Equilibrium is a state in which there are no observable changes as time goes by.

Chemical equilibrium is a state in which the rate of the forward reaction equals the rate of the backward reaction.

Chemical equilibrium is achieved when:

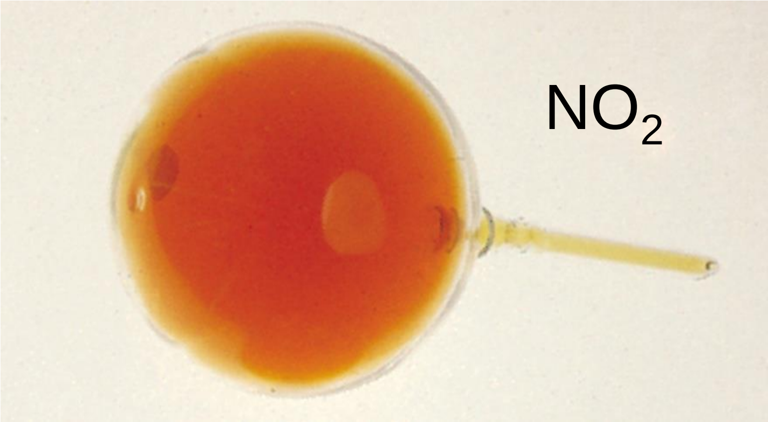
- the rates of the forward and reverse reactions are equal and
- the concentrations of the reactants and products remain constant

Physical equilibrium

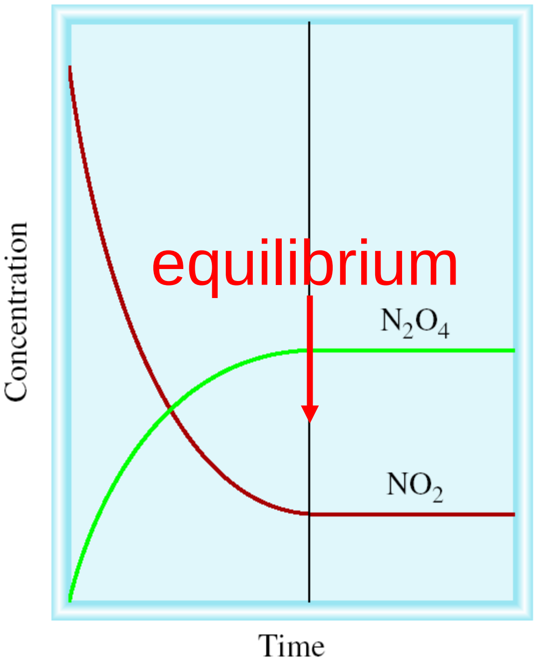
$$H_2O\ (l) \rightleftarrows H_2O\ (g)$$

Chemical equilibrium

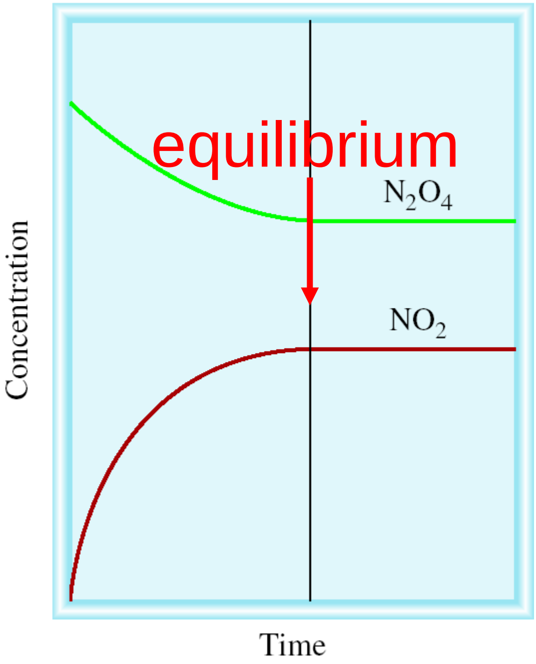
$$N_2O_4\ (g) \rightleftarrows 2NO_2\ (g)$$



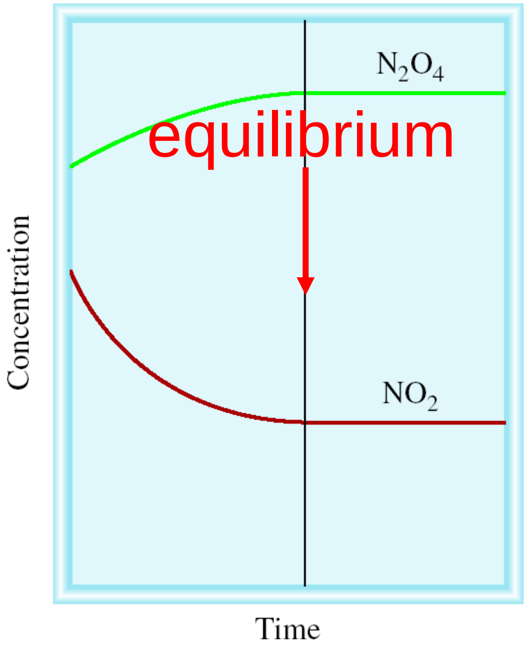
$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$



