Chapter 16: Chemical Equilibrium

Chem 102
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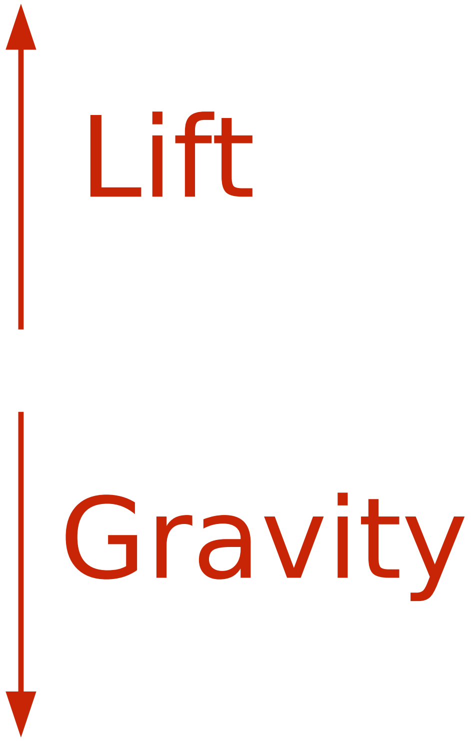
Equilibrium

State in which competing processes are balanced so that no observable change takes place as time passes.



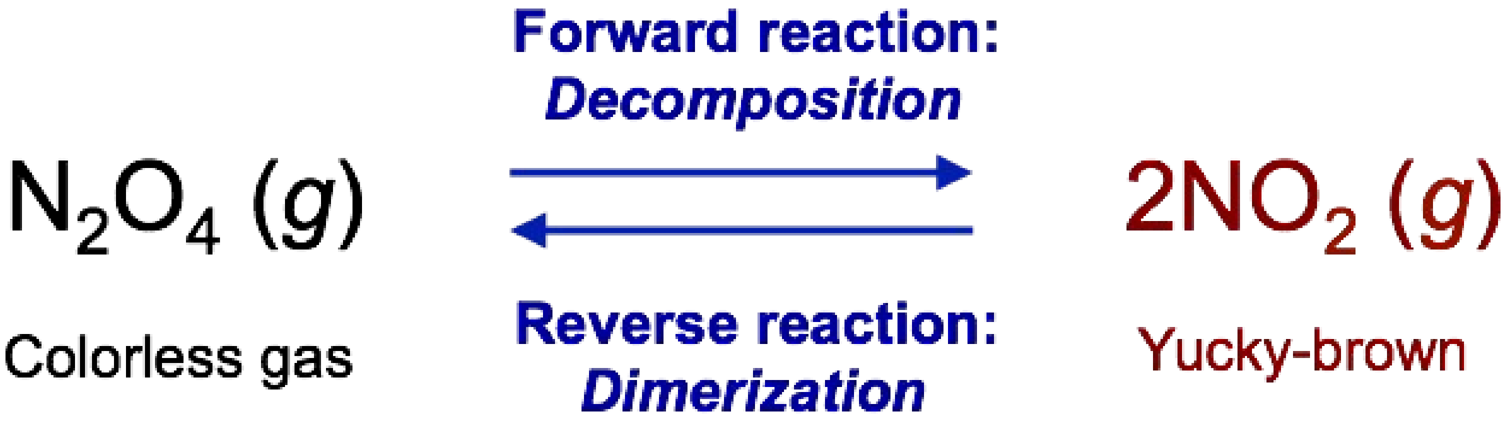
Sometimes called “dynamic equilibrium”

Physical Equilibrium

- Balance of competing physical processes:
  - Evaporation vs. condensation
  - Freezing vs. melting
- At equilibrium: **rate** of evaporation equals **rate** of condensation
- Net result: No observable change (individual molecules move in a balanced way)

Chemical Equilibrium

- Balance of two or more chemical reactions



Forward reaction: ***Decomposition***

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

Reverse reaction: ***Dimerization***

Colorless gas

Yucky-brown

- At equilibrium: **rate** of decomposition equals **rate** of dimerization
- $[N_2O_4]$ and $[NO_2]$ do not change over time
- Individual molecules react but in a balanced way

Dynamic equilibrium

rate of forward reaction = **rate** of reverse reaction

- Reactions are still occurring, but the rates are equal
- An individual molecule could react (or not)
- No net change in concentrations of reactants or products over time
- Concentrations of reactants and products are not necessarily equal to each other!
- All chemical reactions are theoretically reversible, but sometimes this can be ignored because reverse rate is very small

Dynamic Equilibrium

$$\mathrm{H_2(g) + I_2(g) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2\ HI(g)}$$

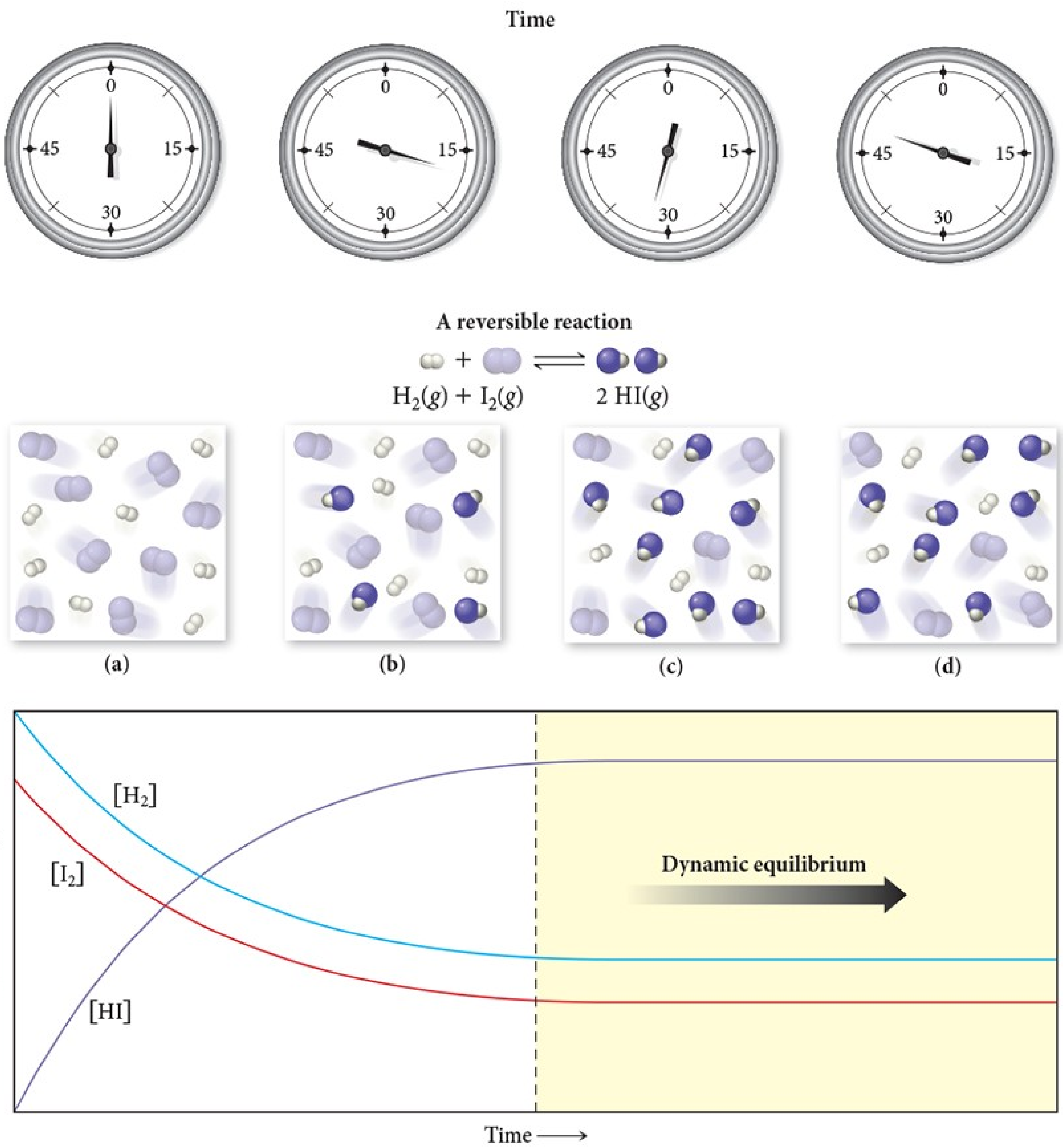
- At equilibrium:
  - forward rate = reverse rate
  - Note: k_f does not necessarily equal k_r

