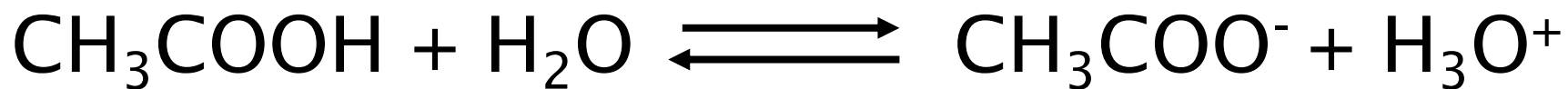


Chapter 16

Chemical Equilibrium



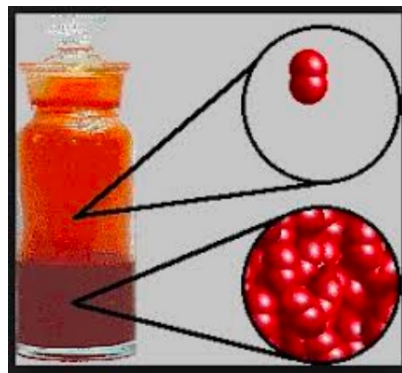
Equilibrium: A Dynamic Process

Opposing processes occur at equal rates

- Forward & reverse reactions occur at equal rates
- No outward change is observed
- **Ratio** of reactants to products is constant
- Temperature dependent
- Other factors can also shift equilibrium toward products or reactants
- Represented by double arrows (\rightleftharpoons or \longleftrightarrow)

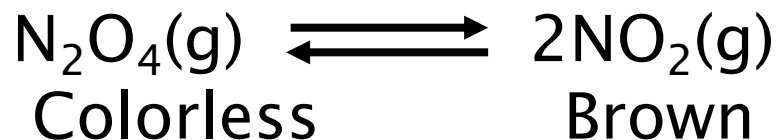
Physical Equilibrium

Ex: Equilibrium between phases



Chemical Equilibrium

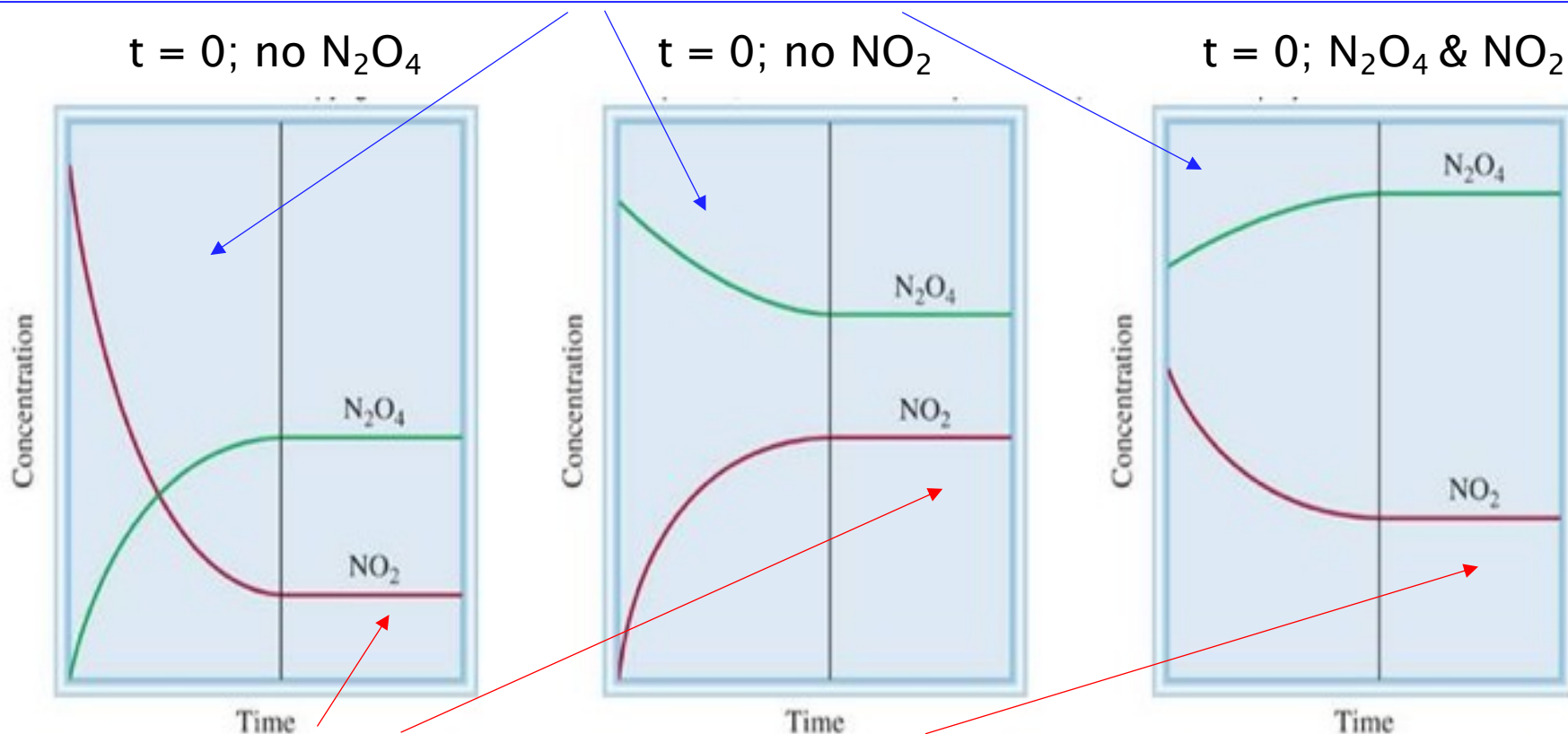
Equilibrium between reactants & products



Initial conditions may vary – concentrations will adjust to establish equilibrium

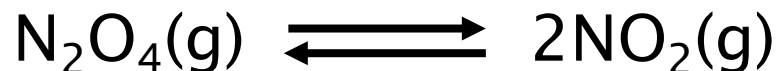


As a system **approaches** equilibrium, both the forward and reverse reactions are occurring



At **equilibrium**, the forward and reverse reactions are proceeding at the same rate, so the relative concentrations remain constant.