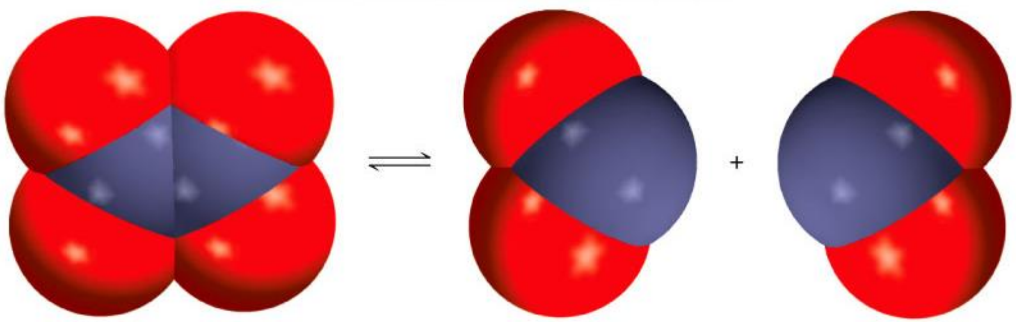
Start with NO_2

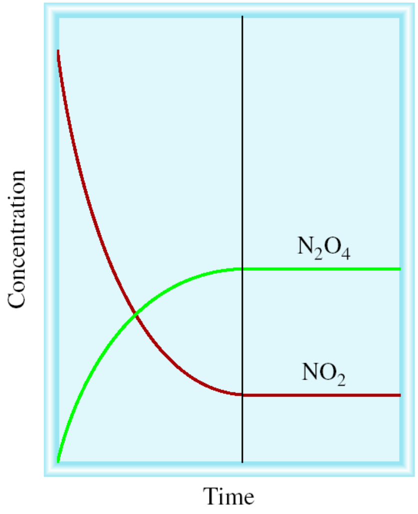


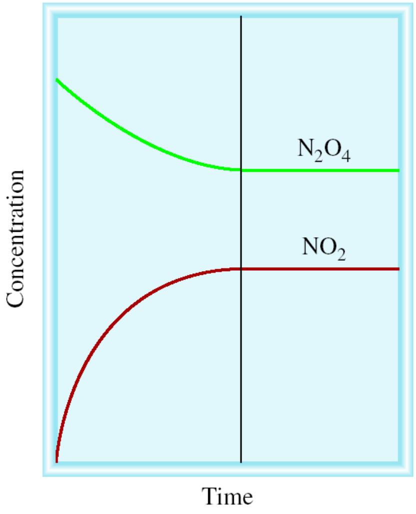
Start with N_2O_4

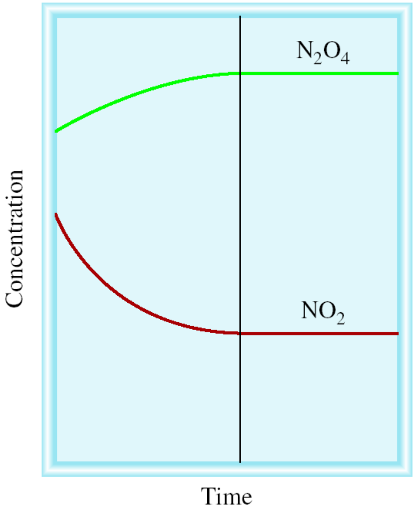


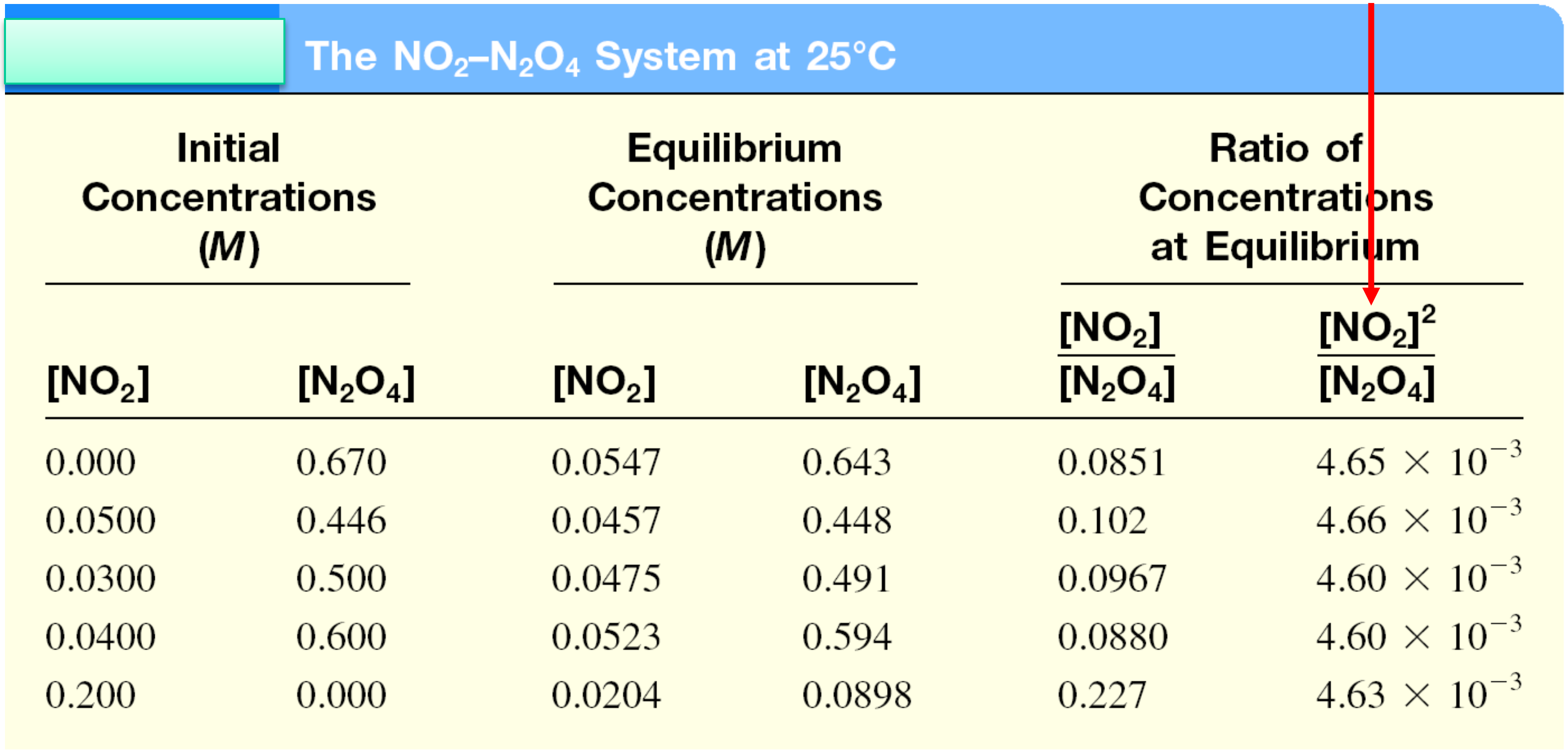
Start with NO_2 & N_2O_4











constant

The NO_2–N_2O_4 System at 25°C

Initial Concentrations (*M*)		Equilibrium Concentrations (*M*)		Ratio of Concentrations at Equilibrium	
$[NO_2]$	$[N_2O_4]$	$[NO_2]$	$[N_2O_4]$	$\frac{[NO_2]}{[N_2O_4]}$	$\frac{[NO_2]^2}{[N_2O_4]}$
0.000	0.670	0.0547	0.643	0.0851	4.65×10^{-3}
0.0500	0.446	0.0457	0.448	0.102	4.66×10^{-3}
0.0300	0.500	0.0475	0.491	0.0967	4.60×10^{-3}
0.0400	0.600	0.0523	0.594	0.0880	4.60×10^{-3}
0.200	0.000	0.0204	0.0898	0.227	4.63×10^{-3}

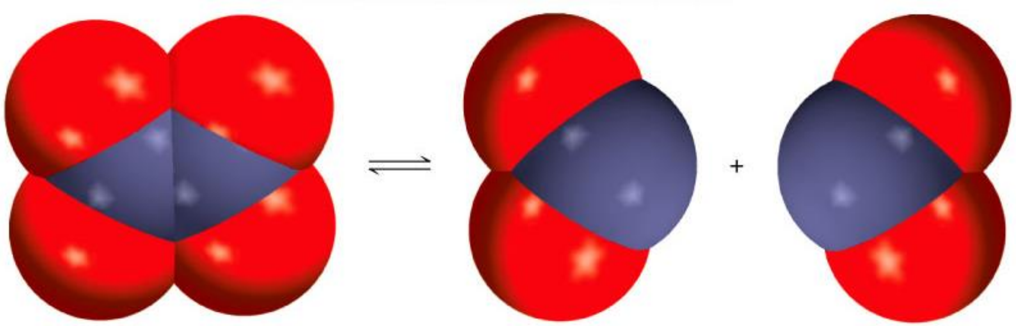
$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$

$$K = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3}$$

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

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

Law of Mass Action

