

Lecture 15

Thermodynamics I

Heat vs. Temperature

Enthalpy and Work

Endothermic and Exothermic Reactions

Average Bond Enthalpy

Thermodynamics

- The relationship between chemical reactions and heat.
- What causes chemical reactions to occur?
- The concepts of Enthalpy, Entropy, and Free Energy.

Heat vs. Temperature

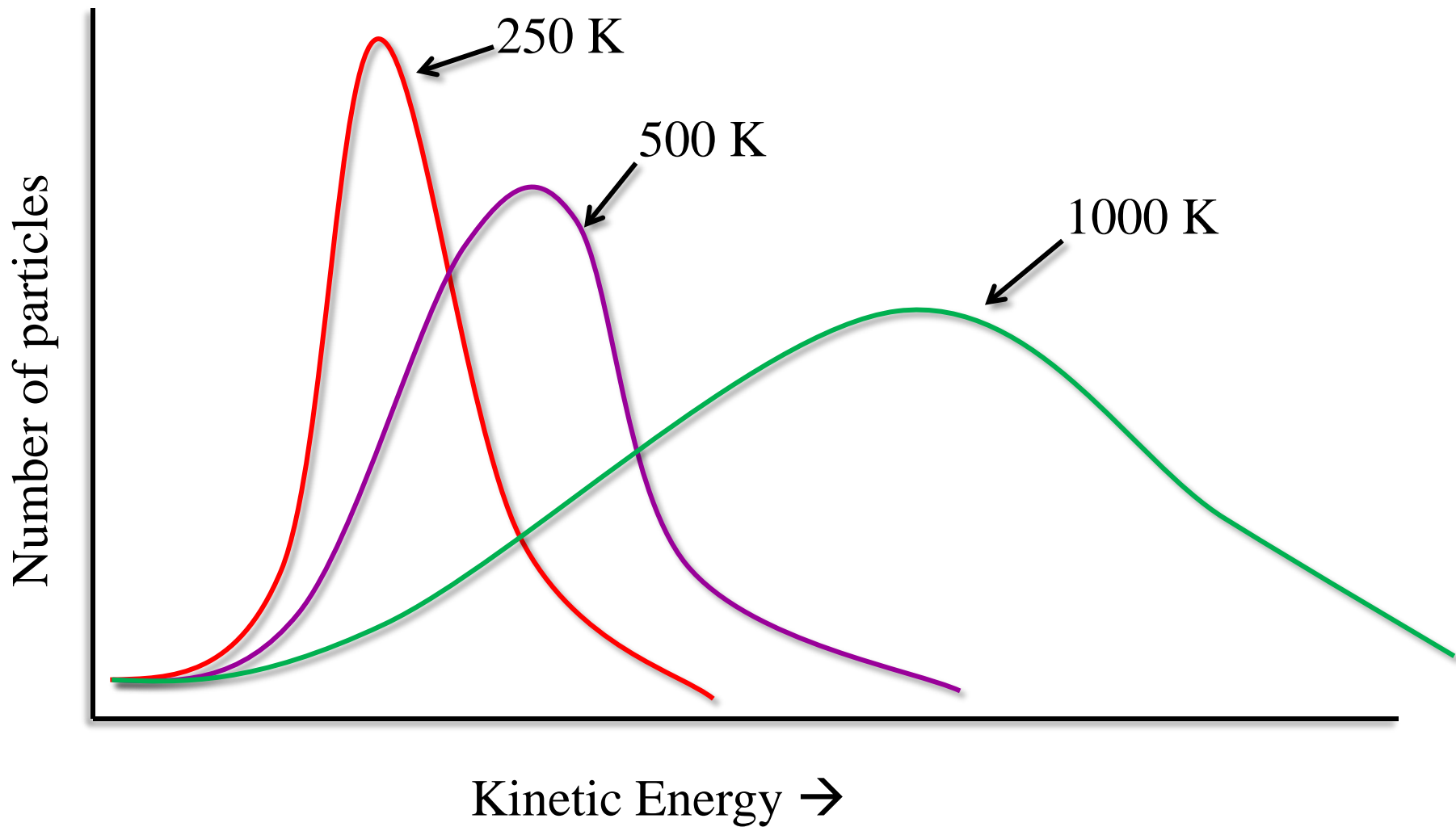
Heat

- A form of energy measured in Joules (J).