Equilibrium Constant (K_c)



At equilibrium, $[\text{N}_2\text{O}_4]$ & $[\text{NO}_2]$ are constant

- **NOT EQUAL**

- Not static – both forward & reverse reactions continue
- Actual amounts depend on system

Rate (forward) = Rate (reverse): $k_1[\text{N}_2\text{O}_4] = k_{-1}[\text{NO}_2]^2$

$$\frac{k_1}{k_{-1}} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = K_c$$

TABLE 15.1 The NO_2 – N_2O_4 System at 25° C					
Initial Concentrations (M)		Equilibrium Concentrations (M)		Ratio of Concentrations at Equilibrium	
$[\text{NO}_2]$	$[\text{N}_2\text{O}_4]$	$[\text{NO}_2]$	$[\text{N}_2\text{O}_4]$	$\frac{[\text{NO}_2]}{[\text{N}_2\text{O}_4]}$	$\frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$
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}

[conc]
not equal

Ratio
is equal

Equilibrium Expression

For the reaction: $aA + bB + \dots \rightleftharpoons cC + dD + \dots$

The Equilibrium Expression is: $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

For an Equilibrium Expression:

- Concentrations of products are in numerator
- Concentrations of reactants are in denominator
- They are the concentrations at equilibrium
- Exponents ARE coefficients from balanced equation
- Units generally not included
- Also known as a Mass Action Expression

Note difference from rate equation – equilibrium expression IS BASED ON BALANCED EQUATION

Impact of How an Equation is Balanced

Reaction A



$$K_c = \frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]^{1/2}}$$

Reaction B



$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$$

Equilibrium constants change if the reaction is balanced differently

Numerical values for K_c are related, but different

$$K_c (\text{reaction B}) = [K_c (\text{reaction A})]^2$$

It is essential to know how the reaction was balanced

K_p The Pressure Version of K_c

Remember the Gas Laws – Chapter 5!

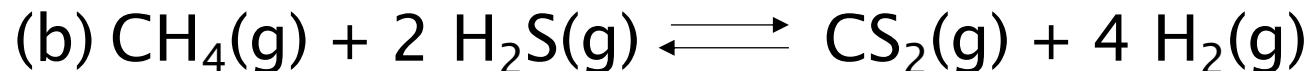
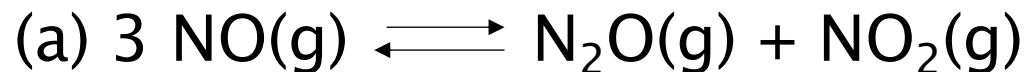
- In a closed system, pressure \propto concentration
 - The equilibrium expression can also be written in terms of pressure
 - Very useful since gas phase reactions are often monitored via pressure

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

\propto = proportional to

Writing Equilibrium Expressions

Write the equilibrium constant expression K_p and K_c for:

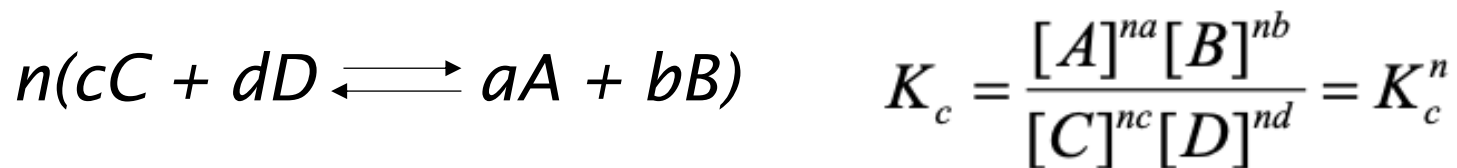


Manipulating Chemical Equations & K_c

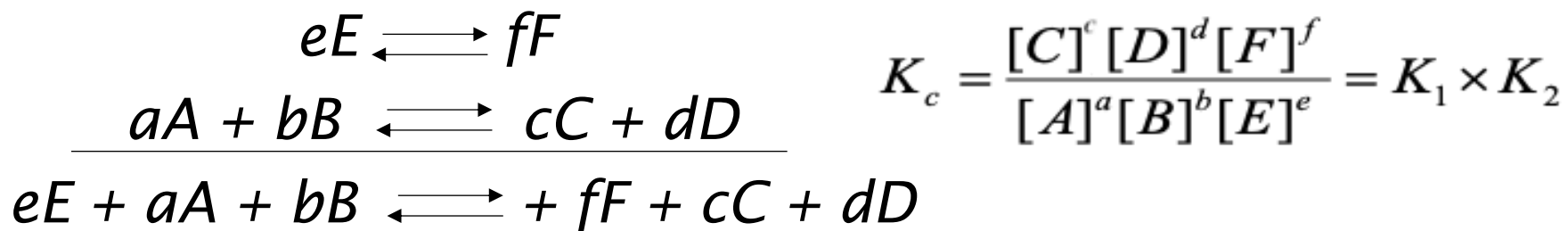
When reversing a chemical equation, invert K_c



When multiplying coefficients by n, raise K_c to n^{th} power

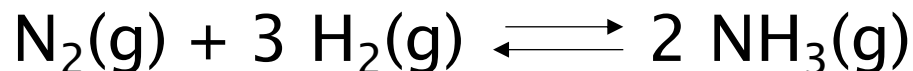


When adding equations, multiply the K_c values



Manipulating K values

1. For the formation of NH_3 from N_2 and H_2



$K_p = 4.34 \times 10^{-3}$ at 300°C . What is the value of K_p for the reverse reaction?

