_p

From the ideal-gas law we know that

$$PV = nRT$$

- Rearranging it, we get

$$P = \frac{n}{V}\,RT$$

Relationship Between K_c and K_p

Plugging this into the expression for K_p, for each substance, the relationship between K_c and K_p becomes

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

where

Δn = (moles of gaseous product) – (moles of gaseous reactant)

17.28 Determine Δn_{gas} for each of the following reactions:

(a) $2KClO_3(s) \rightleftharpoons 2KCl(s) + 3O_2(g)$

(b) $2PbO(s) + O_2(g) \rightleftharpoons 2PbO_2(s)$

(c) $I_2(s) + 3XeF_2(s) \rightleftharpoons 2IF_3(s) + 3Xe(g)$

Δn:

a.) Δn = 3 mol – 0 mol = 3

b.) Δn = 0 mol – 1 mol = –1

c.) Δn = 3

17.30 Calculate K_c for each of the following equilibria:

(a) $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$; $K_p = 3.9 \times 10^{-2}$ at 1000. K

(b) $S_2(g) + C(s) \rightleftharpoons CS_2(g)$; $K_p = 28.5$ at 500. K

a.) $K_p = \frac{(P_{COCl_2})}{(P_{CO})(P_{Cl_2})} = 3.9 \times 10^{-2}$

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

$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{(3.9 \times 10^{-2})}{\left[(0.08206 \frac{L\cdot atm}{K\cdot mol})(1000 K)\right]^{-1}}$

$= 3.20$

17.32 Calculate K_p for each of the following equilibria:

(a) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$; $K_c = 6.1 \times 10^{-3}$ at 298 K

(b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $K_c = 2.4 \times 10^{-3}$ at 1000. K

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

$= (2.4 \times 10^{-3})\left[(0.08206 \frac{L\cdot atm}{K\cdot mol})(1000 K)\right]^{-2} =$

$= \frac{2.4 \times 10^{-3}}{[(0.08206)(1000)]^2} = 3.56 \times 10^{-7}$

February 14, 2018

Solving Equilibrium Problems

1. Balance the equation.
2. Write the equilibrium expression.
3. List the initial concentrations. I
4. Calculate Q and determine the shift to equilibrium. Δ

Solving Equilibrium Problems (continued)

5. Define equilibrium concentrations. E
6. Substitute equilibrium concentrations into equilibrium expression and solve.
7. Check calculated concentrations by calculating K.

17.40 For a problem involving the catalyzed reaction of methane and steam, the following reaction table was prepared:

Pressure (atm)	$CH_4(g)$	+	$2H_2O(g)$	⇌	$CO_2(g)$	+	$4H_2(g)$
Initial	0.30 M		0.40 M		0		0
Change	$-x$		$-2x$		$+x$		$+4x$
Equilibrium	$0.30 - x$		$0.40 - 2x$		x		$4x$

Explain the entries in the "Change" and "Equilibrium" rows.

shift right →

$$K = \frac{[CO_2][H_2]^4}{[CH_4][H_2O]^2} = \frac{(x)(4x)^4}{(0.30-x)(0.40-2x)^2}$$

17.42 In an experiment to study the formation of HI(g),

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

$H_2(g)$ and $I_2(g)$ were placed in a sealed container at a certain temperature. At equilibrium, $[H_2] = 6.50\times10^{-5}$ M, $[I_2] = 1.06\times10^{-3}$ M, and $[HI] = 1.87\times10^{-3}$ M. Calculate K_c for the reaction at this temperature.

$$H_2 + I_2 \rightleftharpoons 2HI$$

I

Δ

E 6.5×10^{-5} 1.06×10^{-3} 1.87×10^{-3}

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.87\times10^{-3})^2}{(6.5\times10^{-5})(1.06\times10^{-3})} = 50.8$$

17.46 For the following reaction, $K_p = 6.5\times10^4$ at 308 K:

$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$$

At equilibrium, $P_{NO} = 0.35$ atm and $P_{Cl_2} = 0.10$ atm. What is the equilibrium partial pressure of NOCl(g)?

$$2NO + Cl_2 \rightleftharpoons 2NOCl$$

I

Δ

E 0.35 0.10 ?

$$K_p = \frac{(P_{NOCl})^2}{(P_{NO})^2(P_{Cl_2})} = 6.5\times10^4$$

$$P_{NOCl} = \left[K_p (P_{NO})^2 (P_{Cl_2})\right]^{1/2} = 28 \text{ atm}$$

17.44 Gaseous PCl_5 decomposes according to the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

In one experiment, 0.15 mol of $PCl_5(g)$ was introduced into a 2.0-L container. Construct the reaction table for this process.

If the equilibrium concentration of Cl_2 is 0.025 M, what is K_c? What is K_p at 25°C?

