



# An Introduction to Kinetics & Thermodynamics

*Unit 9 - Advanced Topic*

# What is Thermodynamics?

- Heat Energy in relation to work done within a system.
- We can use an equation to represent the relationship between Spontaneity and Favorability
- Three Concepts
  1. *Enthalpy - heat of reaction ( $\Delta H$ )*
    - *Endothermic vs. Exothermic*
  2. *Entropy - disorder of reaction ( $\Delta S$ )*
    - *Is disorder increasing or decreasing as the reaction proceeds?*
  3. *Free Energy - energy the system has to do work ( $\Delta G$ )*
    - *Is the reaction spontaneous or not?*

# Bond Enthalpy

- Predicting Endothermic or Exothermic
- Bond Energy (E to break bonds)



$$\Delta H_{rxn} = \sum[\text{bonds broken}] - \sum[\text{bonds formed}]$$

$$\Delta H_{rxn} = [436 \text{ kJ/mol} + 155 \text{ kJ/mol}] - [2(567 \text{ kJ/mol})]$$

$$\Delta H_{rxn} = -543 \text{ kJ/mol}$$

$\Delta H$  values will be given to you!

# Hess's Law



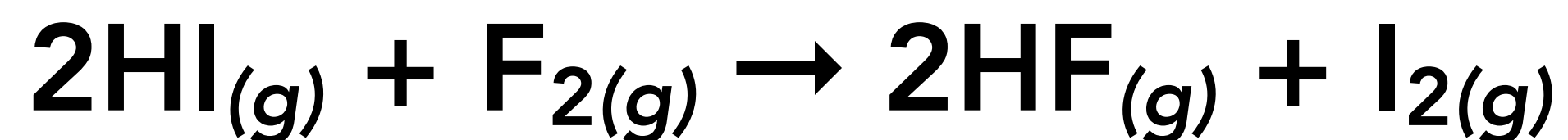
- Determining  $\Delta H$  for a reaction is possible regardless of the number of steps to get to the product.

$$\Delta H = \Delta H_A + \Delta H_B + \Delta H_C + \dots$$

## General Rules:

1. Manipulate equations so they add together to give desired results.
2. Enthalpy of formation of an **element** under STP is 0.
3. When the reaction is reversed, enthalpy is reversed.
4. If a balanced equation is multiplied by a coefficient, so is the enthalpy.
5. Substances on both sides of equation can be subtracted out.

# Hess's Law



$\Delta H$  of formation! ( $\Delta H_f$ )

## STANDARD ENERGIES OF FORMATION OF COMPOUNDS AT 1 atm AND 298 K

Compound	Heat (Enthalpy) of Formation * kJ/mol ( $\Delta H_f^\circ$ )	Free Energy of Formation kJ/mol ( $\Delta G_f^\circ$ )
Aluminum oxide $\text{Al}_2\text{O}_3(\text{s})$	-1674.1	-1580.9
Ammonia $\text{NH}_3(\text{g})$	-46.0	-16.3
Barium sulfate $\text{BaSO}_4(\text{s})$	-1471.8	-1361.0
Calcium hydroxide $\text{Ca}(\text{OH})_2(\text{s})$	-985.2	-897.9
Carbon dioxide $\text{CO}_2(\text{g})$	-393.3	-394.2
Carbon monoxide $\text{CO}(\text{g})$	-110.4	-137.1
Copper (II) sulfate $\text{CuSO}_4(\text{s})$	-770.8	-661.3
Ethane $\text{C}_2\text{H}_6(\text{g})$	-84.4	-33.0
Ethene (ethylene) $\text{C}_2\text{H}_4(\text{g})$	52.3	68.1
Ethyne (acetylene) $\text{C}_2\text{H}_2(\text{g})$	226.6	209.0
Hydrogen fluoride $\text{HF}(\text{g})$	-270.9	-273.0
Hydrogen iodide $\text{HI}(\text{g})$	26.3	1.7
Iodine chloride $\text{ICl}(\text{g})$	18.0	-5.4
Lead (II) oxide $\text{PbO}(\text{s})$	-215.3	-188.1
Magnesium oxide $\text{MgO}(\text{s})$	-601.1	-568.9
Nitrogen monoxide $\text{NO}(\text{g})$	90.3	86.5
Nitrogen dioxide $\text{NO}_2(\text{g})$	33.0	51.4
Potassium chloride $\text{KCl}(\text{s})$	-436.4	-408.8
Sodium chloride $\text{NaCl}(\text{s})$	-410.9	-383.7
Sulfur dioxide $\text{SO}_2(\text{g})$	-296.4	-299.7
Water $\text{H}_2\text{O}(\text{g})$	-241.6	-228.2
Water $\text{H}_2\text{O}(\text{l})$	-285.5	-237.0

\* Minus sign indicates an exothermic reaction.