Side note:
IUPAC prefers: ⇌
May use: ⇄
Do not use ⟷, ⇔, ⇀

$$Rate_f = k_f[H_2]^a[I_2]^b$$
$$Rate_r = k_r[HI]^c$$

$$k_f[H_2]^a[I_2]^b = k_r[HI]^c$$

Dynamic Equilibrium



As concentration of product increases, and concentrations of reactants decrease, rate of forward reaction slows down, and rate of reverse reaction speeds up.

Dynamic equilibrium: Rate of forward reaction = rate of reverse reaction. Concentrations of reactant(s) and product(s) no longer change.

The Equilibrium Constant, *K*

- Concentrations of the reactants and products are not necessarily equal at equilibrium
- Quantify relative concentrations (<u>at equilibrium</u>) with the equilibrium constant (K)

$$\mathrm{aA + bB \rightleftharpoons cC + dD}$$

Law of mass action:

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

Products

Reactants

Note: Upper case K and lower case k are different quantities!

Relationship between *K* and *k*

For an **elementary step** at equilibrium (= we know the reaction order from the coefficients):

$$\mathrm{aA + bB \underset{k_r}{\overset{k_f}{\rightleftharpoons}} cC + dD}$$

$$Rate_f = Rate_r$$

$$k_f[A]^a[B]^b = k_r[C]^c[D]^d$$

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

Equilibrium constant - notes

- Do not include pure liquids or solids in *K* expression
  (later: their activity is equal to one)
- Solutions: Use <u>molarity</u> (M) units
- Gases: Use <u>pressure</u> in atmospheres (atm)
- *K* has <u>no units</u>, regardless of the form of the equation
  (you can learn more about this in Chem 321/351)
- *K* is temperature dependent
- More later:
  K_c for solutions (concentration - M)
  K_p for gases (partial pressure - atm)

Significance of *K*

- What does the magnitude of *K* tell us about the reaction at equilibrium?

$$\mathrm{H_2 + Br_2 \rightleftharpoons 2\,HBr} \qquad K = \frac{[HBr]^2}{[H_2][Br_2]} = 1.9 \times 10^{19}$$

- At equilibrium, would you expect a higher concentration of reactants or products?

(equilibrium is far to the right)

Significance of *K*

- What does the magnitude of *K* tell us about the reaction at equilibrium?

$$N_2 + O_2 \rightleftharpoons 2\,NO \qquad K = \frac{[NO]^2}{[N_2][O_2]} = 4.1 \times 10^{-31}$$

- At equilibrium, would you expect a higher concentration of reactants or products?

(equilibrium is far to the left)

K math rules

If you reverse the reaction (as written), invert *K*:

$$\mathrm{A} + 2\,\mathrm{B} \rightleftharpoons 3\,\mathrm{C} \quad K_{forward} = \frac{[C]^3}{[A][B]^2}$$

$$3\,\mathrm{C} \rightleftharpoons \mathrm{A} + 2\,\mathrm{B} \quad K_{reverse} = \frac{[A][B]^2}{[C]^3}$$

$$K_{reverse} = \frac{1}{K_{forward}}$$

K math rules

If you multiply an equation by a factor, raise the equilibrium constant to the same factor:

$$\mathrm{A} + 2\,\mathrm{B} \rightleftharpoons 3\,\mathrm{C} \qquad K_{forward} = \frac{[C]^3}{[A][B]^2}$$

$$2 \times (\mathrm{A} + 2\,\mathrm{B} \rightleftharpoons 3\,\mathrm{C})$$

$$2\,\mathrm{A} + 4\,\mathrm{B} \rightleftharpoons 6\,\mathrm{C}$$

$$K' = \frac{[C]^6}{[A]^2[B]^4} = \left(\frac{[C]^3}{[A][B]^2}\right)^2$$

So, $K' = K_{forward}^2$.

K math rules

If you add two equations to get an overall reaction, multiply the equilibrium constants to get the overall equilibrium constant:

$$\mathrm{A} \rightleftharpoons 2\,\mathrm{B} \quad K_1 = \frac{[B]^2}{[A]}$$

$$2\,\mathrm{B} \rightleftharpoons 3\,\mathrm{C} \quad K_2 = \frac{[C]^3}{[B]^2}$$

$$+ \quad \overline{\phantom{\mathrm{A} \rightleftharpoons 3\,\mathrm{C}\quad}}$$

$$\mathrm{A} \rightleftharpoons 3\,\mathrm{C} \quad K_{overall} = K_1 \times K_2 = \frac{[C]^3}{[A]}$$

K_c and K_p

- K_c refers to K with units of molarity
- K_p refers to K using the partial pressure of the gases in units of atmospheres:

$$\mathrm{aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)} \quad K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

- The two are related to one another via the ideal gas law:

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

- Here: $R = 8.314$ J / (K mol) or 0.08206 L atm / (mol K)
- Δn = difference in total moles of gas (= gas moles in products minus gas moles in reactants)

Heterogeneous equilibria

- Heterogeneous: More than one state present (solid, liquid, gas)
- Remember: do not include pure solids or liquids in *K*