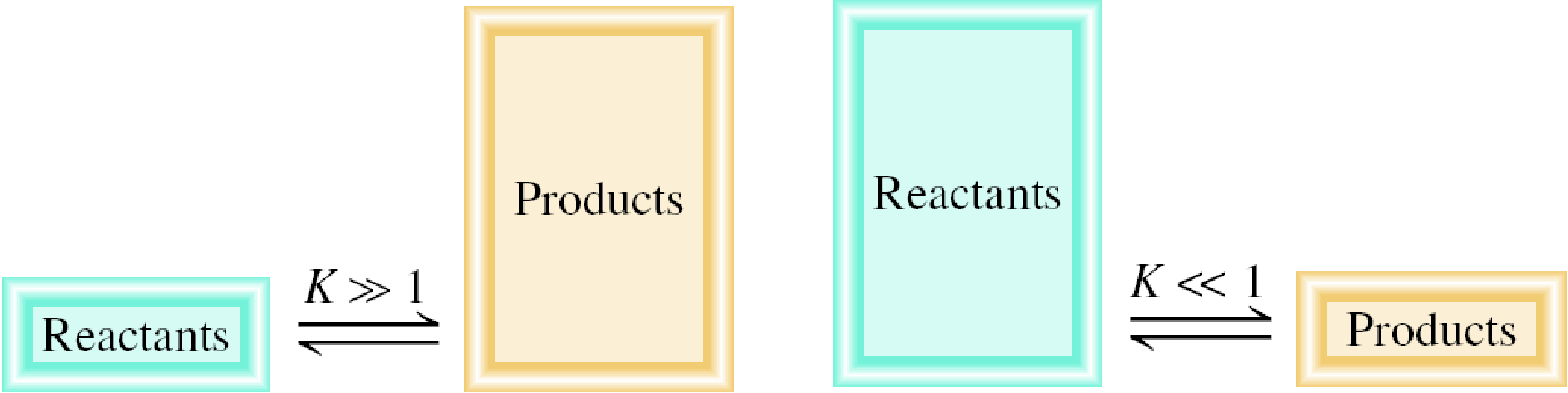


$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

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

Equilibrium Will

$K >> 1$	Lie to the right	Favor products
$K << 1$	Lie to the left	Favor reactants



Homogenous equilibrium applies to reactions in which all reacting species **are in the same phase.**

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

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} \qquad\qquad K_p = \frac{P_{NO_2}^{\,2}}{P_{N_2O_4}}$$

In most cases

$$K_c \neq K_p$$

$$aA\,(g) + bB\,(g) \rightleftharpoons cC\,(g) + dD\,(g)$$

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

Δn = moles of gaseous products – moles of gaseous reactants

$= (c + d) – (a + b)$

Homogeneous Equilibrium

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

$$K_c' = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]}$$

$[H_2O]$ = constant

$$K_c = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = K_c'\ [H_2O]$$

General practice **not** to include units for the equilibrium constant.