A: 2.30×10^2

2. How does the magnitude of the equilibrium constant K_p for the reaction



change if the equilibrium is written as



A: K_p is cubed

3. Given that, at 700 K, $K_p = 54.0$ for the reaction:



and $K_p = 1.04 \times 10^{-4}$ for the reaction:



determine the value of K_p for the following reaction at 700K:

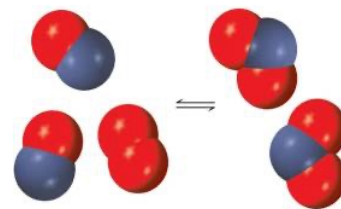


Types of Equilibria: Homogeneous (K_c & K_p)

All products & reactants are in the same phase

K_c : All chemicals are in units of molarity (mol/L)
Can be either **gas** or **aqueous** solutions

K_p : All chemicals in **gas** phase
Pressure is the partial pressure
– units often atmospheres



K_c & K_p are related: $K_p = K_c \cdot (RT)^{\Delta n}$

- Derived from ideal gas law
- R = gas constant (0.0821 L · atm/mol · K)
- T = temperature in Kelvin
- Δn = moles gaseous products – moles gaseous reactants

$K_p = K_c$ if moles product gas = moles reactant gas
If moles product gas \neq moles reactant gas, there will be a
change in pressure

Calculating K_p from K_c

Calculate K_p for the following reactions at 1500°C .



$$K_c = 12800$$

$$\Delta n_{\text{gas}} = -1$$



$$K_c = 12800$$

$$\Delta n_{\text{gas}} = 0$$

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

A: 87.9

A: 12800

Types of Equilibria: Heterogeneous

Are the equilibrium constants for the following two reactions the same?



$$“K_1” = \frac{[\text{H}_2\text{SO}_4(\text{g})]}{[\text{SO}_3(\text{g})] [\text{H}_2\text{O}(\text{g})]}$$

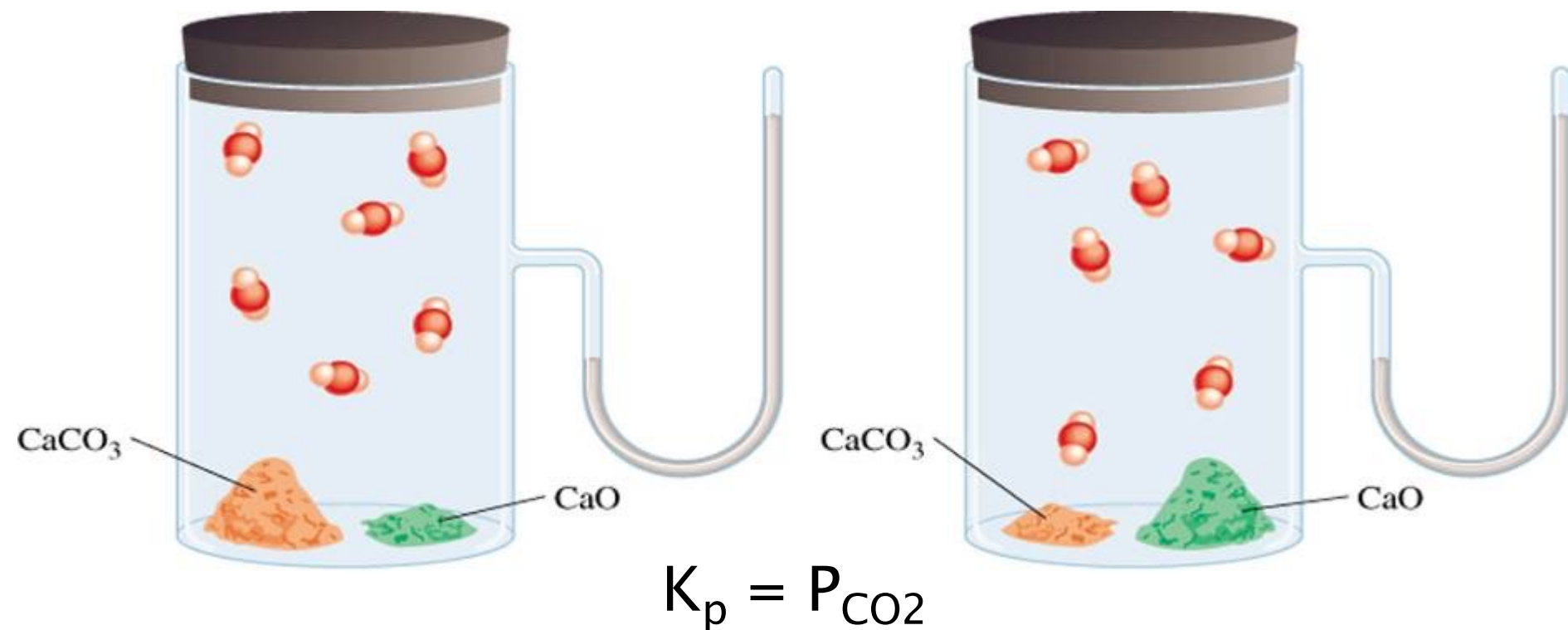
$$“K_2” = \frac{[\text{H}_2\text{SO}_4(\text{aq})]}{[\text{SO}_3(\text{g})] [\text{H}_2\text{O}(\text{l})]}$$

“K₁” would equal “K₂” ONLY IF [H₂SO₄(g)] = [H₂SO₄(aq)]
AND [H₂O(g)] = [H₂O(l)]

[H ₂ SO ₄ (g)]	dependent on partial pressure	variable
[H ₂ SO ₄ (aq)]	# moles dissolved in water	variable
[H ₂ O(g)]	dependent on partial pressure	variable
[H ₂ O(l)]	1 g/mL = 1000 g/L	56M
	for 1L: 1000g(1 mol/18g) = 56 mol	

The two equilibrium constants are NOT the same!
THE PHASE MATTERS!

Equilibria Involving Pure Solids & Liquids



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

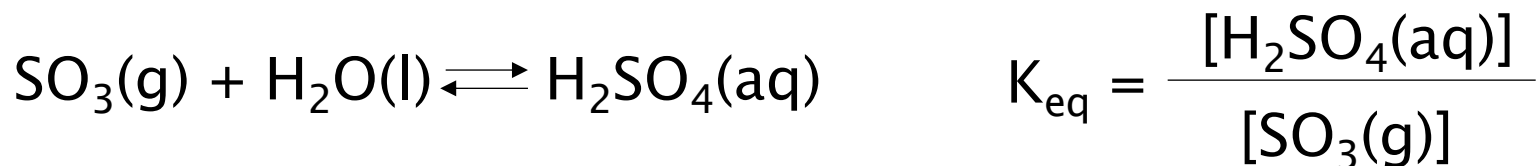
As long as there is some CaCO_3 & CaO in the system, the amount of CO_2 above the solid will remain the same

Equilibria Involving Mixed Phases (i.e. Heterogeneous)

The subscript “eq” is for general equilibria

K_c & K_p are specific types of K_{eq}

Equilibrium expressions only include gaseous & aqueous materials (solids & liquid are NOT included)