$$2\,\mathrm{CO(g)} \rightleftharpoons \mathrm{CO_2(g)} + \mathrm{C(s)}$$

$$K_c = \frac{[CO_2]\cancelto{1}{[C]}}{[CO]^2} = \frac{[CO_2]}{[CO]^2}$$

Heterogeneous equilibrium example

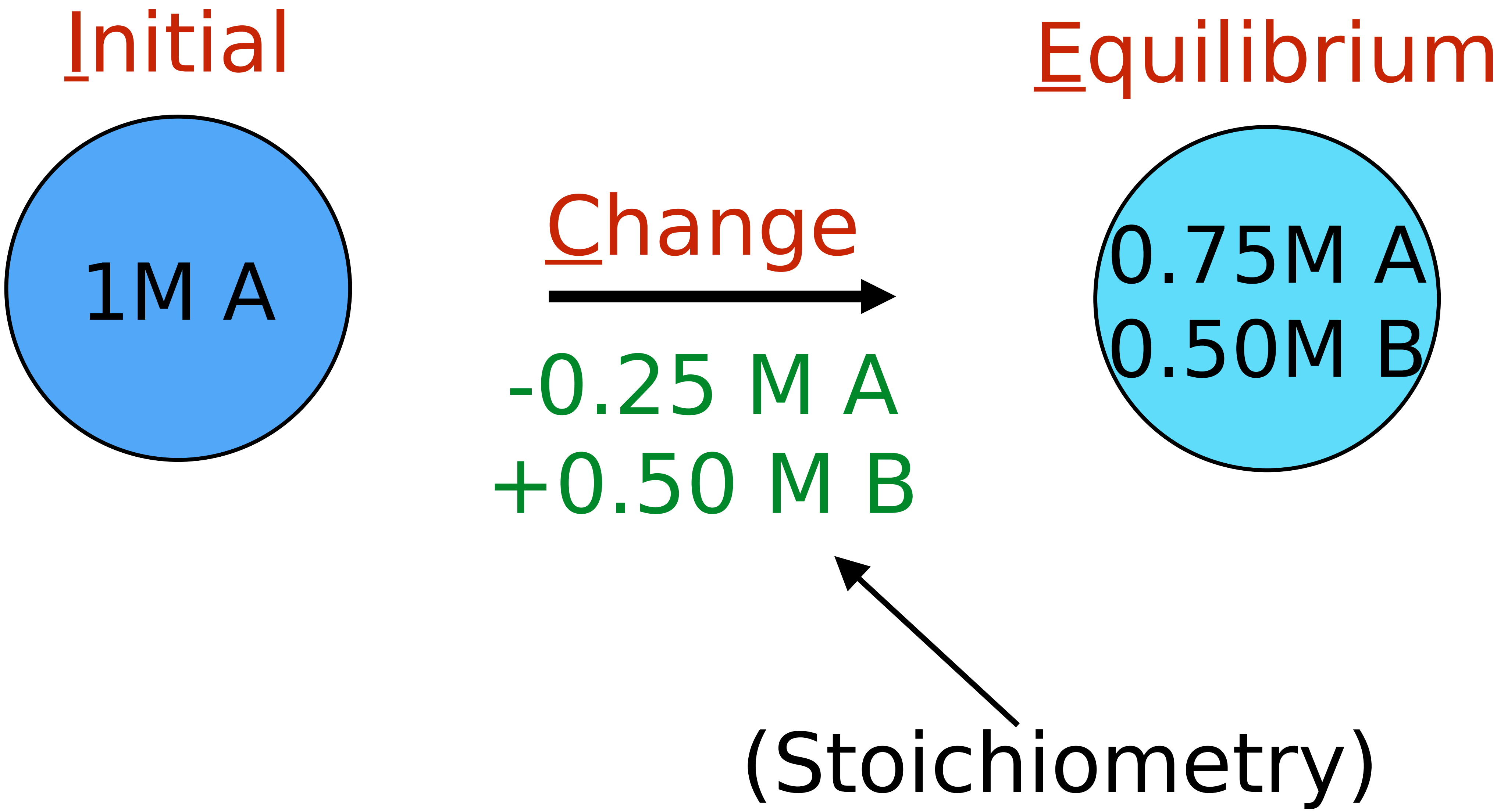
- Write *K* expression for:

$$CO_2(g) + H_2O(\ell) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

$$K_c = \frac{[H^+][HCO_3^-]}{[CO_2]}$$

Concentration changes during a reaction to reach equilibrium

Given the following balanced reaction: A(g) ⇌ 2 B(g)



Initial

1M A

Change

-0.25 M A

+0.50 M B

Equilibrium

0.75M A

0.50M B

(Stoichiometry)

The Reaction Quotient, *Q*

- Given a set of conditions, can we predict which way the reaction will proceed?
- *Q* is defined the same way as *K*, except *Q* is the ***actual*** ratio of products to reactants under given conditions, ***not necessarily at equilibrium***

$$\mathrm{aA} + \mathrm{bB} \rightleftharpoons \mathrm{cC} + \mathrm{dD}$$

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

K is always evaluated using equilibrium concentrations!

Q example

$$\mathrm{aA} + \mathrm{bB} \rightleftharpoons \mathrm{cC} + \mathrm{dD}$$

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

- Say you start a reaction with mostly reactants present
    - Q = 0
- Say you start a reaction with mostly products present
    - Q = large
- Say you have equilibrium concentrations of reactants and products
    - Q = K

Reaction quotient, *Q*

We can compare Q and K to determine

- Is the reaction at equilibrium?
- If not at equilibrium, which direction would the reaction need to proceed to reach equilibrium?

Relationship	Condition	Direction
$Q = K$	At equilibrium	At equilibrium (no change)
$Q < K$	Too little product / too much reactant	Toward products (to the right)
$Q > K$	Too much product / too little reactant	Toward reactants (to the left)

Reaction quotient, *Q*

Given the following concentrations, which way would the reaction proceed to try to reach equilibrium?

$$A \rightleftharpoons B \qquad K = \frac{[B]}{[A]} = 5 \qquad Q = \frac{[B]}{[A]}$$

Equilibrium concentrations!

[A] (M)	[B] (M)	*Q*	Reaction direction?
3.0	1.0		
1.0	1.0		
5.0	1.0		
3.0	1.5		

ICE Charts or ICE Tables (aka BRA Charts)

Set up a table to describe what will happen in the reaction

- Units are always M or atm (we should really be using Pascals...)
- Use *Q* to determine which way the reaction will proceed

$$A \rightleftharpoons B$$

	A	$\rightleftharpoons$	B
Initial	Initial [A] (M)		Initial [B] (M)
Change	Quantity changed in the reaction (M)		Quantity changed in the reaction (M)
Equilibrium	Equilibrium [A] (M)		Equilibrium [B] (M)

ICE Charts: Example 1

Given an initial set of conditions, and a value for *K*, can we determine the equilibrium concentrations?

$$A \rightleftharpoons B \qquad K = \frac{[B]}{[A]} = 5$$

	A	⇌	B
Initial	1.0 (M)		0.0 (M)
Change	-x		+x
Equilibrium	1.0 - x		x

Plug in and solve:

$$K = \frac{[B]}{[A]} = 5 = \frac{x}{1-x}$$

$$5 - 5x = x$$

$$5 = 6x$$

$$x = 0.83$$

At equilibrium:
[A] = 0.17 M = 1 - 0.83
[B] = 0.83 M

ICE Charts: Example 2

A ⇌ B

$$K = \frac{[B]}{[A]} = 5$$

$$Q = \frac{[B]}{[A]} = \frac{1.0\ M}{1.0\ M} = 1$$

	A	⇌	B
Initial	1.0 (M)		1.0 (M)
Change	-x		+x
Equilibrium	1.0 - x		1.0 + x

$$K = \frac{1.0 + x}{1.0 - x} = 5$$

$$x = 0.67\ M$$

At equilibrium:
[A] = 0.33 M
[B] = 1.67 M

Stoichiometry matters: Example 3

$Cl_2(g) \rightleftharpoons 2\,Cl(g)$, $K = 0.2$ (not really, used for simplicity)

	$Cl_2(g)$	$\rightleftharpoons$	$2\,Cl(g)$
Initial	1.0 (M)		0.0 (M)
Change	$-x$		$+2x$
Equilibrium	$1.0 - x$		$2x$

$$K = \frac{[Cl]^2}{[Cl_2]}$$

$$0.2 = \frac{(2x)^2}{1-x} = \frac{4x^2}{1-x}$$

$$0.2 - 0.2x = 4x^2$$

$$4x^2 + 0.2x - 0.2 = 0$$

Quadratic equation!!!

Quadratic Equation

$$For\ ax^2 + bx + c = 0 \qquad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$4x^2 + 0.2x - 0.2 = 0$$

$$x = \frac{-0.2 \pm \sqrt{0.2^2 - 4 \times 4 \times (-0.2)}}{2 \times 4}$$

$$x = 0.2 \text{ M or } x = -0.25 \text{ M}$$

Cannot have a negative concentration, so x = 0.2 M.