The equilibrium concentrations for the reaction between carbon monoxide and molecular chlorine to form $COCl_2$ (*g*) at 74^0C are [CO] = 0.012 *M*, $[Cl_2]$ = 0.054 *M*, and $[COCl_2]$ = 0.14 *M*. Calculate the equilibrium constants K_c and K_p.

$$CO\ (g) + Cl_2\ (g) \rightleftharpoons COCl_2\ (g)$$

$$K_c = \frac{[COCl_2]}{[CO][Cl_2]} = \frac{0.14}{0.012 \times 0.054} = 220$$

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

$$\Delta n = 1 - 2 = -1 \qquad R = 0.0821 \qquad T = 273 + 74 = 347\ \text{K}$$

$$K_p = 220 \times (0.0821 \times 347)^{-1} = 7.7$$

The equilibrium constant K_p for the reaction

$$2NO_2\,(g) \rightleftarrows 2NO\,(g) + O_2\,(g)$$

is 158 at 1000K. What is the equilibrium pressure of O_2 if the $P_{NO_2} = 0.400$ atm and $P_{NO} = 0.270$ atm?

$$K_p = \frac{P_{NO}^2\, P_{O_2}}{P_{NO_2}^2}$$

$$P_{O_2} = K_p \frac{P_{NO_2}^2}{P_{NO}^2}$$

$$P_{O_2} = 158 \times (0.400)^2/(0.270)^2 = 347 \text{ atm}$$

Heterogenous equilibrium applies to reactions in which reactants and products **are in different phases.**

$$CaCO_3\boxed{(s)} \rightleftharpoons CaO\boxed{(s)} + CO_2\boxed{(g)}$$

$$K'_c = \frac{[CaO][CO_2]}{[CaCO_3]}$$

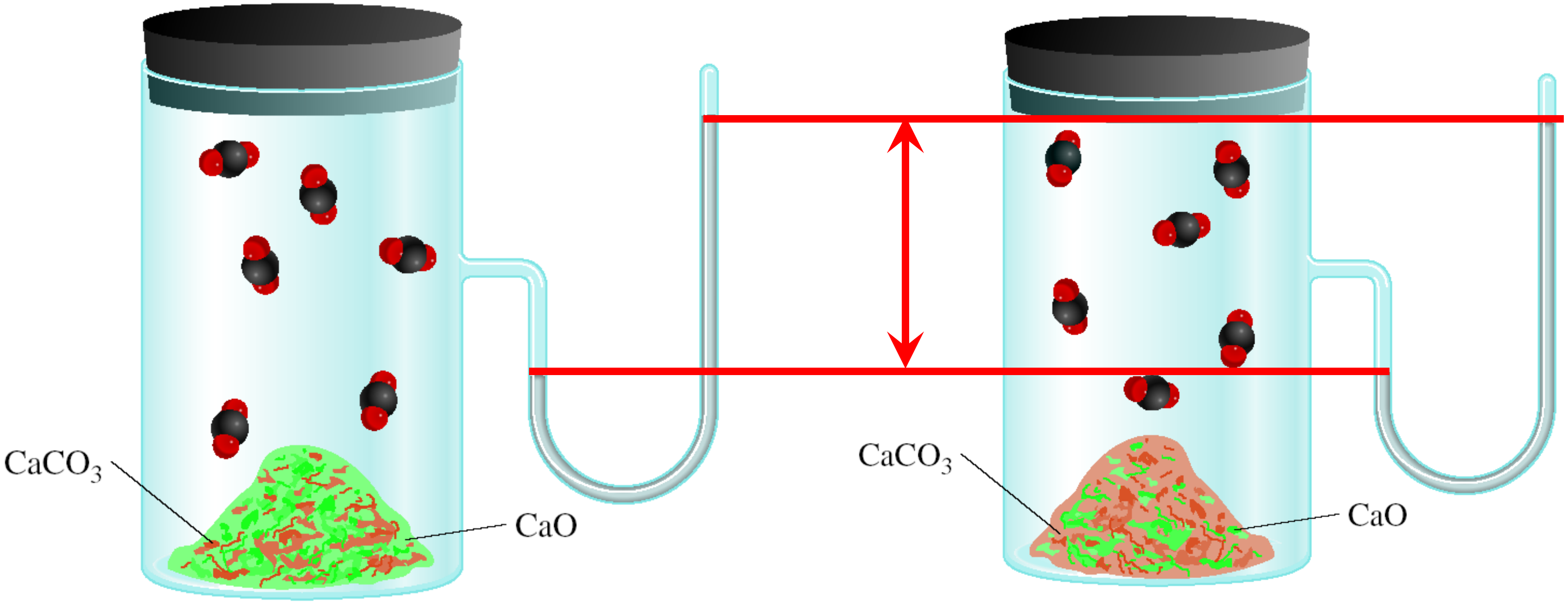
$[CaCO_3]$ = constant
$[CaO]$ = constant

$$K_c = [CO_2] = K'_c \text{ x } \frac{[CaCO_3]}{[CaO]}$$

$$K_p = P_{CO_2}$$

The concentration of **solids** and **pure liquids** are not included in the expression for the equilibrium constant.

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



$$P_{CO_2} = K_p$$

P_{CO_2} does not depend on the amount of $CaCO_3$ or CaO

Consider the following equilibrium at 295 K:

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

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

$$K_p = P_{NH_3}P_{H_2S} = 0.265 \text{ x } 0.265 = 0.0702$$

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

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

$$\Delta n = 2 - 0 = 2 \qquad T = 295 \text{ K}$$

$$K_c = 0.0702 \text{ x } (0.0821 \text{ x } 295)^{-2} = 1.20 \text{ x } 10^{-4}$$

$$\begin{array}{ll} A + B \rightleftharpoons \cancel{C} + \cancel{D} & K_c' \\ \cancel{C} + \cancel{D} \rightleftharpoons E + F & K_c'' \\ \hline A + B \rightleftharpoons E + F & K_c \end{array}$$

$$K_c' = \frac{[C][D]}{[A][B]} \qquad K_c'' = \frac{[E][F]}{[C][D]}$$

$$K_c = \frac{[E][F]}{[A][B]}$$

$$K_c = K_c' \text{ x } K_c''$$

If a reaction can be expressed as the 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.

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

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

$$K = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3}$$

$$K' = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{K} = 216$$

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

Writing Equilibrium Constant Expressions

1. The concentrations of the reacting species in the condensed phase are expressed in *M*. In the gaseous phase, the concentrations can be expressed in *M* or in atm.
2. The concentrations of pure solids, pure liquids and solvents do not appear in the equilibrium constant expressions.
3. The equilibrium constant is a dimensionless quantity.
4. In quoting a value for the equilibrium constant, you must specify the balanced equation and the temperature.
5. If a reaction can be expressed as a 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.