Temperature

- A measure of the average kinetic energy of atoms and molecules in a system.
 - The Kelvin (K) temperature scale is proportional to this.
 - When KE doubles, the Kelvin temperature doubles.

Boltzmann Distribution and Temperature

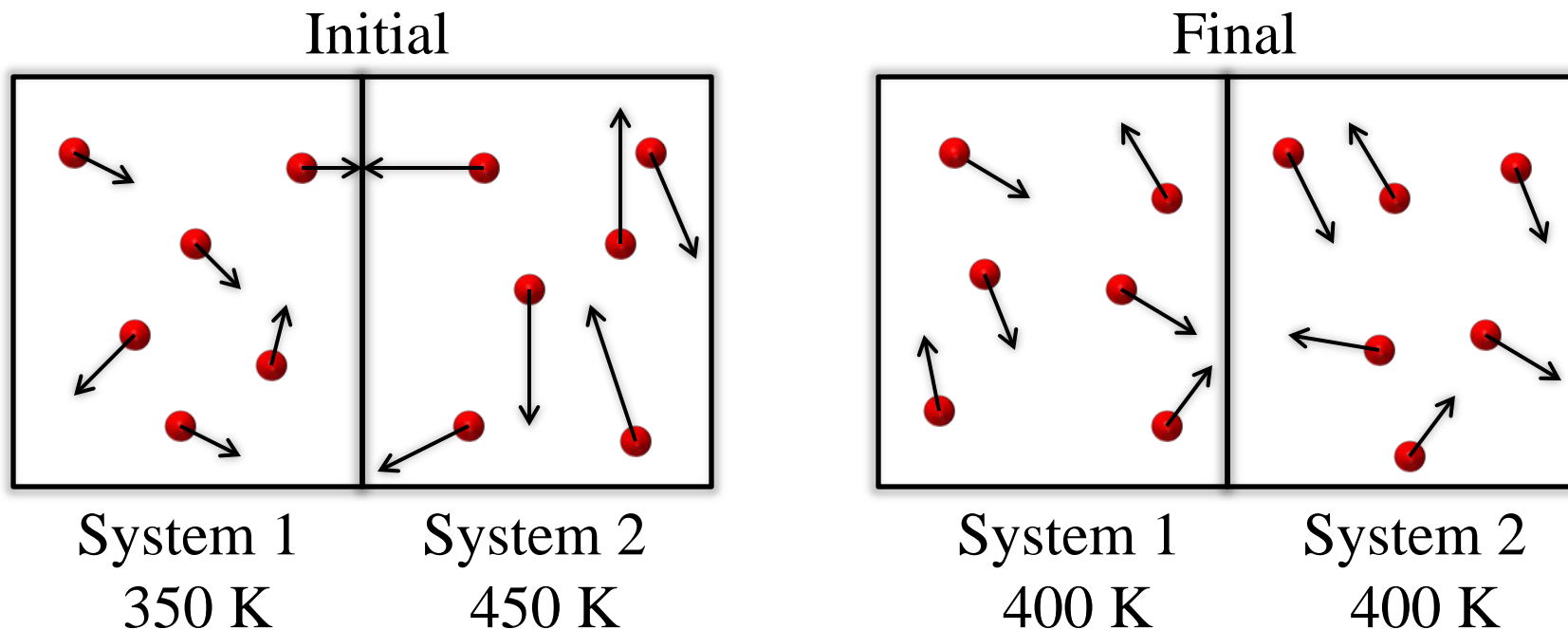


Boltzmann Distribution and Temperature

- The distribution of kinetic energies increases as temperature increases.
- The average kinetic energy of the particles in a system increases as temperature increases.

Energy Transfer Between Systems

- Two systems at different temperatures that are in thermal contact with one another will exchange energy (heat).
- The energy transferred to system 1 is equal to the energy transferred from system 2.