Sample equations:



$$\Delta H = \Delta H_A + \Delta H_B + \Delta H_C + \dots$$

# Gibbs Free Energy

$$\Delta G = \Delta H - T\Delta S$$

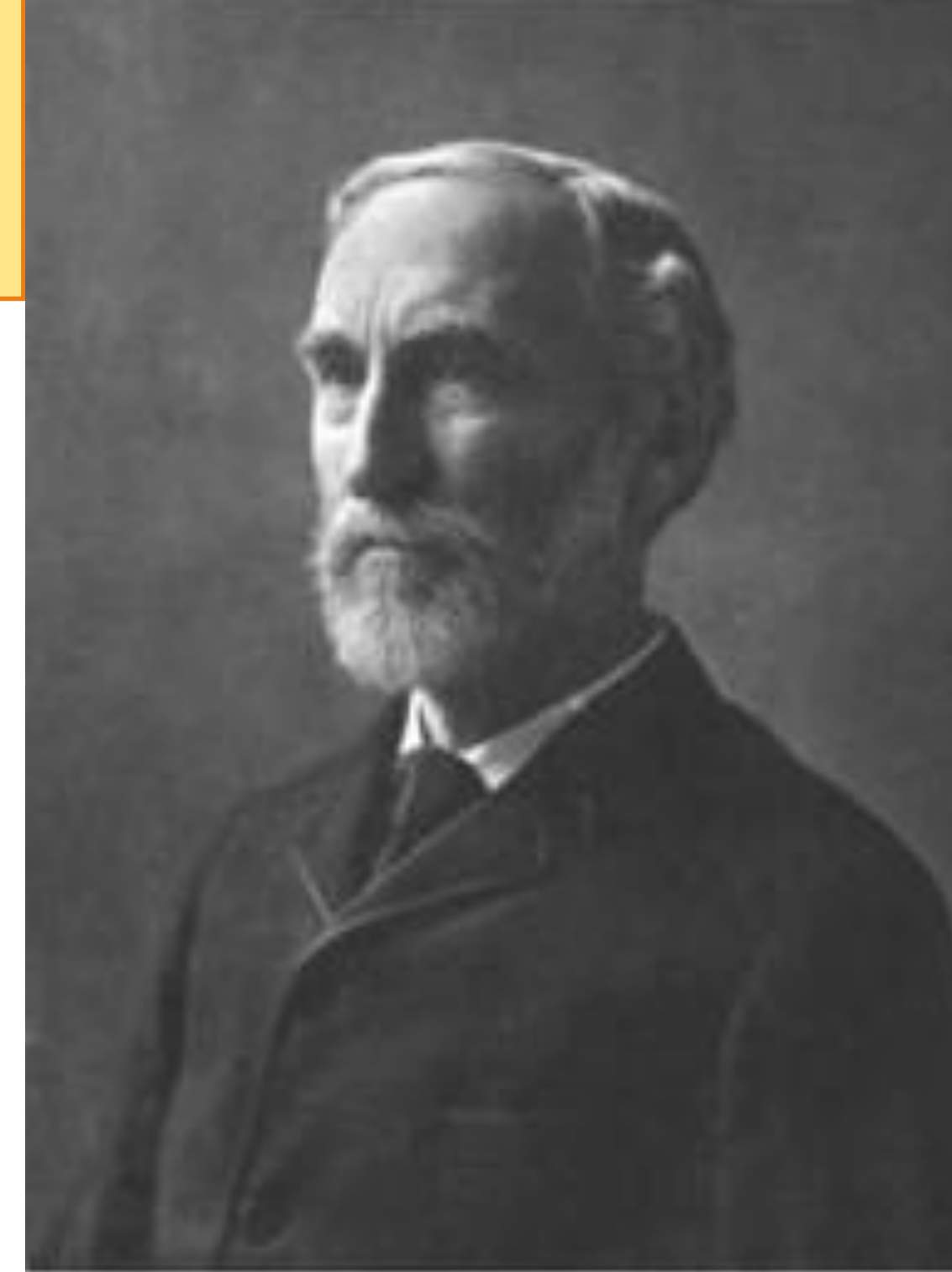
$\Delta G$  = Change in Gibbs free energy