Chemical Kinetics and Chemical Equilibrium

$$A + 2B \underset{k_r}{\overset{k_f}{\rightleftarrows}} AB_2$$

$$\text{rate}_f = k_f\,[A][B]^2$$

$$\text{rate}_r = k_r\,[AB_2]$$

Equilibrium

$$\text{rate}_f = \text{rate}_r$$

$$k_f\,[A][B]^2 = k_r\,[AB_2]$$

$$\frac{k_f}{k_r} = K_c = \frac{[AB_2]}{[A][B]^2}$$

The equilibrium constant K_c for the reaction

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

is 54.3 at 430°C. Suppose that in a certain experiment we place 0.243 mole of H_2, 0.146 mole of I_2, and 1.98 moles of HI all in a 1.00-L container at 430°C. Will there be a net reaction to form more H_2 and I_2 or more HI? Inserting the starting concentrations in the equilibrium constant expression, we write

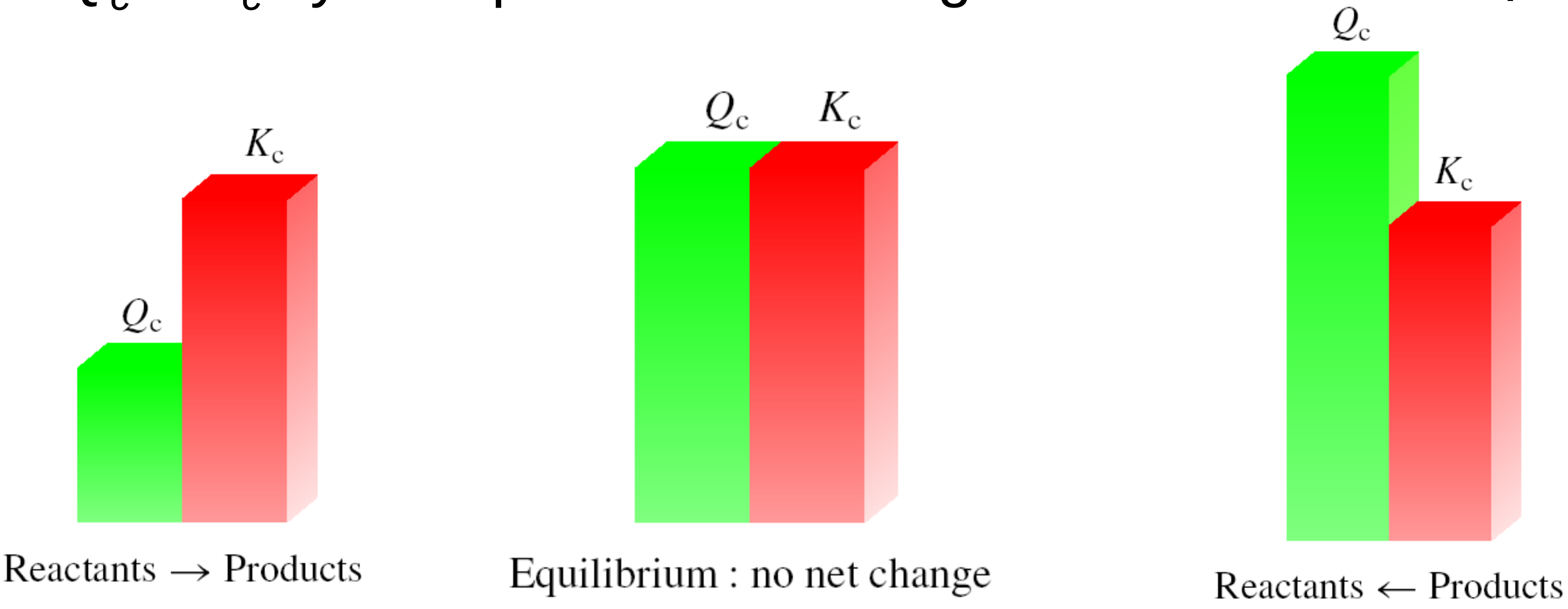
$$\frac{[HI]_0^2}{[H_2]_0[I_2]_0} = \frac{(1.98)^2}{(0.243)(0.146)} = 111$$

where the subscript 0 indicates initial concentrations. Because the calculated quotient $[HI]_0^2/[H_2]_0[I_2]_0$ is greater than K_c, this system is not at equilibrium. Consequently, some of the HI will react to form more H_2 and I_2 (decreasing the value of the quotient). Thus, the net reaction proceeds from right to left to reach equilibrium.

The ***reaction quotient (Q_c)*** is calculated by substituting the initial concentrations of the reactants and products into the equilibrium constant (K_c) expression.

IF

- $Q_c < K_c$ system proceeds from left to right to reach equilibrium
- $Q_c = K_c$ the system is at equilibrium
- $Q_c > K_c$ system proceeds from right to left to reach equilibrium



Calculating Equilibrium Concentrations

1. Express the equilibrium concentrations of all species in terms of the initial concentrations and a single unknown x, which represents the change in concentration.
2. Write the equilibrium constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant, solve for x.
3. Having solved for x, calculate the equilibrium concentrations of all species.

A mixture of 0.500 mol H_2 and 0.500 mol I_2 was placed in a 1.00-L stainless-steel flask at 430°C. The equilibrium constant K_c for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 54.3 at this temperature. Calculate the concentrations of H_2, I_2, and HI at equilibrium.

Strategy We are given the initial amounts of the gases (in moles) in a vessel of known volume (in liters), so we can calculate their molar concentrations. Because initially no HI was present, the system could not be at equilibrium. Therefore, some H_2 would react with the same amount of I_2 (why?) to form HI until equilibrium was established.

Solution We follow the preceding procedure to calculate the equilibrium concentrations.