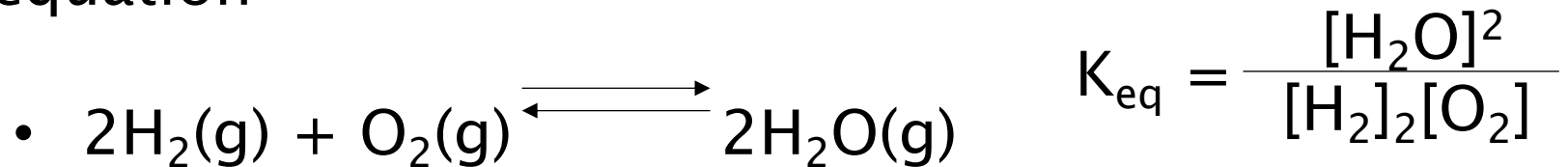
K_p for liquid-vapor equilibrium = vapor pressure of liquid



To write an appropriate equilibrium expression from a balanced equation, the equation **MUST** show the phase of each reactant & product.

Determination of K_{eq} values:

- The equilibrium expression comes from the balanced equation



- The value of K is experimentally determined
 - Allow the reaction to run until it reaches equilibrium.
 - Once equilibrium is reached, measure the concentration of all components in the equilibrium expression.
 - Plug the equilibrium concentrations into the equilibrium expression to calculate K_{eq} .

Equilibria Involving Solids & Liquids

A mixture of H_2 , S, and H_2S is held in a 1.0L vessel at 90°C and reacts according to the equation:



An equilibrium mixture contains 0.46g H_2S & 0.40g H_2 .

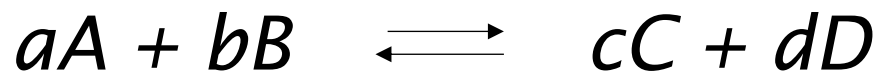
(a) Write the equilibrium constant expression for this reaction.

(b) What is the value of K_c for the reaction at this temp.?

A: 0.068

(c) Why can we ignore the amount of S when doing the calculation in part b?

What Equilibrium Constants Can Tell Us



At Equilibrium:

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

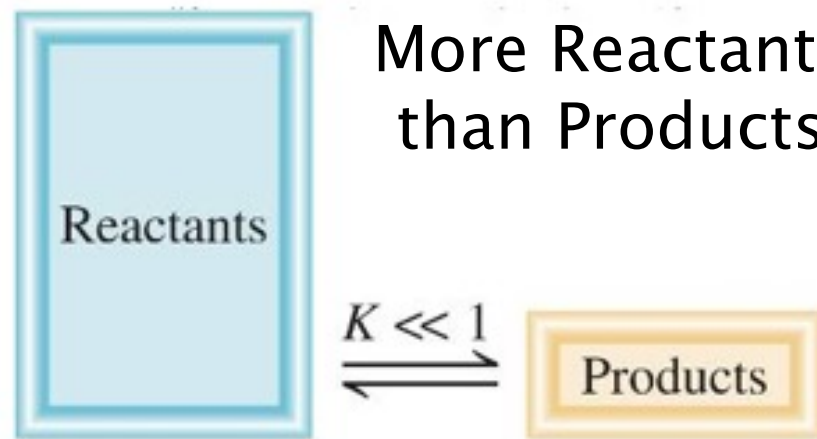
$K > 1$

More Products
than Reactants



$K < 1$

More Reactants
than Products



As K goes to infinity, reaction goes to completion.
As K goes to zero, no reaction occurs.

Analyzing K_p/K_c Values

For the reaction: $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$

$K_p = 794$ at 298K and $K_p = 54$ at 700K

Is the formation of HI more favored at the higher or lower temperature?

Using the Equilibrium Expression

1. Nitrogen monoxide exists in equilibrium with nitrogen and oxygen gas. At a given temperature, 0.100 moles of NO were added to a 2.00L vessel. At equilibrium, 0.044 moles of NO were remaining. What is the value of K_c ?

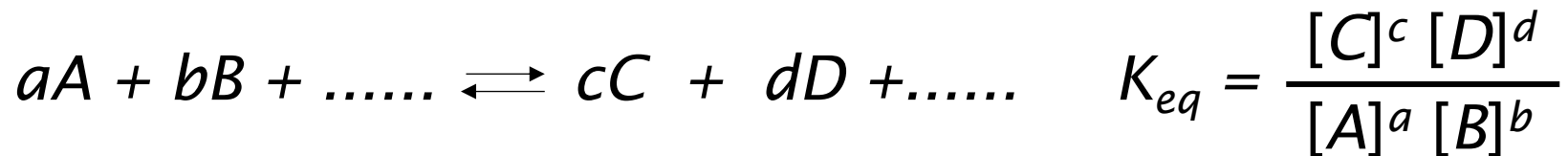
1. Write the balanced equation & equilibrium constant expression.

2. Find equilibrium molarities of reactants and products.

We are using concentration, so make sure to convert to Molarity!

3. Calculate K_c

Predicting the Direction of a Reaction



If the value of K_{eq} is very large

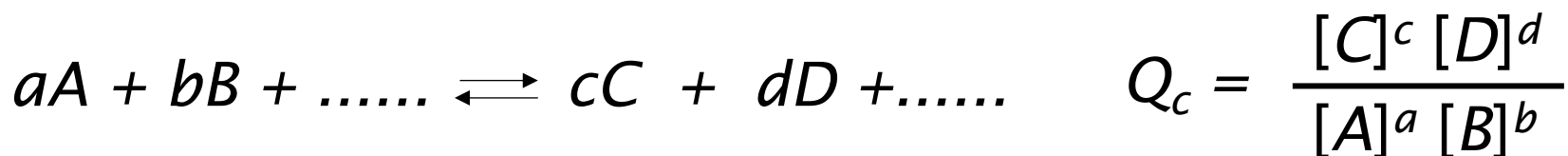
- $[C]$ & $[D]$ very large or $[A]$ & $[B]$ very small
- Reaction will go to completion
- Equilibrium favors products

If the value of K_{eq} is very small

- $[C]$ & $[D]$ very small or $[A]$ & $[B]$ very large
- Reaction proceeds very slowly or no reaction (NR) at all
- Equilibrium favors reactants

Note that K_{eq} has its origins in thermodynamics, but kinetics are also important. The value of K_{eq} does not guarantee that a reaction will occur in either direction.