	PCl_5	⇌	PCl_3	+	Cl_2
I	0.075 M		0		0
Δ	$-x$		$+x$		$+x$
E	$0.075-x$		x		x

$x = 0.025$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(x)(x)}{(0.075-x)} = 0.0125 \text{ M}$$

$$K_p = K_c(RT)^{\Delta n} = (0.0125)\left((0.0820)(298)\right)^1$$

$= 0.306$ atm

17.48 Ammonium hydrogen sulfide decomposes according to the following reaction, for which $K_p = 0.11$ at 250°C:

$$NH_4HS(s) \rightleftharpoons H_2S(g) + NH_3(g)$$

If 55.0 g of $NH_4HS(s)$ is placed in a sealed 5.0-L container, what is the partial pressure of $NH_3(g)$ at equilibrium?

$K_p = (P_{H_2S})(P_{NH_3}) = 0.11$

	NH_4H_3	⇌	H_2S	+	NH_3
I			0		0
Δ	−x		+x		+x
			x		x

$(x)(x) = 0.11$ $x = 0.33$ atm

17.50 Even at high *T*, the formation of NO is not favored:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad K_c = 4.10 \times 10^{-4} \text{ at } 2000°C$$

What is [NO] when a mixture of 0.20 mol of $N_2(g)$ and 0.15 mol of $O_2(g)$ reach equilibrium in a 1.0-L container at 2000°C?

	N_2	+ O_2	⇌ $2NO$
I	0.20 M	0.15 M	0
Δ	−x	−x	+2x
E	0.20−x	0.15−x	2x
	0.1983	0.14826	0.0035 M

$K_c = \frac{[NO]^2}{[N_2][O_2]} = 4.10 \times 10^{-4}$

$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$\frac{(2x)^2}{(0.20-x)(0.15-x)} = 4.10 \times 10^{-4}$

$K = \frac{(0.0035)^2}{(0.1983)(0.1483)} = 4.17 \times 10^{-4}$

$4x^2 = (4.10 \times 10^{-4})(x^2 - 0.35x + 0.030)$

$4x^2 = 4.10 \times 10^{-4}x^2 - 1.44 \times 10^{-4}x + 1.23 \times 10^{-5}$

$4.0x^2 + 1.44 \times 10^{-4}x - 1.23 \times 10^{-5} = 0$ (a, b, c)

$x = \frac{-1.44 \times 10^{-4} \pm \sqrt{(+1.44 \times 10^{-4})^2 - 4(4.0)(-1.23 \times 10^{-5})}}{2(4.0)}$

$x = 0.00174$ or ~~-0.00177~~

5% Rule for small K

$\frac{(2x)^2}{(0.20)(0.15)} = 4.10 \times 10^{-4}$

$\frac{(2x)^2}{(0.20)(0.15)} = 4.1 \times 10^{-4}$ $x =$

$x = \left(\frac{(4.1 \times 10^{-4})(0.20)(0.15)}{4}\right)^{1/2} = 0.00175$

$\frac{x}{0.20} \times 100 = 0.88\%$

17.52 Hydrogen iodide decomposes according to the reaction

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

A sealed 1.50-L container initially holds 0.00623 mol of H_2, 0.00414 mol of I_2, and 0.0244 mol of HI at 703 K. When equilibrium is reached, the concentration of $H_2(g)$ is 0.00467 *M*. What are the concentrations of HI(g) and $I_2(g)$?

Calculate K

	$2HI$	⇌ H_2	+ I_2
I	1.63×10^{-2}	4.2×10^{-3}	2.76×10^{-3}
Δ	−2x	+x	+x
E	$1.63 \times 10^{-2} - 2x$ = 0.0154	0.00467	$2.76 \times 10^{-3} + x$ = 0.00323

$4.2 \times 10^{-3} + x = 0.00467$

$x = 4.70 \times 10^{-4}$

$K = \frac{[H_2][I_2]}{[HI]^2} = \frac{(0.00467)(0.00323)}{(0.0154)^2} = 0.064$

17.54 In an analysis of interhalogen reactivity, 0.500 mol of ICl was placed in a 5.00-L flask, where it decomposed at a high *T*:

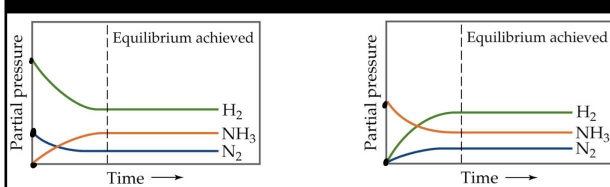
$$2ICl(g) \rightleftharpoons I_2(g) + Cl_2(g)$$

Calculate the equilibrium concentrations of I_2, Cl_2, and ICl ($K_c = 0.110$ at this temperature).

Reaction Quotient

. . . helps to determine the direction of the move toward equilibrium.

The law of mass action is applied with initial concentrations.



(a) (b)

$3H_2 + N_2 \rightleftharpoons 2NH_3$ $K = \frac{[NH_3]^2}{[H_2]^3[N_2]}$

The Reaction Quotient (Q)

Q gives the same ratio the equilibrium expression gives, but for a system that is *not* at equilibrium.

To calculate *Q*, one substitutes the initial concentrations on reactants and products into the equilibrium expression.