$[Cl_2] = 1.0 - x = 0.8$ M $\quad [Cl] = 2x = 0.4$ M

Multiple reactants/products: Example 4

$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \quad K = 4.3\text{x}10^{-7}$

	$H_2CO_3(aq)$	$\rightleftharpoons$	$H^+(aq)$	$HCO_3^-(aq)$
Initial	0.1 M		0 M	0 M
Change	$-x$		$+x$	$+x$
Equilibrium	$0.1 - x$		x	x

$$K = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = \frac{x^2}{0.1 - x} = 4.3 \times 10^{-7}$$

$$x = 0.000207\ M$$

A shortcut for quadratic equations

If *x* < 5% of the term you compare it with, you can ignore it in the denominator to simplify the equation:

$$K = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = \frac{x^2}{0.1 - x} = 4.3 \times 10^{-7}$$

Assume *x* is small compared to 0.1

$$K = \frac{x^2}{0.1} = 4.3 \times 10^{-7}$$

Much easier to solve: $x = 0.000207\ M$

Must test our assumption to see if it was valid

In the previous case, we assumed *x* < 5% of 0.1.

Is this true?

$$\frac{0.000207\ \mathrm{M}}{0.1\ \mathrm{M}} \times 100\% = 0.21\%$$

In this case, we made a good assumption (0.21% < 5%)

Notice that we got the same answer (within rounding).

Note: *x* is not zero, just small.

Method of successive approximations

$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$ $K = 7.2\text{x}10^{-4}$

	HF(aq)	$\rightleftharpoons$	$H^+(aq)$	$F^-(aq)$
Initial	0.01 M		0 M	0 M
Change	$-x$		$+x$	$+x$
Equilibrium	$0.01 - x$		x	x

$$\frac{x^2}{0.01 - x} = 7.2 \times 10^{-4}$$

Method of Successive Approximations

$$\frac{x^2}{0.01 - x} = 7.2 \times 10^{-4}$$

$$\frac{x^2}{0.01} = 7.2 \times 10^{-4}$$

$$x = 0.00268\ M$$

$$\frac{0.00268\ M}{0.01\ M} \times 100\% = 27\%$$

- Clearly, our assumption was bad, > 5 %!
- Cannot use this answer
- Must solve exactly with quadratic equation

$$\frac{x^2}{0.01 - x} = 7.2 \times 10^{-4}$$

$$x = 0.00235\ M$$

Method of Successive Approximations

- Quadratic equation slows down calculations
- Often it is also possible to obtain the solution by iteration:

  Take your answer from assuming *x* was small

  First approximation

$$\frac{x^2}{0.01 - x} = 7.2 \times 10^{-4}$$

$$\frac{x^2}{0.01} = 7.2 \times 10^{-4}$$

$$x = 0.00268\ M$$

Method of successive approximations

Plug back into your equation and solve for *x* again:

$$\frac{x^2}{0.01 - x} = 7.2 \times 10^{-4}$$

$$\frac{x^2}{0.01} = 7.2 \times 10^{-4}$$

$$x = 0.00268\ M$$

2nd approximation

$$\frac{x^2}{0.01 - 0.00268} = 7.2 \times 10^{-4}$$

$$\frac{x^2}{0.00732} = 7.2 \times 10^{-4}$$

$$x = 0.00230$$

3rd approximation

Method of successive approximations

Plug back into your equation and solve for *x* again:

$$\frac{x^2}{0.01 - 0.00230} = 7.2 \times 10^{-4}$$

$$x = 0.00236\ M$$

4th approximation

$$\frac{x^2}{0.01 - 0.00236} = 7.2 \times 10^{-4}$$

$$x = 0.00230$$

$$x = 0.00235\ M$$

5th approximation

Usually within 3-5 iterations, *x* will be obtained with sufficient accuracy

Method of successive approximations

$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq) \qquad K = 7.2\times10^{-4}$

	$HF(aq)$	$\rightleftharpoons$	$H^+(aq)$	$F^-(aq)$
Initial	0.01 M		0 M	0 M
Change	$-x$		$+x$	$+x$
Equilibrium	$0.01 - x$		x	x

$$x = 0.00235\ M$$

At equilibrium: $[H^+] = 0.002$ M
$[HF] = 0.008$ M $[F^-] = 0.002$ M

(after rounding to correct sig. figs.)

Le Chatelier’s Principle

How does a system at equilibrium respond to disturbances?

Henry Louis Le Châtelier
1850 - 1936

When a chemical system at equilibrium is disturbed, the system shifts in a direction that minimizes the disturbance.