Conservation of Energy

- Energy can be neither created nor destroyed, but it can be transformed from one form to another.
 - The energy of a system changes during a:
 - chemical reaction,
 - phase change, or
 - change in temperature.
 - This results in energy being transferred into or out of the system in the form of heat or work.

Systems and Surroundings

System

- The actual chemical reaction that is taking place.

Surroundings

- The entire universe outside of the chemical reaction.

Change in a System's Internal Energy (ΔE)

$$\Delta E = q + w$$

ΔE = Change in the *PE* and *KE* of the particles in a system

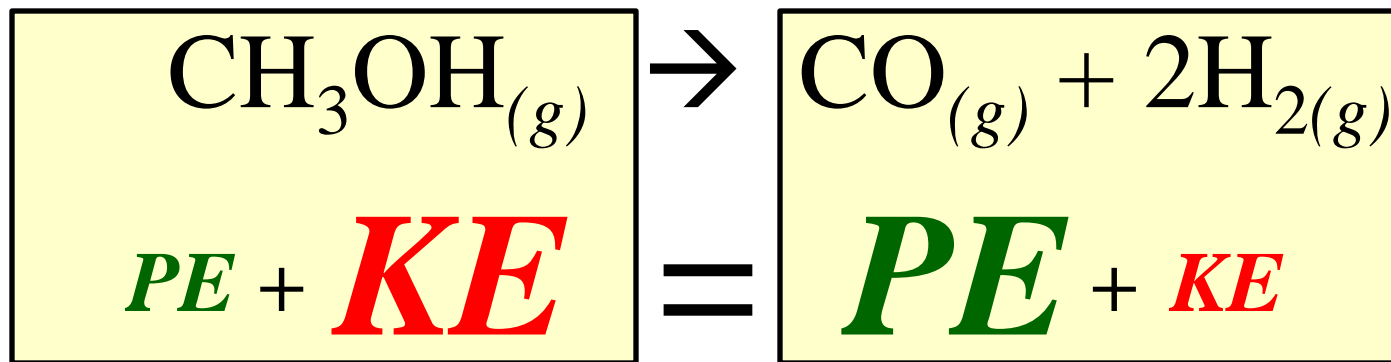
q = Heat that is transferred into (+ value) or out of (– value) the system

w = Work done on the system by the surroundings (+ value as energy flows into the system) or work done on the surrounding by the system (– value as energy flows out of the system)

- Work results from changes in the volume of a gas.

Heat and Endothermic Processes

In an isolated system, energy is conserved.



$$\Delta H = +90.7 \text{ kJ}$$

As the bonds in the products contain more *PE*, the product molecules must contain less *KE*.

- This is why the products of an endothermic reaction are at a lower temperature.

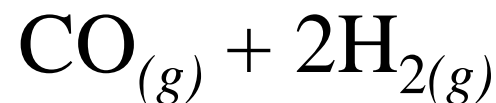
Heat and Endothermic Processes

Because the products are at a lower temperature than the surroundings...