$\Delta H$  = Change in Enthalpy (heat)

$T$  = Temperature (K)

$\Delta S$  = Change in Entropy

- Things to Consider in the system:
  - Endo vs. Exo (enthalpy,  $\Delta H$ )
  - Order vs. Disorder (entropy,  $\Delta S$ )
  - The temperature at which the change occurs



# Is the Reaction Favorable/Spontaneous?

Favorable Reaction	Unfavorable Reaction
<ul style="list-style-type: none"><li>• <math>\Delta H &lt; 0</math></li><li>• <math>\Delta S &gt; 0</math></li><li>• Exothermic Rxn.</li><li>• Increased entropy</li></ul>	<ul style="list-style-type: none"><li>• <math>\Delta H &gt; 0</math></li><li>• <math>\Delta S &lt; 0</math></li><li>• Endothermic Rxn.</li><li>• Decreased entropy</li></ul>

$$\Delta G = \Delta H - T\Delta S$$

A reaction will always be spontaneous if the  $\Delta G$  is NEGATIVE.

# Gibbs' Practice

$$\Delta G = \Delta H - T\Delta S$$

For the decomposition reaction of  $\text{CaCO}_3$  to  $\text{CaO}$  and  $\text{CO}_2$  at 298K, the  $\Delta H$  is 178.5 kJ/mol and the  $\Delta S$  is 161.6 J/mol•K. Is the reaction spontaneous or non-spontaneous at this temperature?

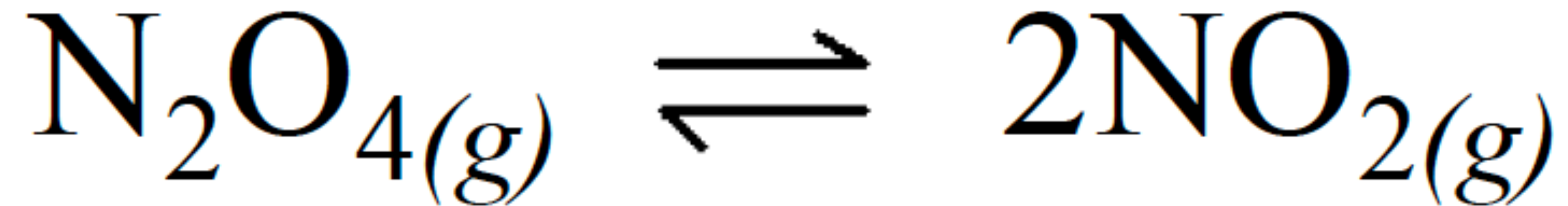
What temperature would make this decomposition spontaneous?