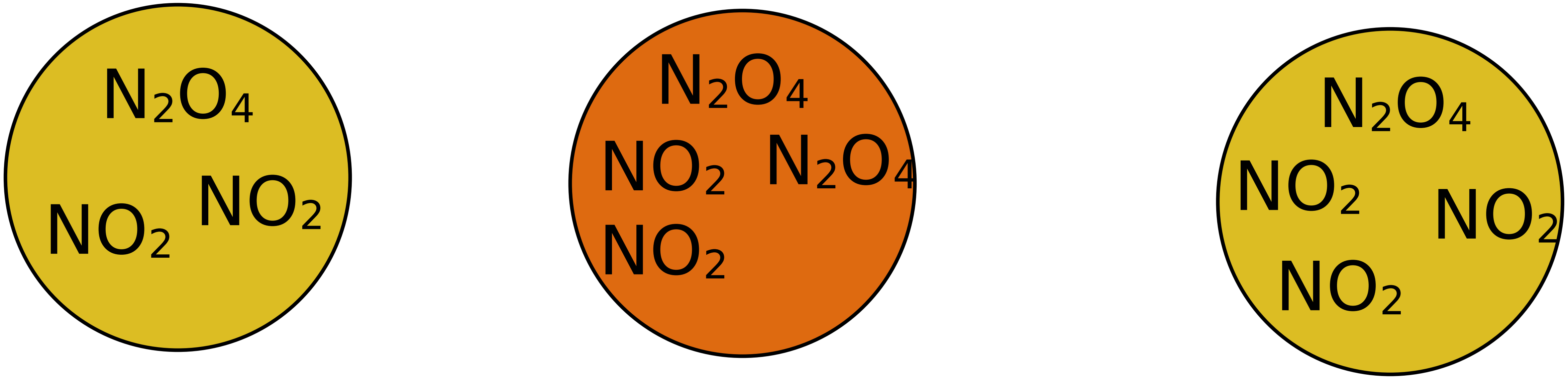
Example - Changing concentration

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

At equilibrium

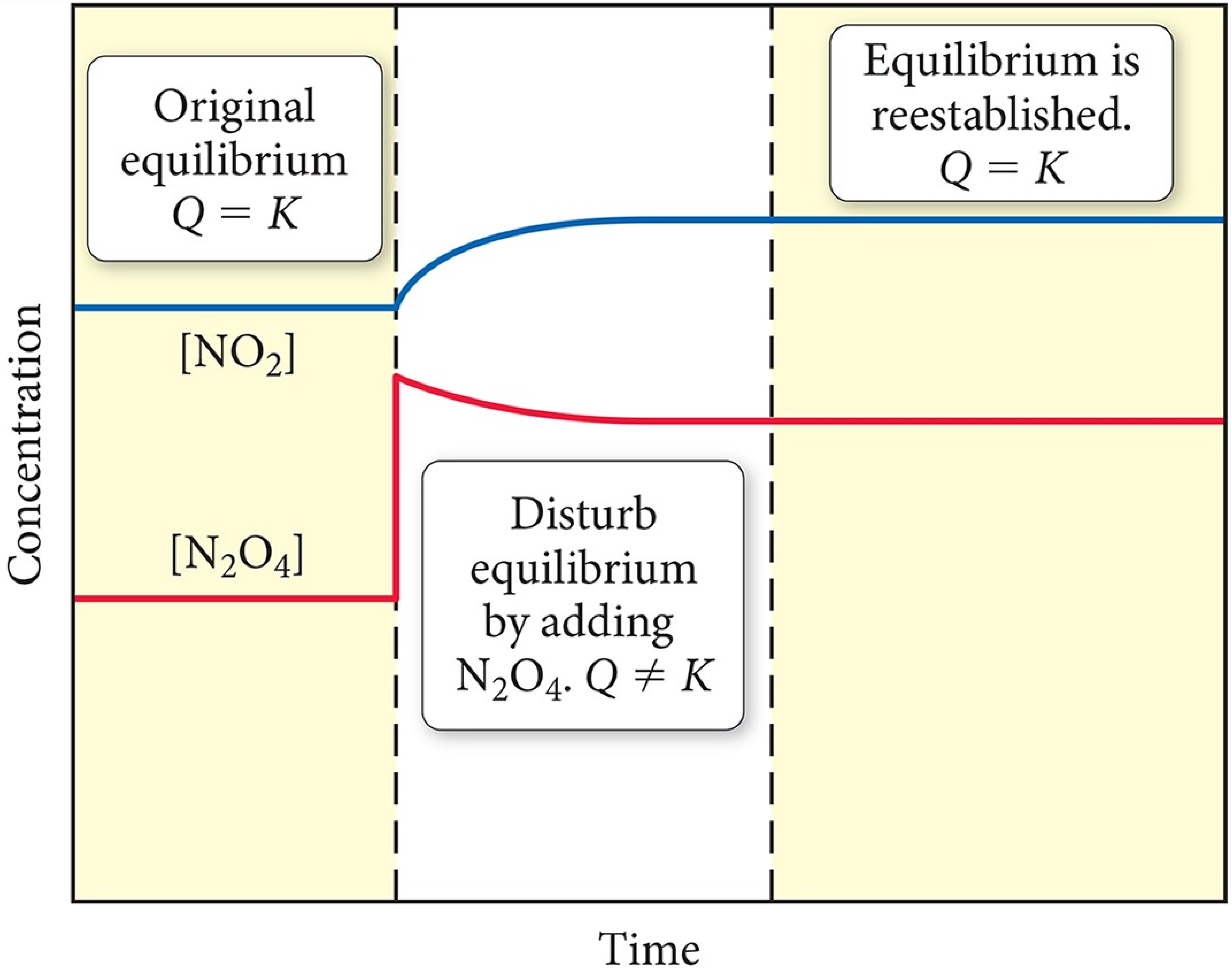
Add extra N_2O_4

N_2O_4 will react to reach equilibrium again



Adding a higher concentration of reactant will cause the equilibrium to shift right to attempt to reach equilibrium again ($Q = K$)

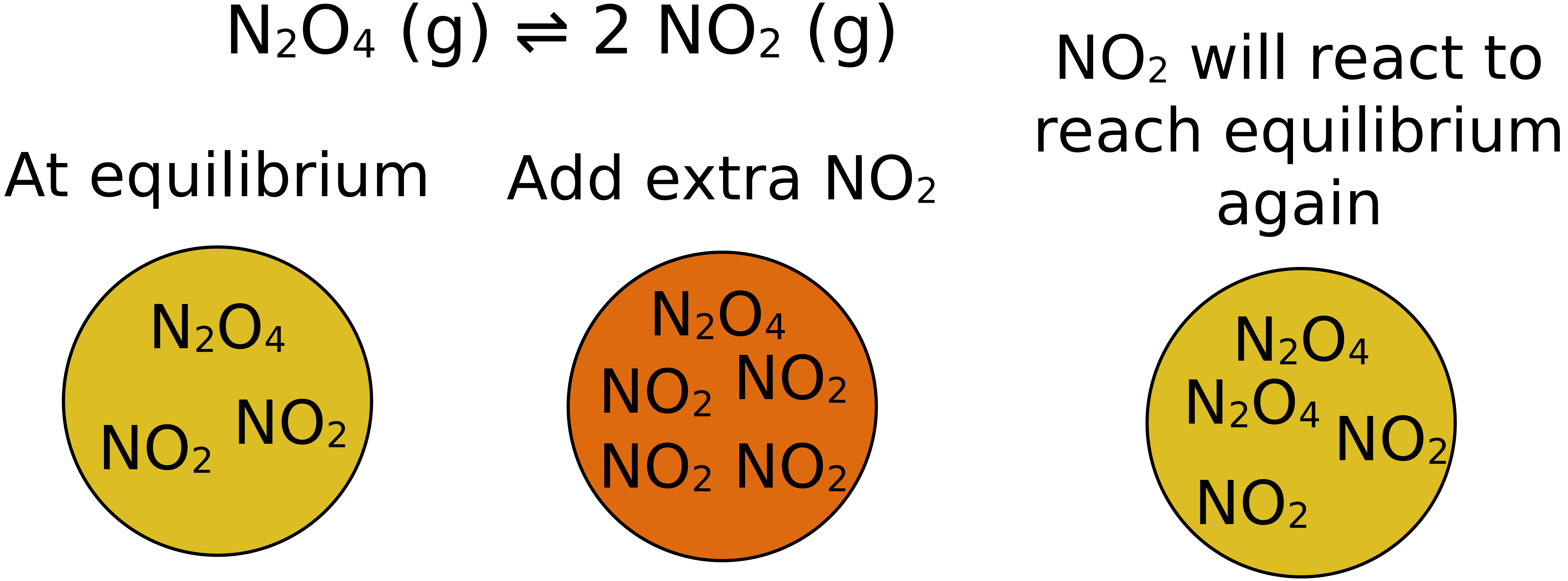
$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$



(b)