Surroundings



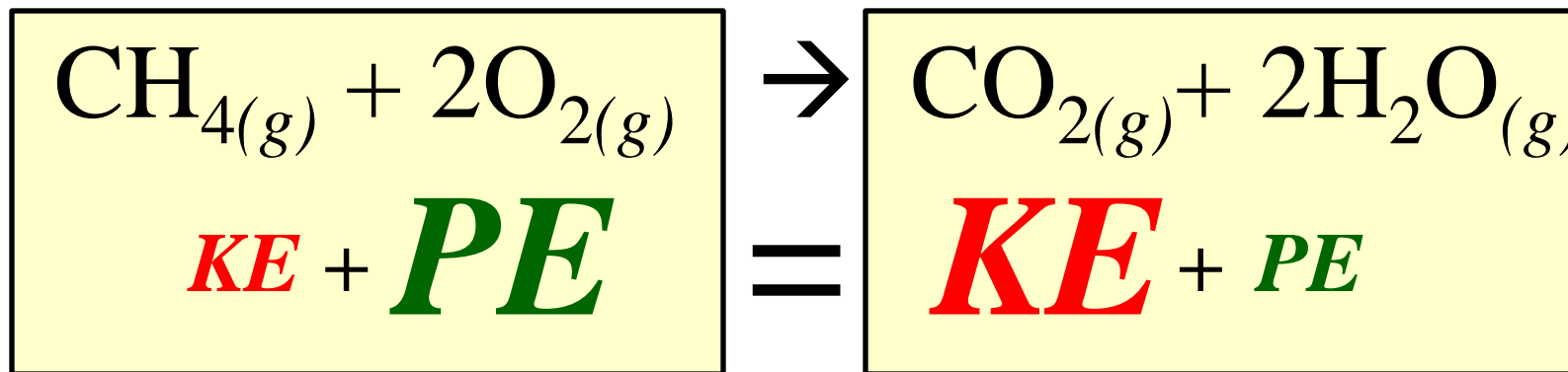
System after an
endothermic reaction



heat must flow from the surroundings into the system until thermal equilibrium is established.

Heat and Exothermic Processes

In an isolated system, energy is conserved.



As the bonds in the products contain less *PE*, the product molecules must contain more *KE*.

- This is why the products of an exothermic reaction are at a higher temperature.

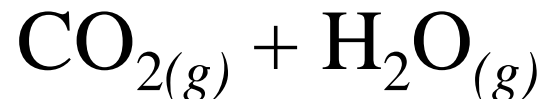
Heat and Exothermic Processes

Because the products are at a higher temperature than the surroundings...

Surroundings



System after an
exothermic reaction

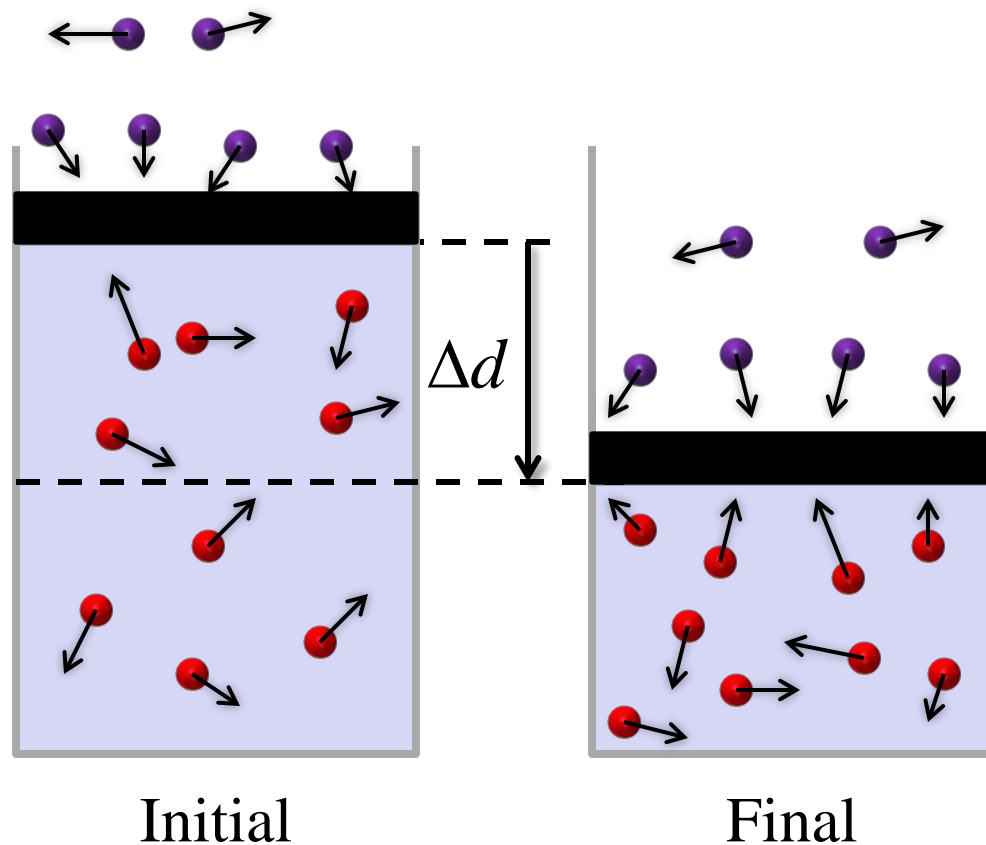


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Work and Endothermic Processes

- If the pressure caused by gas particles colliding with the piston on the outside of the cylinder is greater than that inside the cylinder...