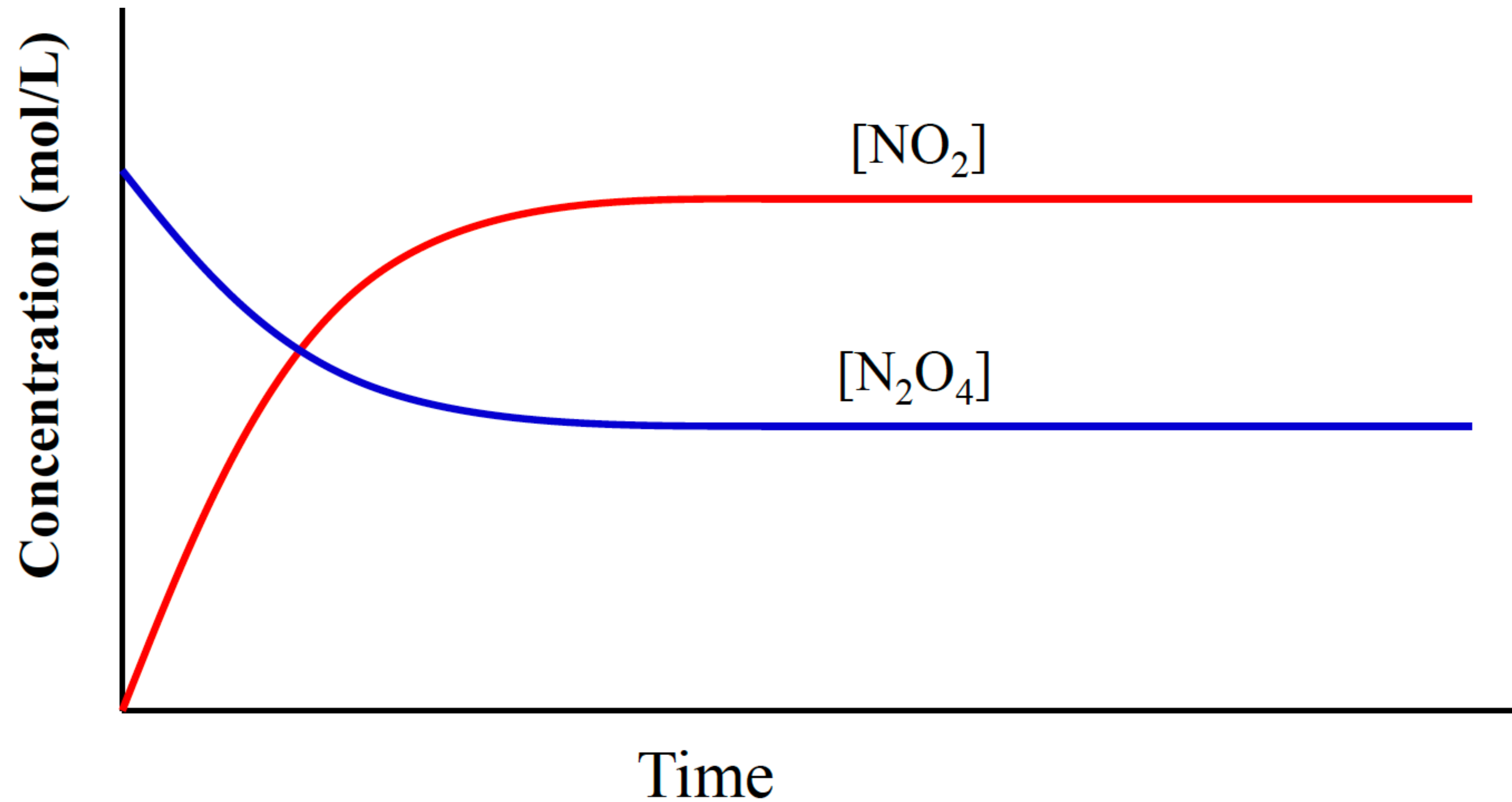
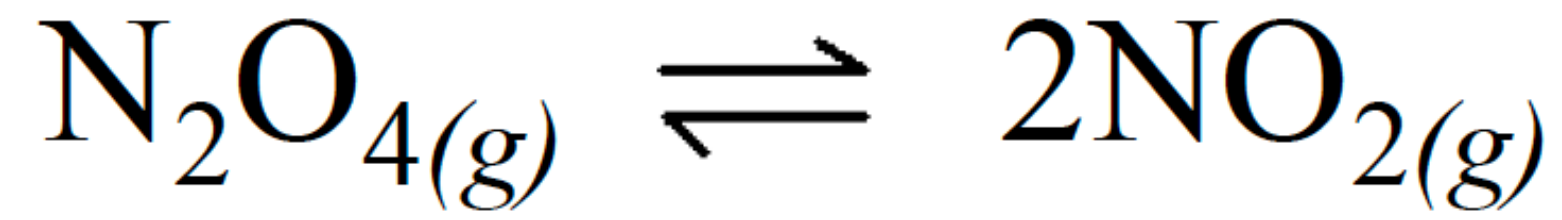
# Dynamic Equilibrium

Most reactions do not go to completion.

- Here, all of the reactants **do not** get used up.
- The system reaches a dynamic state where reactants are continually turning into products, and products are continually turning back into reactants.