Example - Changing concentration

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



At equilibrium

N_2O_4

NO_2 NO_2

Add extra NO_2

N_2O_4

NO_2 NO_2

NO_2 NO_2

NO_2 will react to reach equilibrium again

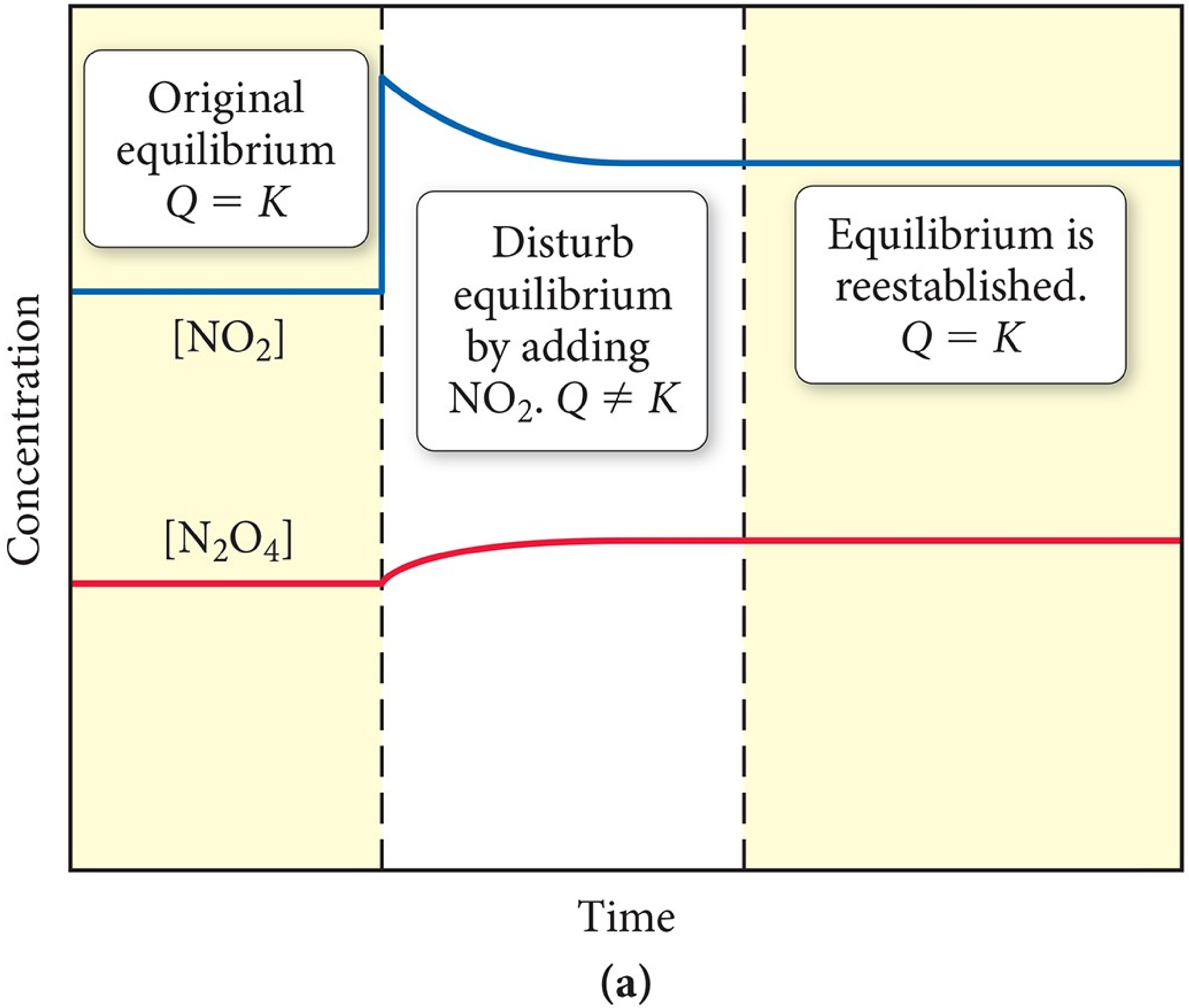
N_2O_4

N_2O_4 NO_2

NO_2

- Adding a higher concentration of product will cause the equilibrium to shift left to attempt to reach equilibrium again ($Q = K$)

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



Effect of concentration change on equilibrium

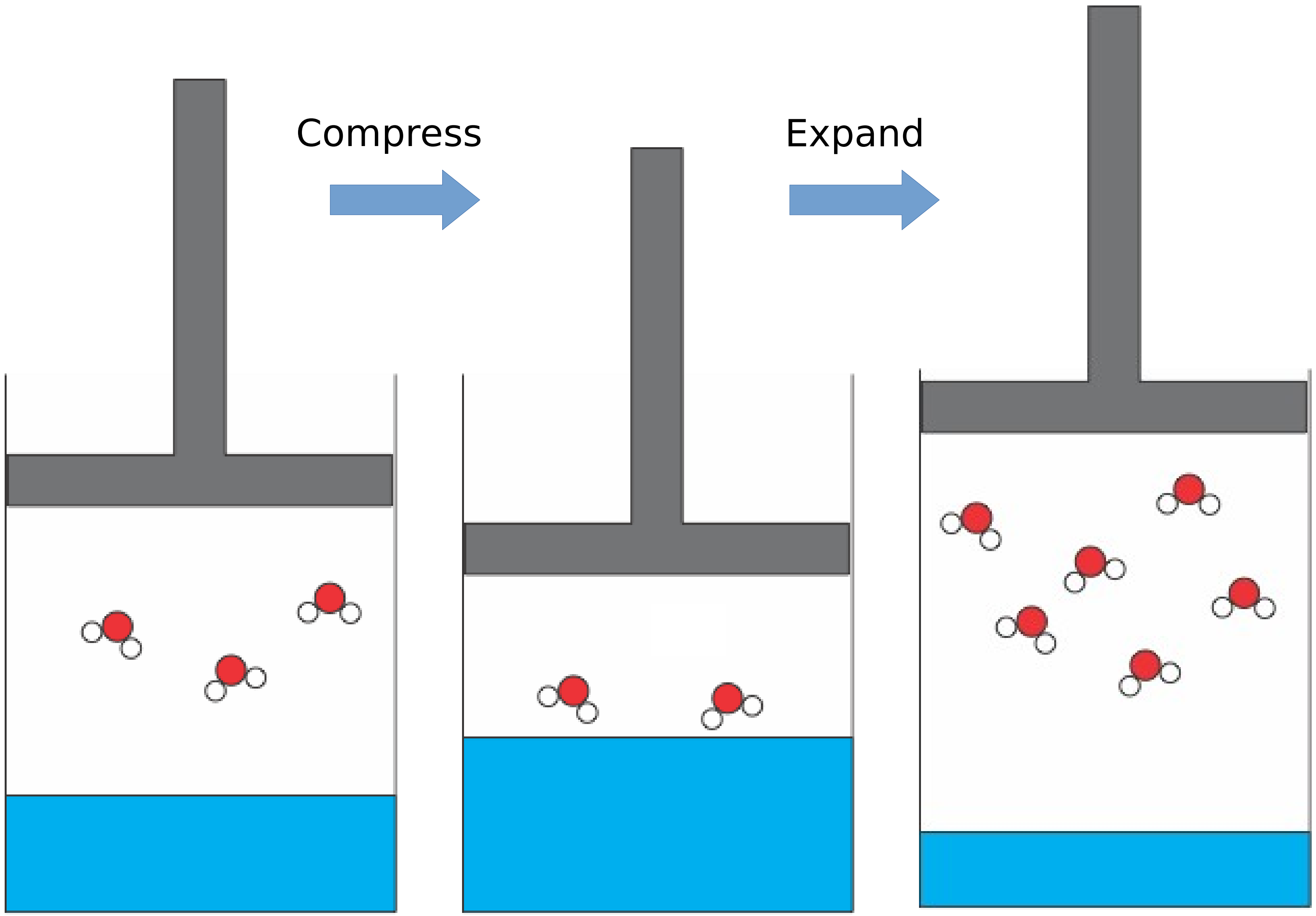
- Increasing concentration of one or more reactant ($Q < K$)
  Reaction will shift right (toward products)
- Increasing concentration of one or more products ($Q > K$)
  Reaction will shift left (toward reactants)

- Decreasing concentration of one or more reactants ($Q > K$)
  Reaction will shift left (toward reactants)
- Decreasing concentration of one or more products ($Q < K$)
  Reaction will shift right (toward products)

K is constant, concentrations are changing such that $Q \rightarrow K$

Volume/Pressure changes in equilibrium

$$H_2O\ (\ell) \rightleftharpoons H_2O\ (g)$$



Higher *P*:
Equilibrium shifts left
(away from gas)

Lower *P*:
Equilibrium shifts right
(toward gas)

“Gas would like to occupy more space than liquid”