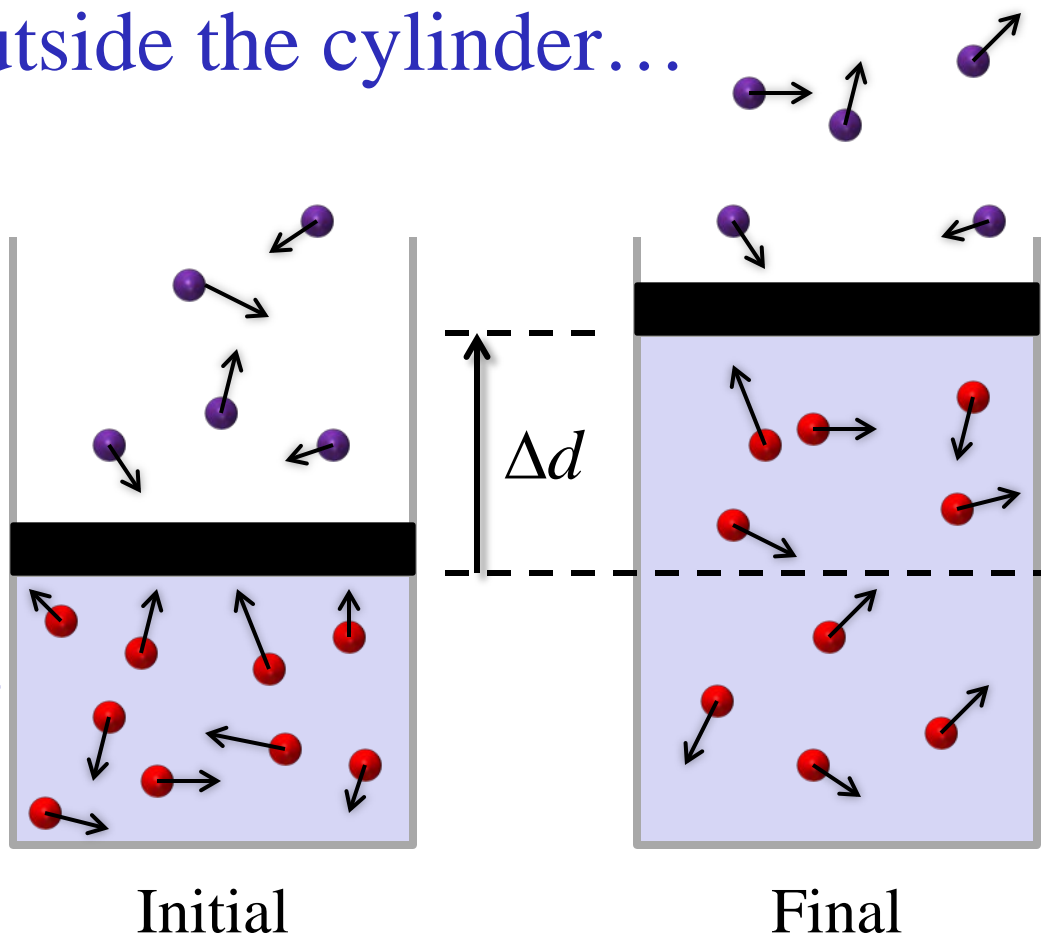
the gas outside does work on the piston, energy is transferred from the gas to the piston, and the gas inside the cylinder contracts.



Work and Exothermic Processes

- If the pressure caused by gas particles colliding with the piston on the inside of the cylinder is greater than that outside the cylinder...

the gas inside does work on the piston, energy is transferred from the gas to the piston, and the gas inside the cylinder expands.



Transfer of Energy Through Work

- Associated with changes in the volume of a gas.