The Reaction Quotient (Q_c or Q_p)

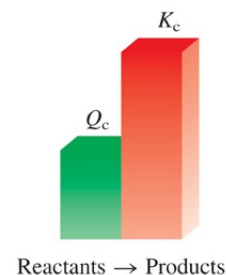


Essentially K_{eq} but at non-equilibrium conditions

- Indicates direction of reaction to get to equilibrium

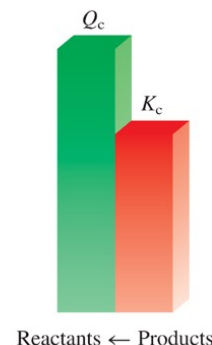
$Q < K$

- $[Products] < \text{equilibrium concentration}$
- Higher rate in forward direction



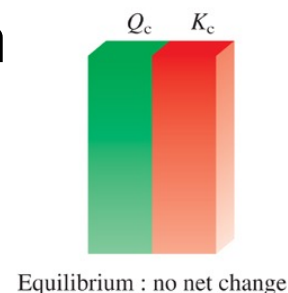
$Q > K$

- $[Products] > \text{equilibrium concentration}$
- Higher rate in reverse direction



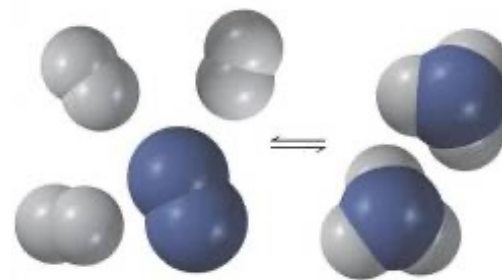
$Q = K$

- $[Products] = \text{equilibrium concentration}$
- Forward rate = Reverse rate
- No macroscopic changes observed



Reaction Quotient

1. For the reaction of hydrogen with nitrogen to form ammonia at 25°C, $K_c = 4.0 \times 10^8$. The equilibrium concentrations were found to be $1.0 \times 10^{-3} \text{M}$ in both hydrogen & nitrogen and 0.020M in ammonia. If you add 0.010M nitrogen, in which direction does the reaction shift?



2. At 1000K, the value of K_p for the following reaction is 0.338.



Given the following pressures:

$$P_{\text{SO}_3} = 0.16 \text{ atm}; P_{\text{SO}_2} = 0.41 \text{ atm}; P_{\text{O}_2} = 2.5 \text{ atm}$$

(a) Is the system at equilibrium? **A: No**

(b) If not, predict the direction in which the reaction will shift to reach equilibrium. **A: toward reactants**

Free Energy & Equilibrium

During a reaction, not all of the reactants and products will be in their standard state. Under any conditions (standard or nonstandard), the free energy change is:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$R = 8.314 \times 10^{-3} \text{ kJ/mol K}$$

T = temperature in K

Q = reaction quotient

(Under standard conditions, all concentrations are 1 M, so $Q = 1$, $\ln Q = 0$, and $\Delta G = \Delta G^\circ$)

At equilibrium: $\Delta G = 0$ and $Q = K$ (K is equilibrium constant)

So the equation becomes: $0 = \Delta G^\circ + RT \ln K$

Therefore, at equilibrium: $\Delta G^\circ = -RT \ln K$

Gibbs Free Energy & Equilibrium

K	$\ln K$	ΔG°	Comments
> 1	Positive	Negative	Products are favored over reactants at equilibrium.
$= 1$	0	0	Products and reactants are equally favored at equilibrium.
< 1	Negative	Positive	Reactants are favored over products at equilibrium.

$\Delta G^\circ < 0$ (negative), the forward reaction is spontaneous

$\Delta G^\circ > 0$ (positive), the reverse reaction is spontaneous

$\Delta G^\circ = 0$ the reaction is at equilibrium

The magnitude of ΔG° indicates how far the standard state is from equilibrium
(more negative ΔG° = larger K)

Free Energy & Equilibrium

1. Calculate ΔG° for the following reaction at 25°C.



K_{sp} for Fe(OH)_2 is 1.6×10^{-14}

A: 79kJ/mol

2. For the following reaction:



A: (a) -5.41 kJ/mol
(b) 0.295 kJ/mol

- (a) Using data from Appendix 2, calculate ΔG° at 298K
(b) Calculate ΔG at 298K if the partial pressure of NO_2 and N_2O_4 are 0.40atm and 1.60atm, respectively.

Using K_{eq} to Find Equilibrium Concentrations

1. Write the properly balanced chemical equation.
 - Need the stoichiometry & species involved in the reaction.
2. Set up a table of concentrations for all components.
 - Use coefficients from balanced equation to express all unknown concentrations in terms of a single reactant or product, x .
3. Write out the equilibrium constant expression for the reaction (i.e. the equation for K).
4. Substitute the values from step 2 into the K_{eq} equation.
5. Solve the equation for x .
6. Substitute the value you calculated for x into the expressions for the other equilibrium concentrations.

“Ice Tables” will be used in most of the remaining chapters!

Using K_{eq} to Find Equilibrium Concentrations

1. The decomposition of BrCl to bromine & chlorine has a K_c of 0.14 at 350K. If the initial concentration of BrCl is 0.062M, what are the equilibrium concentrations of all components?

1. Balanced Equation:

2. ICE Table

3. K_{eq} Expression

6. Use x to determine conc.

4 & 5. Substitute values from table & Solve for x

2. Carbon monoxide reacts with water at 1000°C to give carbon dioxide and hydrogen with $K_c = 0.58$. A reaction was started with the following composition: CO_2 0.20M; H_2 1.20M; H_2O 0.50M; CO 1.00M. What are the equilibrium concentrations of all components?

1. Balanced Equation:

2. ICE Table

3. K_{eq} Expression

4. Substitute values from table

Need quadratic equation!