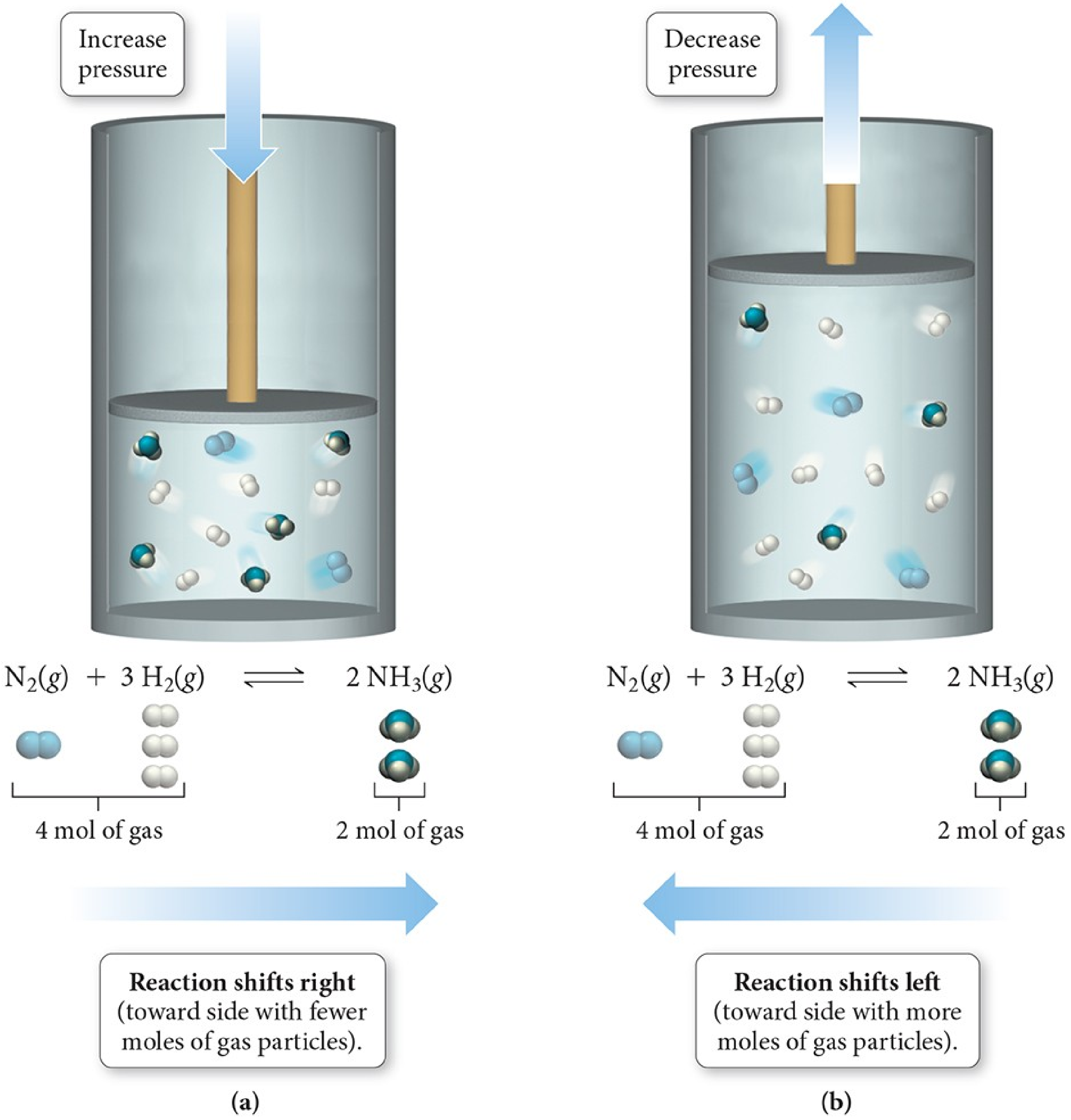
Volume/Pressure changes in equilibrium

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

Higher *P*:
Equilibrium shifts
toward fewer moles of gas

Lower *P*:
Equilibrium shifts
toward more moles of gas

Le Châtelier's Principle: Changing Pressure



Effect of volume (or pressure) change on equilibrium

- Decreasing volume (increasing pressure) causes equilibrium to shift to fewer moles of gas particles
- Increasing volume (decreasing pressure) causes equilibrium to shift to more moles of gas particles

- If equal number of moles of gas on both sides of the reaction, change in volume or pressure has no effect
- Adding an inert gas to a mixture (at fixed volume) has no effect

- *K* is constant as long as *T* is constant

Le Chatelier's Principle and Temperature

- Think of heat as a "reactant" or "product"

- Exothermic reaction: $A + B \rightleftharpoons C + D$ + "heat"
- Endothermic reaction: $A + B$ + "heat" $\rightleftharpoons C + D$

- Adding or removing heat will change the equilibrium

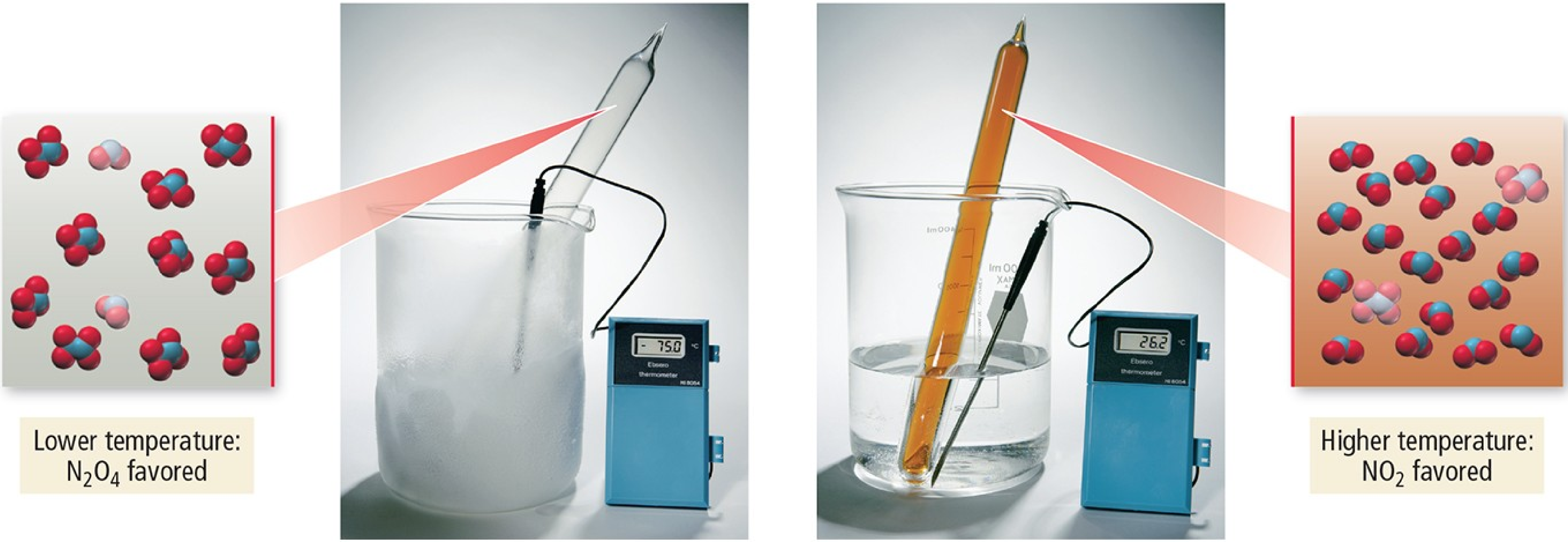
  removing heat = lowering *T*

  adding heat = increasing *T*
- *K* is changing in this case, K = K(T).

Le Châtelier's Principle: Changing Temperature

$$\underset{\text{colorless}}{N_2O_4(g)} + \text{heat} \rightleftharpoons \underset{\text{brown}}{2\,NO_2(g)}$$

Endothermic reaction



Lower temperature: N_2O_4 favored

Higher temperature: NO_2 favored

Le Chatelier’s Principle and Temperature

- Increasing temperature: Exothermic reaction shifts toward reactants
- Increasing temperature: Endothermic reaction shifts toward products

- Decreasing temperature: Exothermic reaction shifts toward products
- Decreasing temperature: Endothermic reaction shifts toward reactants

- Adding heat favors endothermic reaction
- Removing heat favors exothermic reaction

General tips for this section

- Understand definitions:

  Dynamic equilibrium, how rates relate, equilibrium constant, K_c vs. K_p, reversibility, etc.
- Understand Q vs. K:

  Which way will the reaction proceed?
- Understand ICE charts - be able to solve any ice chart:
  - May need quadratic equation or successive approx.
  - Understand the 5 % validity test
- Le Chatelier's principle: concentration change, pressure/ volume change, temperature change.