Step 1: The stoichiometry of the reaction is 1 mol H_2 reacting with 1 mol I_2 to yield 2 mol HI. Let x be the depletion in concentration (mol/L) of H_2 and I_2 at equilibrium. It follows that the equilibrium concentration of HI must be $2x$. We summarize the changes in concentrations as follows:

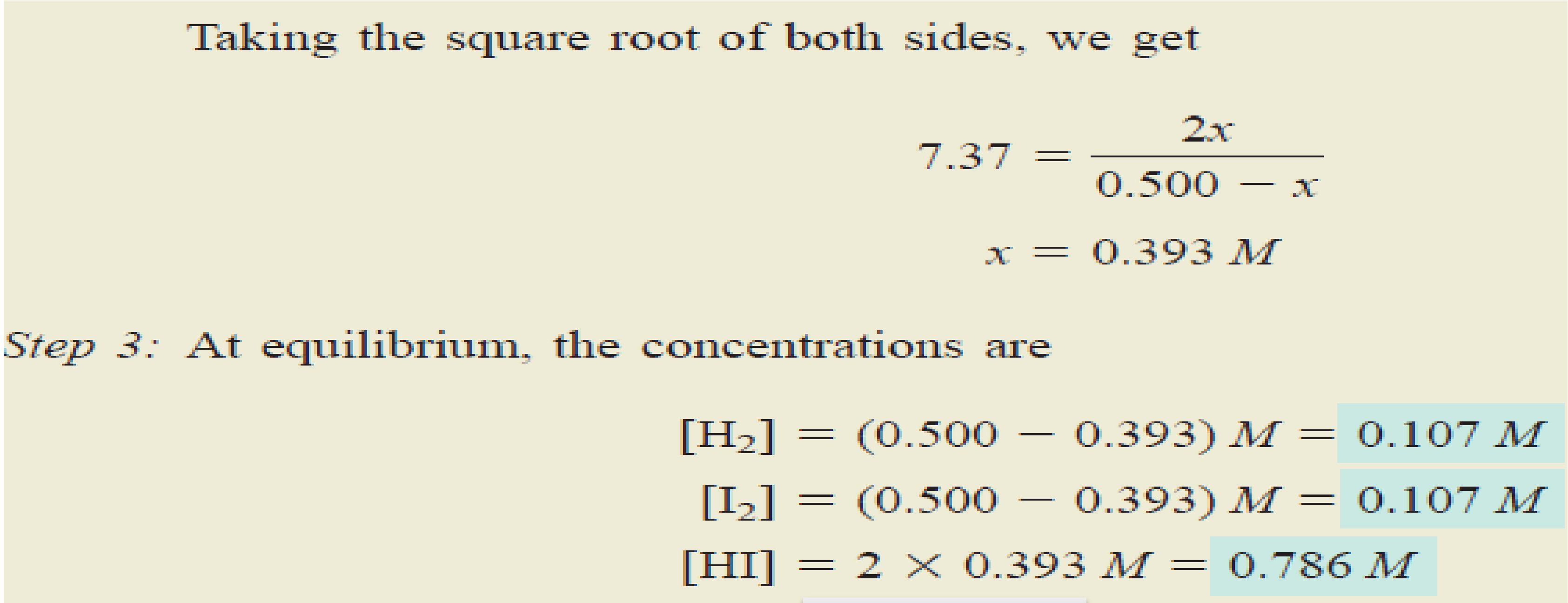
	H_2	+	I_2	$\rightleftharpoons$	2HI
Initial (*M*):	0.500		0.500		0.000
Change (*M*):	$-x$		$-x$		$+2x$
Equilibrium (*M*):	$(0.500 - x)$		$(0.500 - x)$		$2x$

Step 2: The equilibrium constant is given by

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

Substituting, we get

$$54.3 = \frac{(2x)^2}{(0.500 - x)(0.500 - x)}$$



Taking the square root of both sides, we get

$$7.37 = \frac{2x}{0.500 - x}$$

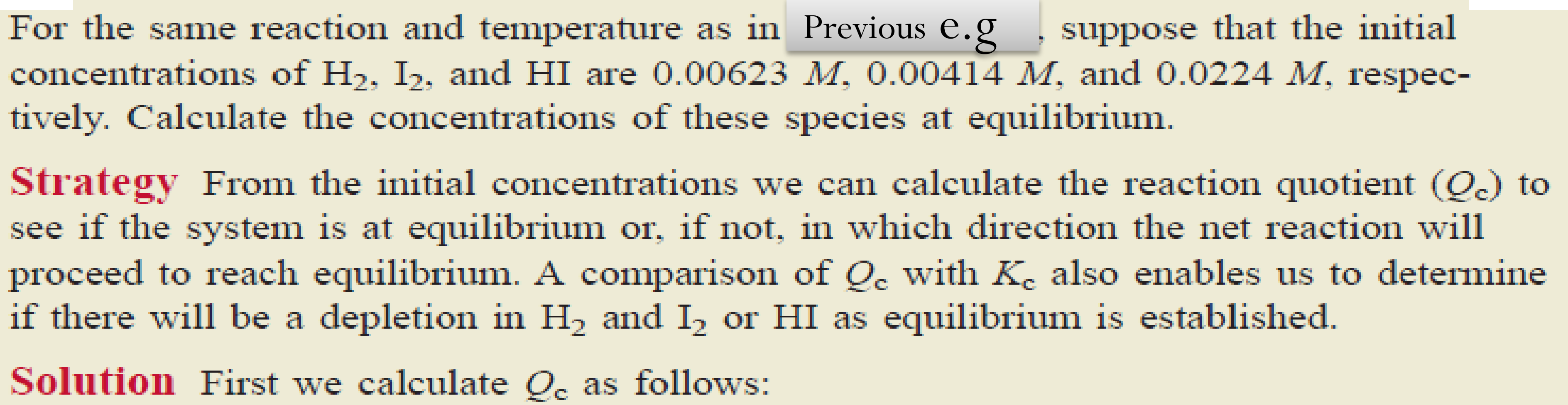
$$x = 0.393\ M$$

Step 3: At equilibrium, the concentrations are

$$[H_2] = (0.500 - 0.393)\ M = 0.107\ M$$

$$[I_2] = (0.500 - 0.393)\ M = 0.107\ M$$

$$[HI] = 2 \times 0.393\ M = 0.786\ M$$



For the same reaction and temperature as in Previous e.g, suppose that the initial concentrations of H_2, I_2, and HI are 0.00623 M, 0.00414 M, and 0.0224 M, respectively. Calculate the concentrations of these species at equilibrium.