5. Solve for x using quadratic equation: $\frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

6. Use x to determine concentrations

3. Compare the molar solubility of lead chloride ($[\text{Pb}^{2+}]$) at 25°C and 90°C.



K_{sp} for PbCl_2 is 1.6×10^{-5} at 25°C

From Table:

$\Delta H^{\circ}_{\text{f}}$ (kJ/mol)

S° (J/molK)

$\text{PbCl}_2(\text{s}) = -359$

$\text{PbCl}_2(\text{s}) = 136$

$\text{Pb}^{2+}(\text{aq}) = -1.7$

$\text{Pb}^{2+}(\text{aq}) = 10.5$

$\text{Cl}^{-}(\text{aq}) = -167.2$

$\text{Cl}^{-}(\text{aq}) = 56.5$

Molar solubility = amt. moles dissolved = equilibrium concentration!

A: solubility at 90°C about double the solubility at 25°C

Making Approximations in Equilibrium Calculations (do we need to use the Quadratic Equation?)

Answer: Only if the percent difference between X and the equilibrium concentration is >5%

Example A:

Find [HClO] for a 0.010M solution of hypochlorous acid (HClO) at 25°C. $\text{HClO(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{ClO}^-(\text{aq})$ where $K_a = 2.9 \times 10^{-8}$.

	HClO	H ₃ O ⁺	ClO ⁻
I	0.010	0	0
C	-X	+X	+X
E	0.010-X	X	X

$$2.9 \times 10^{-8} = \frac{X^2}{0.010}$$

$$X^2 = 2.9 \times 10^{-10}$$
$$X = 0.000017$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$
$$2.9 \times 10^{-8} = \frac{[\text{X}][\text{X}]}{[0.010 - \text{X}]}$$

Ignore this X

$$[\text{HClO}] = 0.010 - 0.000017 \sim 0.010$$

$$(0.000017/0.010) \times 100 = 0.17\%$$

Approximation OK

Making Approximations in Equilibrium Calculations (do we need to use the Quadratic Equation?)

Answer: Only if the percent difference between X and the equilibrium concentration is >5%

Example B:

Find $[\text{HNO}_2]$ for a 0.010M solution of nitrous acid (HNO_2) at 25°C. $\text{HNO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NO}_2^-(\text{aq})$ where $K_a = 4.5 \times 10^{-4}$.

	HNO_2	H_3O^+	NO_2^-
I	0.010	0	0
C	-X	+X	+X
E	$0.010 - X$	X	X

$$4.5 \times 10^{-4} = \frac{X^2}{0.010}$$

$$X^2 = 4.5 \times 10^{-6}$$
$$X = 0.0021$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

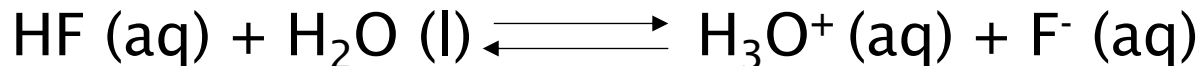
$$4.5 \times 10^{-4} = \frac{[X][X]}{[0.010 - X]}$$

Ignore this X

$$[\text{HNO}_2] = 0.010 - 0.0021 \sim 0.008$$

$(0.0021/0.008) \times 100 = 26\%$
Approximation **NOT** acceptable

Hydrofluoric acid dissociates in water to yield hydronium ions and fluoride ions according to the equation:



The K_{eq} for this process is 7.1×10^{-4} . If you start with a 1.2M solution of HF, what are the equilibrium concentrations for all components?

1. Balanced Equation:

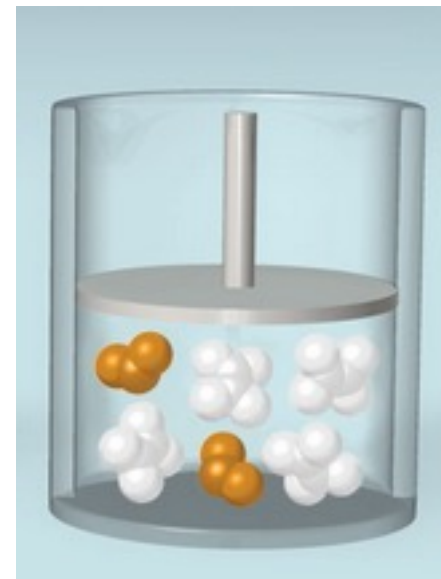
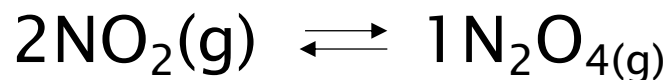
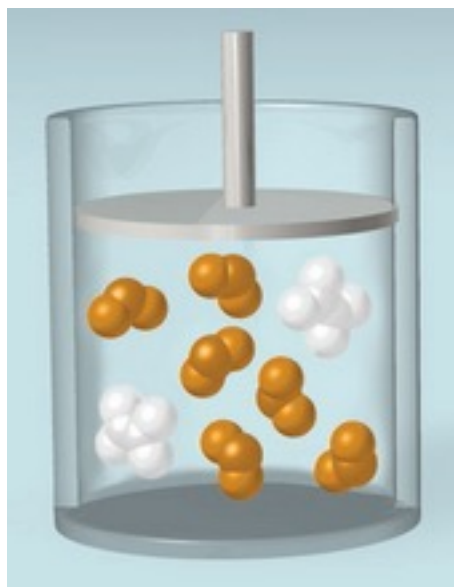
2. ICE Table