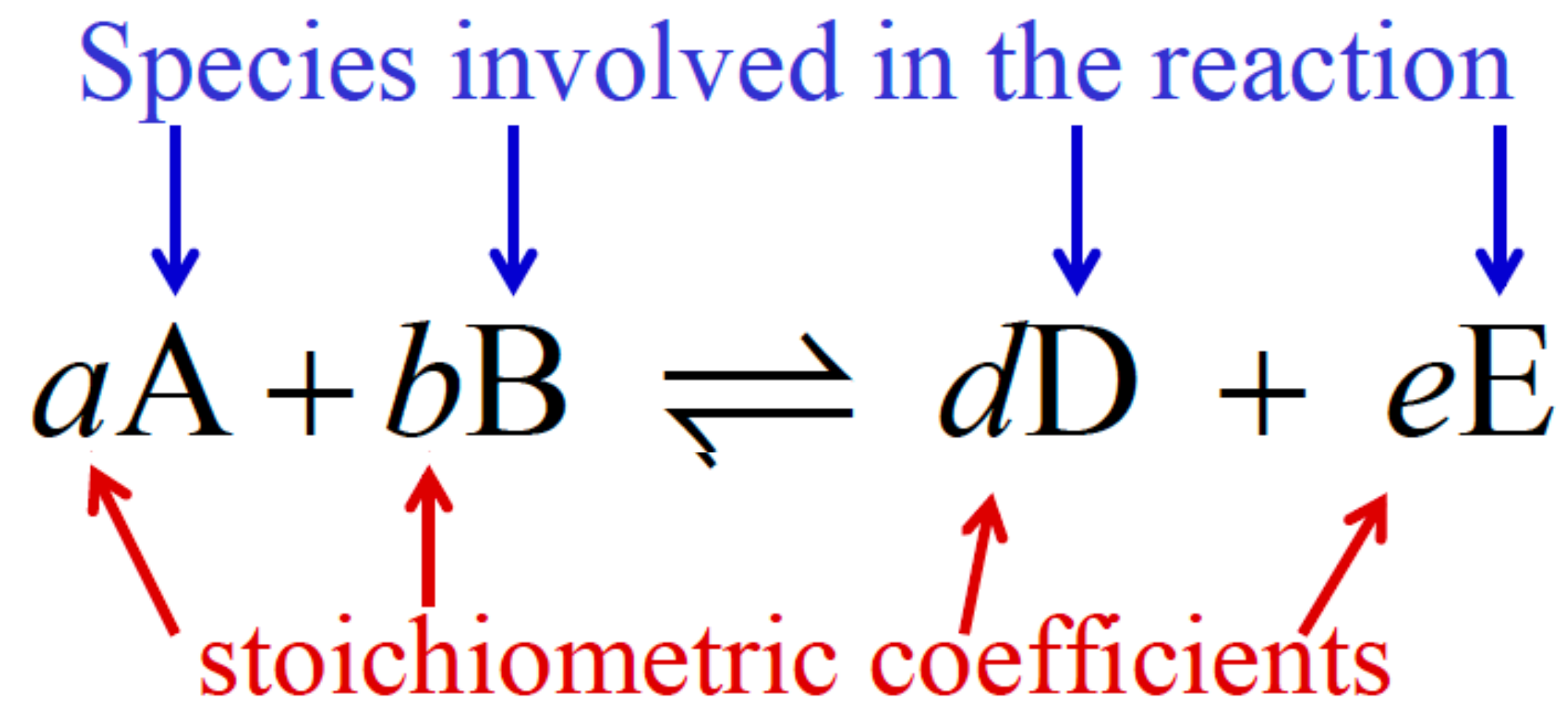


# Dynamic Equilibrium



In this example, the system *initially contains only reactants,  $\text{N}_2\text{O}_4$ , and eventually establishes equilibrium.*

# The Equilibrium Constant ( $K_{eq}$ )



concentration constant

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

square brackets represent concentration in [mol/L]

Units for Concentration  
mol/L =  $M$

# Example: Equilibrium Expression ( $K_c$ )

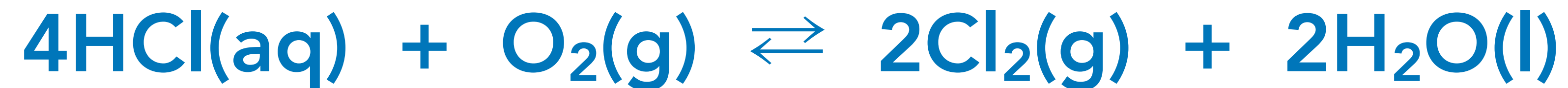
Write the equilibrium expression,  $K_c$ , for:



$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

# Example: Equilibrium Expression ( $K_c$ )

Write the equilibrium expression,  $K_c$ , for:



$$K_c = \frac{[\text{Cl}_2]^2}{[\text{HCl}]^4 [\text{O}_2]}$$

Adding or taking away small amounts of water in a reaction that takes place in an aqueous solution does not affect the overall concentration of  $\text{H}_2\text{O}$

# Details About the Equilibrium Constant, $K$

- $K$  indicates how far a reaction will proceed towards the products at a given temperature.
- Small  $K$  means little to no reaction
- Large  $K$  means the reaction goes to or near completion
- Intermediate  $K$  means significant amounts of reactants and products are present at equilibrium.