Strategy From the initial concentrations we can calculate the reaction quotient (Q_c) to see if the system is at equilibrium or, if not, in which direction the net reaction will proceed to reach equilibrium. A comparison of Q_c with K_c also enables us to determine if there will be a depletion in H_2 and I_2 or HI as equilibrium is established.

Solution First we calculate Q_c as follows:

$$Q_c = \frac{[HI]_0^2}{[H_2]_0[I_2]_0} = \frac{(0.0224)^2}{(0.00623)(0.00414)} = 19.5$$

	H_2	+	I_2	$\rightleftharpoons$	$2HI$
Initial (*M*):	0.00623		0.00414		0.0224
Change (*M*):	$-x$		$-x$		$+2x$
Equilibrium (*M*):	$(0.00623 - x)$		$(0.00414 - x)$		$(0.0224 + 2x)$

Step 2: The equilibrium constant is

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

Substituting, we get

$$54.3 = \frac{(0.0224 + 2x)^2}{(0.00623 - x)(0.00414 - x)}$$

$$54.3(2.58 \times 10^{-5} - 0.0104x + x^2) = 5.02 \times 10^{-4} + 0.0896x + 4x^2$$

Collecting terms, we get

$$50.3x^2 - 0.654x + 8.98 \times 10^{-4} = 0$$

This is a quadratic equation of the form $ax^2 + bx + c = 0$. The solution for a quadratic equation (see Appendix 3) is

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

Here we have $a = 50.3$, $b = -0.654$, and $c = 8.98 \times 10^{-4}$, so that

$$x = \frac{0.654 \pm \sqrt{(-0.654)^2 - 4(50.3)(8.98 \times 10^{-4})}}{2 \times 50.3}$$

$$x = 0.0114\, M \qquad \text{or} \qquad x = 0.00156\, M$$

The first solution is physically impossible because the amounts of H_2 and I_2 reacted would be more than those originally present. The second solution gives the correct answer. Note that in solving quadratic equations of this type, one answer is always physically impossible, so choosing a value for x is easy.

At equilibrium, the concentrations are

$$[H_2] = (0.00623 - 0.00156)\, M = \boxed{0.00467\, M}$$

$$[I_2] = (0.00414 - 0.00156)\, M = \boxed{0.00258\, M}$$

$$[HI] = (0.0224 + 2 \times 0.00156)\, M = \boxed{0.0255\, M}$$

Le Châtelier's Principle

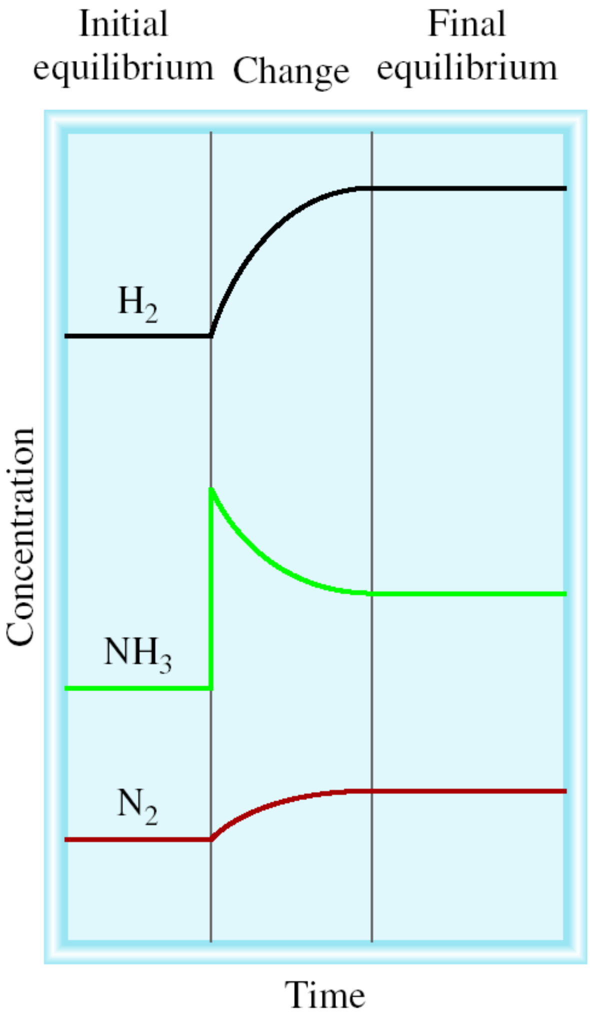
If an external stress is applied to a system at equilibrium, the system adjusts in such a way that the stress is partially offset as the system reaches a new equilibrium position.

- Changes in Concentration

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

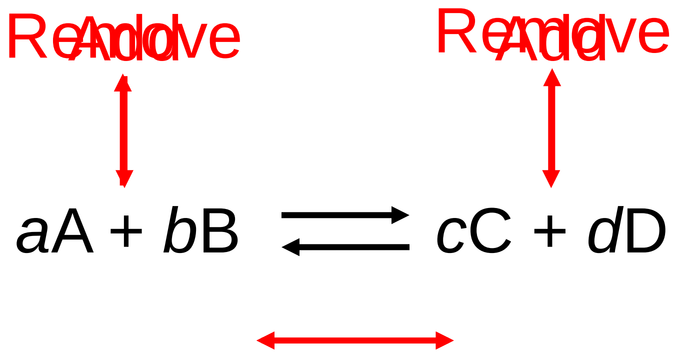
Add NH_3

Equilibrium shifts left to offset stress ←



Le Châtelier's Principle

- Changes in Concentration continued



Remove Add   Remove Add

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

Change	**Shifts the Equilibrium**
Increase concentration of product(s)	left
Decrease concentration of product(s)	right
Increase concentration of reactant(s)	right
Decrease concentration of reactant(s)	left