Additional example #1

What is the value of K_c for the reaction

$$2\ CH_4(g) \rightleftharpoons C_2H_2(g) + 3\ H_2(g)$$

if we start with only CH_4, the initial $[CH_4]$ is 0.300 M and the equilibrium $[C_2H_2] = 0.045$ M?

Note, we have a mixture of some initial and some equilibrium concentrations.

The best way to answer this problem is using an **ICE table.**

Additional example #1

1. First set up the ICE table and add the values in the problem

$$2\ CH_4(g) \rightleftharpoons C_2H_2(g) + 3\ H_2(g)$$

	$[CH_4]$	$[C_2H_2]$	$[H_2]$
Initial	**0.300 M**	**0.000 M**	**0.000 M**
Change			
Equilibrium		**0.045 M**	

Additional example #1

2. For a substance whose initial and equilibrium concentrations are known, complete ‘change’

$$2\ CH_4(g) \rightleftharpoons C_2H_2(g) + 3\ H_2(g)$$

	$[CH_4]$	$[C_2H_2]$	$[H_2]$
Initial	0.300 M	0.000 M	0.000 M
Change		**+0.045 M**	
Equilibrium		0.045 M	

Additional example #1

3. Use reaction stoichiometry to complete the rest of the 'change' row

$$\textcircled{2}\,CH_4(g) \rightleftharpoons C_2H_2(g) + \textcircled{3}\,H_2(g)$$

	$[CH_4]$	$[C_2H_2]$	$[H_2]$
Initial	0.300	0.000	0.000
Change	**-0.090**	← x2 +0.045 x3 →	**+0.135**
Equilibrium		0.045	

Signs are important!

Additional example #1

4. Sum each column to find the equilibrium concentrations of all substances

$$2\ CH_4(g) \rightleftharpoons C_2H_2(g) + 3\ H_2(g)$$

	$[CH_4]$	$[C_2H_2]$	$[H_2]$
Initial	0.300	0.000	0.000
Change	+ -0.090	+0.045	+ +0.135
Equilibrium	= **0.210**	0.045	= **0.135**

Additional example #1

5. Finally, use the **equilibrium concentrations** to calculate K_c

$$2\ CH_4(g) \rightleftharpoons C_2H_2(g) + 3\ H_2(g)$$

$$K_c = \frac{[C_2H_2]\cdot[H_2]^3}{[CH_4]^2}$$

$$= \frac{0.045 \times 0.135^3}{0.210^2}$$

$$= 2.51\text{x}10^{-3}$$

K_c is small, equilibrium lies on the left

We calculated K_c even without all equilibrium concentrations in the problem

Additional example #2

When given K_c and all but one of the equilibrium concentrations, what is the equilibrium $[CO_2]$ in the reaction: $2\ COF_2(g) \rightleftharpoons CO_2(g) + CF_4(g)$

if $K_c = 2.00$ at 1000 °C, the equilibrium $[COF_2] = 0.255$ M and equilibrium $[CF_4] = 0.118$ M?

We know all terms except $[CO_2]$

$$\overset{\checkmark}{K_c} = \frac{[CO_2]\cdot\overset{\checkmark}{[CF_4]}}{\underset{\checkmark}{[COF_2]^2}}$$

Additional example #2

To solve, simply rearrange the K_c equation

$$K_c = \frac{[CO_2]\cdot[CF_4]}{[COF_2]^2}$$

To check, insert values into expression
$K_c = 1.99 \approx 2.00$

$$[CO_2] = \frac{K_c \cdot [COF_2]^2}{[CF_4]}$$

$$= \frac{2.00 \times (0.255\ M)^2}{0.118\ M}$$

$$= 1.10\ M$$

Additional example #3

What is the equilibrium concentration of H_2 for the reaction:

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

if $K_c = 1.67\text{x}10^{-7}$ at 800 °C and the reaction initially contains only 0.0125 mol H_2S in a 0.500 L flask?

Additional example #3

- The initial [H_2S] is 0.0125 mol/0.500 L = 0.025 M
- Notice K_c = 1.67x10^{-7} is very small compared with the initial [H_2S]
- We expect the [H_2S] to change only very slightly from its initial conditions and we can ignore this change in calculations - this simplifies the algebra
- Next, set up an ICE table

Additional example #3

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

	$[H_2S]$	$[H_2]$	$[S_2]$
Initial	0.025	0.000	0.000
Change	**$-2x$**	**$+2x$**	**$+x$**
Equilibrium	**$0.025-2x$**	**$+2x$**	**$+x$**

$[H_2S]$ decreases and $[H_2]$ and $[S_2]$ increase as the system approaches equilibrium

Next, solve for ‘x’

Additional example #3

$$K_c = \frac{[H_2]^2 \cdot [S_2]}{[H_2S]^2}$$

$$1.67\text{x}10^{-7} = \frac{(2x)^2 \cdot x}{(0.0250 - 2x)^2}$$

$$= \frac{4x^3}{(0.0250 - 2x)^2}$$

A cubic equation that is difficult to solve!

If **x is small**, we can ignore it in the denominator of this equation

Additional example #3

$$1.67\times10^{-7} = \frac{4x^3}{(0.0250)^2} = \frac{4x^3}{6.25\times10^{-4}}$$

$$x^3 = \frac{1.67\times10^{-7} \times 6.25\times10^{-4}}{4}$$

$$x = 2.97\times10^{-4}$$

No need to solve a cubic equation!

?

- The equilibrium $[H_2] = 2\cdot x = 5.94\times10^{-4}$ M
- If this value is < 5% of the initial concentration, the assumption error is small and the method is acceptable (in this case 2.4%)

Additional example #4

Consider heterogeneous equilibrium:

$$\mathrm{MgCO_3}(s) \leftrightharpoons \mathrm{MgO}(s) + \mathrm{CO_2}(g) \text{ with } K_p = 0.026$$

When the system is compressed from 10.0 L to 0.1 L at constant temperature of 650 K, how many grams of $MgCO_3$(s) is formed? Assume that CO_2 can be treated as an ideal gas and sufficient amounts of both solids are present.

1. Before compression: $V_1 = 10.0$ L, $P_1 = 0.026$ atm (from $K_p = P_{CO2}$), and $T = 650$ K. Ideal gas law:

$$n_1 = \frac{P_1 V_1}{RT} = \frac{(2634.5 \text{ Pa})(0.01 \text{ m}^3)}{(8.314 \text{ J/(mol K)})(650 \text{ K})} = 4.875 \times 10^{-3} \text{ mol}$$

Additional example #4

2. After compression: V_2 = 0.100 L, P_2 = 0.026 atm (from $K_p = P_{CO2}$), and T = 650 K. Ideal gas law:

$$n_2 = \frac{P_2V_2}{RT} = \frac{(2634.5\ \text{Pa})(0.0001\ \text{m}^3)}{(8.314\ \text{J}/(\text{mol K}))(650\ \text{K})} = 4.875 \times 10^{-5}\ \text{mol}$$

3. The number of moles of CO_2 consumed:

$$\Delta n = n_2 - n_1 = -4.826 \times 10^{-3}\ \text{mol}$$

Based on the stoichiometry, this also gives the number of moles of $MgCO_3$(*s*) formed ($4.826\text{x}10^{-3}$ mol). The mass is:

$$m = (4.826 \times 10^{-3}\ \text{mol}) \times (84.3139\ \frac{\text{g}}{\text{mol}}) = \underline{0.41\ \text{g}}$$

(molar mass of $MgCO_3$ is 84.3130 g/mol)