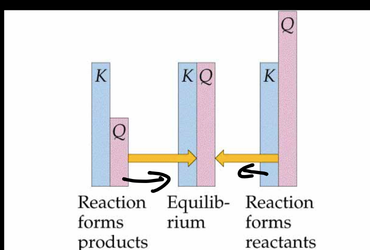
$Q = \frac{[NH_3]_0^2}{[N_2]_0[H_2]_0^3}$

Reaction Quotient
(continued)

$$H_2(g) + F_2(g) \leftrightarrow 2HF(g)$$

$$Q = \frac{[HF]_0^2}{[H_2]_0[F_2]_0}$$

Reaction Quotient



$Q = \frac{[Prod]}{[React]}$

17.38 The water-gas shift reaction plays a central role in the chemical methods for obtaining cleaner fuels from coal:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

At a given temperature, $K_p = 2.7$. If 0.13 mol of CO, 0.56 mol of H_2O, 0.62 mol of CO_2, and 0.43 mol of H_2 are put in a 2.0-L flask, in which direction does the reaction proceed?

	CO	+ H_2O	⇌ CO_2	+ H_2
I	0.065 M	0.28 M	0.31 M	0.215 M
Δ	+x	+x	−x	−x
E	0.065+x	0.28+x	0.31−x	0.215−x

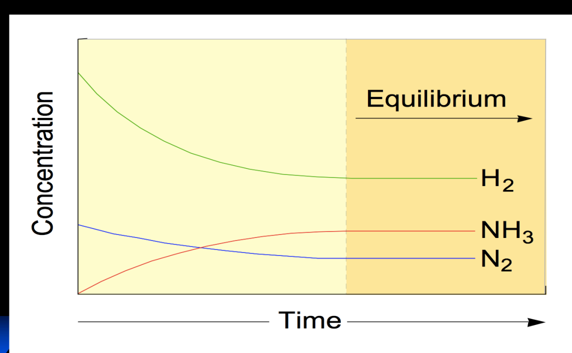
$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = 2.7$

$Q = \frac{[CO_2]_0[H_2]_0}{[CO]_0[H_2O]_0} = \frac{(0.31)(0.215)}{(0.065)(0.28)} = 3.66$

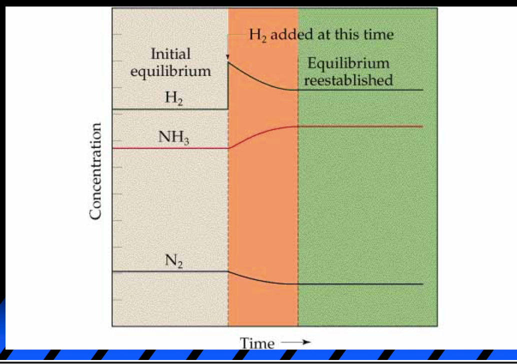
Le Châtelier's Principle

"If a system at equilibrium is disturbed by a change in temperature, pressure, or the concentration of one of the components, the system will shift its equilibrium position so as to counteract the effect of the disturbance."

$N_2 + 3H_2 \leftrightarrow 2NH_3$



$N_2 + 3H_2 \leftrightarrow 2NH_3$



$H_2 + F_2 \leftrightarrow 2HF$

K = 1.00 x 10^2

In an experiment 2.00 moles of F_2 and 2.00 moles of H_2 are introduced into a 1L flask. Calculate the equilibrium concentration of all species.

$H_2 + F_2 \rightleftharpoons 2HF$ $K = 1.00 \times 10^2$

	H_2	F_2	$2HF$
I	2.00 m	2.00 m	0
Δ	−x	−x	+2x
E	2.00 − x	2.00 − x	2x

$K = \frac{[HF]^2}{[H_2][F_2]} = 100$

x = 1.67

$\frac{(2x)^2}{(2.00-x)(2.00-x)} = 100$

$\sqrt{\frac{(2x)^2}{(2.00-x)^2}} = \sqrt{100}$

$\frac{2x}{(2.00-x)} = \sqrt{100}$

$[H_2]_{eq} = [F_2]$ = 0.33 m

$[HF]_{eq} = 2(1.67)$ = 3.34

$H_2 + F_2 \leftrightarrow 2HF$

To the equilibrium mixture in the previous problem, an additional 0.50 moles of H_2 is added. Calculate the new equilibrium concentration of all species.

$H_2 + F_2 \rightleftharpoons 2HF$ K = 100

	H_2	F_2	$2HF$
I	0.33 m + 0.50 m = 0.83 m	0.33 m	3.34 m
Δ	−x	−x	+2x
E	0.83 − x	0.33 − x	3.34 + 2x

$Q = \frac{[HF]_0^2}{[H_2]_0[F_2]_0}$ = 40.7

$\frac{(3.34+2x)^2}{(0.83-x)(0.33-x)} = 100$

x = 0.14

Effects of Changes on the System

1. Concentration: The system will shift away from the added component.
2. Temperature: K will change depending upon the temperature (treat the energy change as a reactant).

A ⇌ B + heat exo

← add T

Effects of Changes on the System (continued)

3. Pressure:

a. Addition of inert gas does not affect the equilibrium position.

b. Decreasing the volume shifts the equilibrium toward the side with fewer moles. of gas

A + B ⇌ C

1 + 1 1

END