3. K_{eq} Expression

4. Substitute values from table

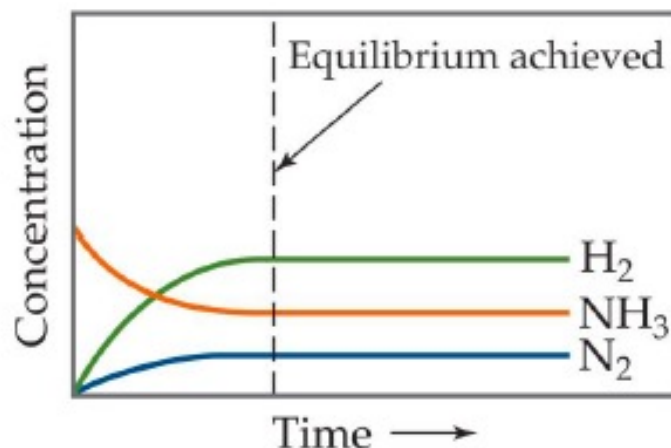
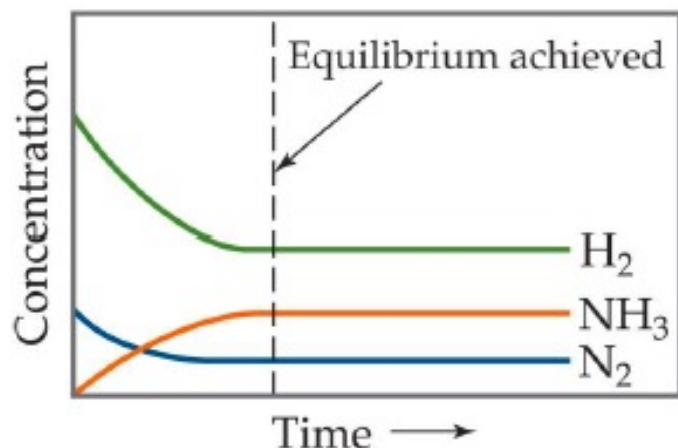
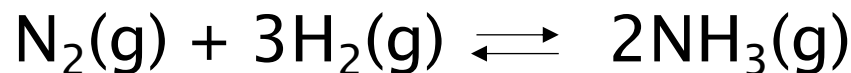
Factors that Affect Chemical Equilibrium: Le Châtelier's Principle

When stress is applied to a system at equilibrium, the system will shift to reduce the applied stress and re-establish equilibrium



Addition of pressure causes the reaction to shift towards products – fewer moles of gas decreases the pressure (i.e. the stress)

Remember: Equilibrium Can Be Reached From Either Direction



It doesn't matter whether you start with N_2 and H_2 or with NH_3 – you will have the same proportions of all three substances at equilibrium

Many different types of stress can affect equilibrium, such as:

Change in components

Change in concentrations

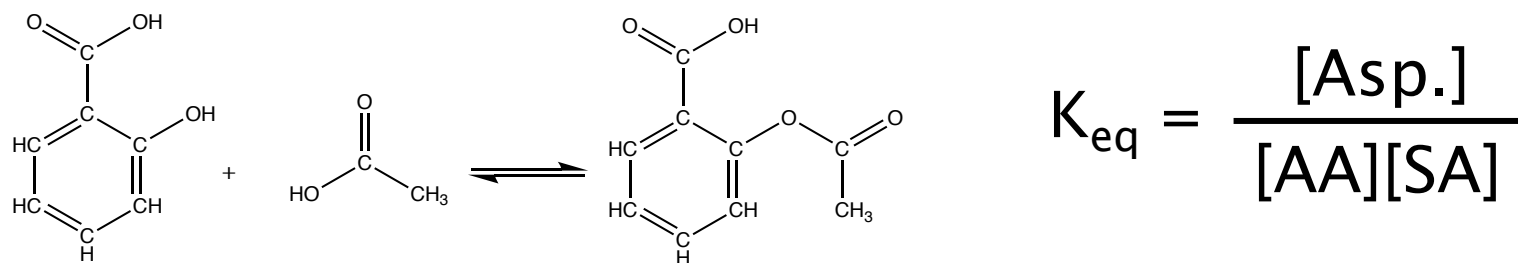
Change in partial pressure

Change in external pressure

Change in total volume

Change in temperature

Changing Components, Concentration, or Partial Pressure



Synthesis of Aspirin from Salicylic Acid & Acetic Acid is an equilibrium process. We want to make as much aspirin as possible.

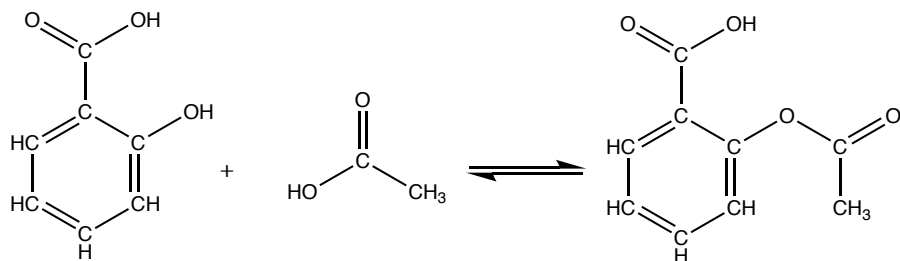
Addition of a component: Add Acetic Acid

K_{eq} must remain constant $\longrightarrow K_{eq} = \frac{[Asp.]}{[AA][SA]}$

If we add more AA, the denominator gets larger

To keep K_{eq} constant, we need to increase the numerator – reaction will shift toward the products (make more aspirin).

Changing Components, Concentration, or Partial Pressure



$$K_{eq} = \frac{[Asp.]}{[AA][SA]}$$

Synthesis of Aspirin from Salicylic Acid & Acetic Acid is an equilibrium process. We want to make as much aspirin as possible.

Decrease in conc. of a component: Remove Aspirin

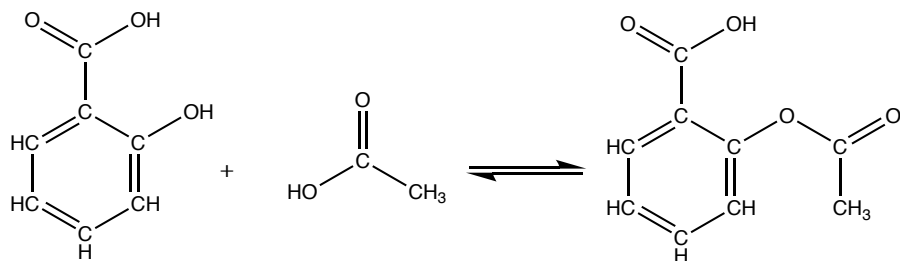
K_{eq} must remain constant

$$K_{eq} = \frac{[Asp.]}{[AA][SA]}$$

To keep K_{eq} constant, we need to decrease the denominator – reaction will shift toward the products (use up AA & SA, & make more aspirin).

If we remove aspirin, the numerator gets smaller

Changing Components, Concentration, or Partial Pressure



$$K_{eq} = \frac{[Asp.]}{[AA][SA]}$$

Synthesis of Aspirin from Salicylic Acid & Acetic Acid is an equilibrium process. We want to make as much aspirin as possible.

What if we added aspirin?