Le Châtelier's Principle

- Changes in Volume and Pressure

$$\mathrm{A}\,(g) + \mathrm{B}\,(g) \underset{\longleftrightarrow}{\rightleftharpoons} \mathrm{C}\,(g)$$

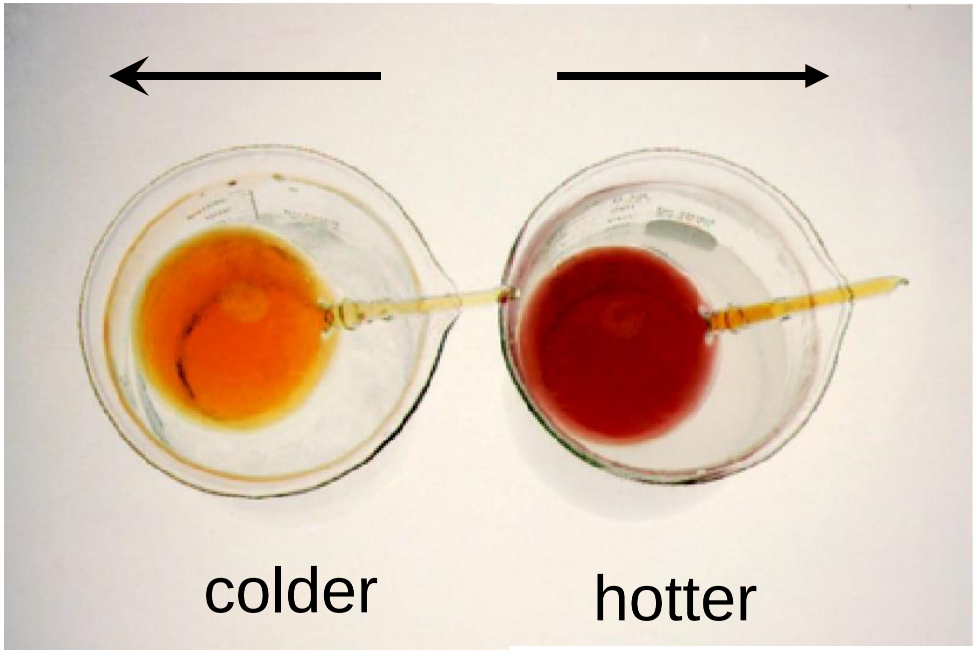
Change	**Shifts the Equilibrium**
Increase pressure	Side with fewest moles of gas
Decrease pressure	Side with most moles of gas
Increase volume	Side with most moles of gas
Decrease volume	Side with fewest moles of gas

Le Châtelier's Principle

- Changes in Temperature

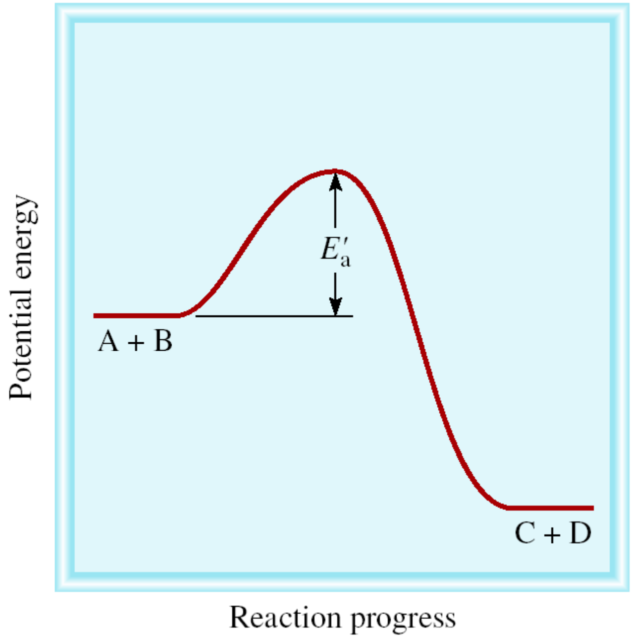
Change	**Exothermic Rx**	**Endothermic Rx**
Increase temperature	*K* decreases	*K* increases
Decrease temperature	*K* increases	*K* decreases

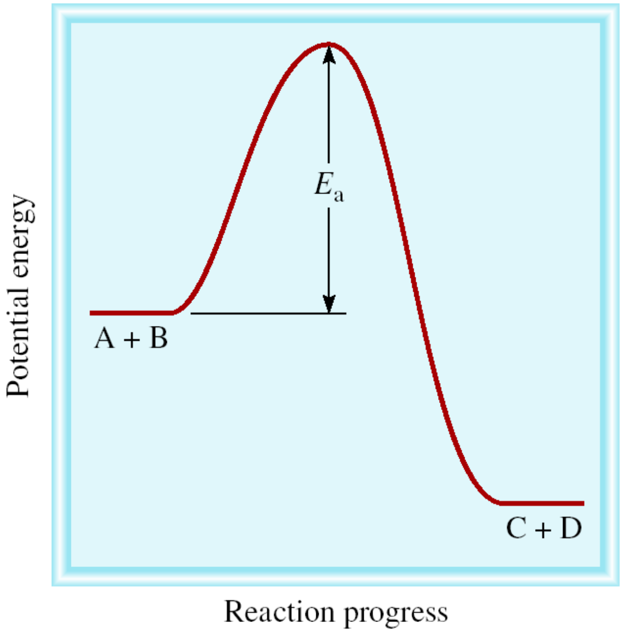
$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$ $\Delta H^\circ = 58.0\ \mathrm{kJ/mol}$



Le Châtelier’s Principle

- Adding a Catalyst
  - does not change *K*
  - does not shift the position of an equilibrium system
  - system will reach equilibrium sooner





Catalyst lowers E_a for **both** forward and reverse reactions.

Catalyst does not change equilibrium constant or shift equilibrium.

Le Châtelier’s Principle - Summary

Change	Shift Equilibrium	Change Equilibrium Constant
Concentration	yes	no
Pressure	yes*	no
Volume	yes*	no
Temperature	yes	yes
Catalyst	no	no

*Dependent on relative moles of gaseous reactants and products