K_{eq} must remain constant \longrightarrow $K_{eq} = \frac{[Asp.]}{[AA][SA]}$

If we add aspirin, the numerator gets larger

To keep K_{eq} constant, we need to increase the denominator – reaction will shift toward the reactants (make more AA & SA).

Changing Components, Concentration, or Partial Pressure

For the following reaction,

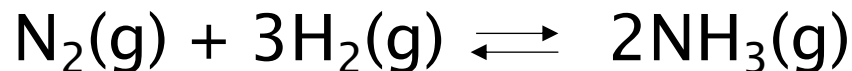


what happens to the equilibrium if:

(a) O_2 is added to the system?

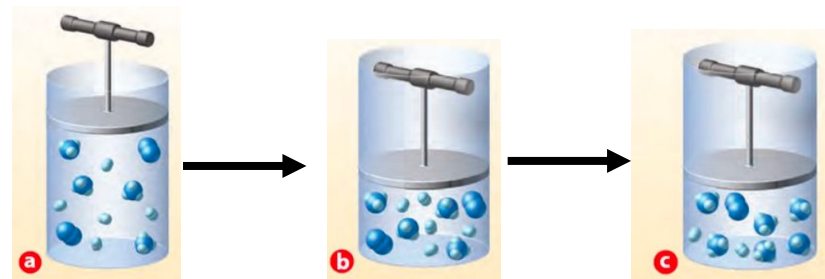
(b) NO is removed?

Changing Volume or External Pressure



When pressure is increased:

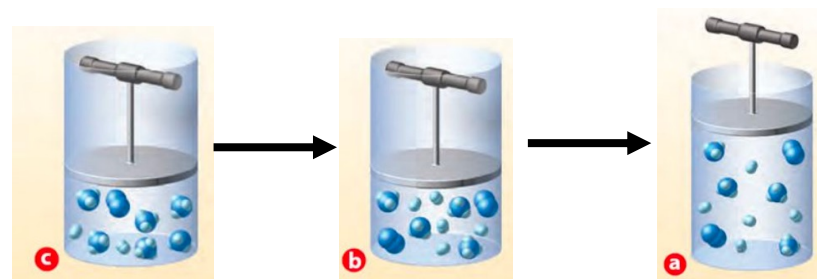
Equilibrium shifts to produce smaller # moles of gas



Toward products – 2 moles < 4 moles

When Pressure is decreased:

Equilibrium shifts to produce larger # moles of gas



Toward reactants – 4 moles > 2 moles

If a reaction has the same number of moles of gas on both sides (e.g. $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$):

Changes in external pressure do not affect equilibrium

Changing Volume or External Pressure

For the following reaction,



what happens to the equilibrium if:

(a) The volume of the system is increased?

(b) The external pressure exerted on the system is increased?

Changing Temperature

Exothermic Reaction:

Heat is released

→ heat is a product

Increase T: K decreases

→ favors reactants

Decrease T: K increases

→ favors products

Endothermic Reaction:

Heat is absorbed

→ heat is a reactant

Increase T: K increases

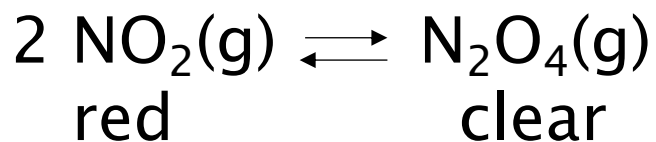
→ favors products

Decrease T: K decreases

→ favors reactants

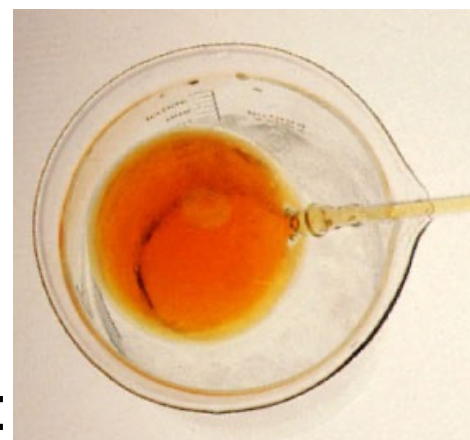


High T:
More NO₂



Exothermic Reaction

$$\Delta H = -58 \text{ kJ/mol}$$



Low T:
More N₂O₄

Adding a Catalyst or Inhibitor

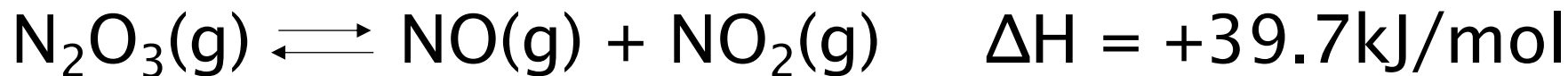
Catalysts:

- Catalysts lower activation energy.
- Cause a reaction to reach equilibrium faster
- DO NOT AFFECT THE EQUILIBRIUM ITSELF

Inhibitors

- Act to slow the rate of a reaction
- Prevent equilibrium from being reached as quickly
- DO NOT AFFECT THE EQUILIBRIUM ITSELF
- It may seem like the reaction is not occurring at all, but in reality it is just infinitely slow.

Which way does the reaction shift if.....



NO is added?

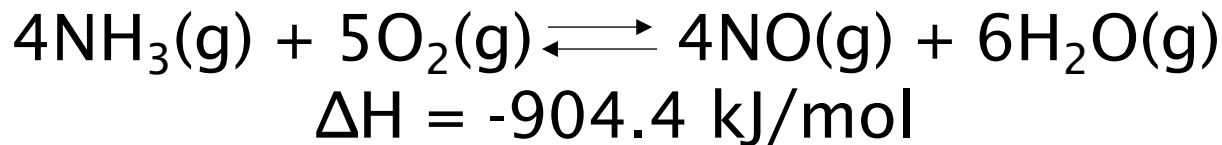
Volume of reaction vessel is reduced?

The total internal pressure is increased by adding He gas?

The temperature is increased?

A catalyst is added?

How does each of the following changes affect the yield of NO at equilibrium?



Increase $[\text{NH}_3]$

Increase $[\text{H}_2\text{O}]$

Decrease $[\text{O}_2]$

Decrease the volume of the container

Add a catalyst

Increase temperature