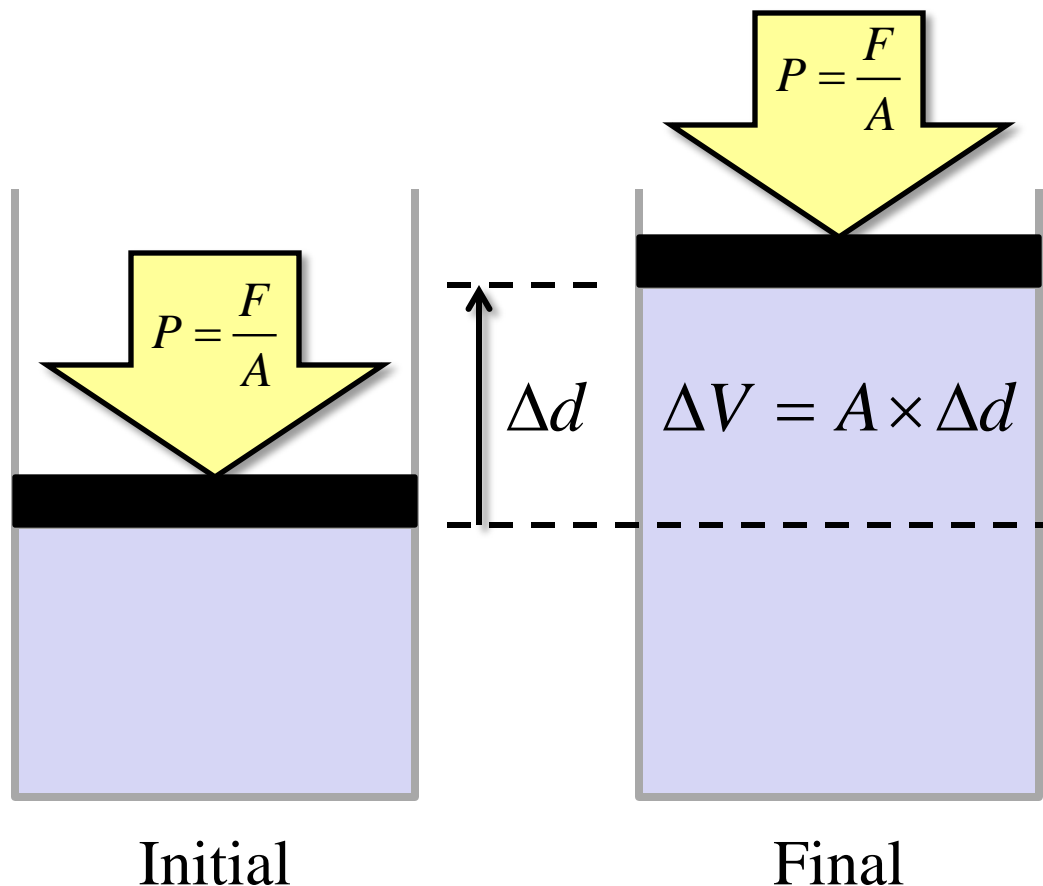
$$w = F \times \Delta d$$

$$w = P \times A \times \Delta d$$

$$w = P\Delta V$$

$$w = -P\Delta V$$

Must be (-) to get the correct sign for w .



Ex1) Transfer of Energy Through Work

Ex1) A gas expands from 0.87 L to 2.46 L in a cylinder under a constant external pressure of 1.05 atm. Calculate the work associated with the expansion of this gas.

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$$w = -1.67 \text{ L} \cdot \text{atm} \times \frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}}$$

$$w = -169 \text{ J}$$

Exothermic – the system expanded into the surroundings

Ex2) Transfer of Energy Through Work

Ex2) 1142 J of heat are added to a cylinder, which causes its contained gas to expand from 1.35 L to 4.18 L under a constant external pressure of 1.03 atm. Calculate ΔE for this process.

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$$w = -1.03 \text{ atm}(4.18 \text{ L} - 1.35 \text{ L})$$

$$w = -2.91 \text{ L} \cdot \text{atm}$$

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$$w = -295 \text{ J}$$

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$$\Delta E = q + w$$

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$$w = -295 \text{ J}$$

$$\Delta E = q + w$$

$$\Delta E = \overset{\uparrow}{+}1142 \text{ J} + (\overset{\uparrow}{-}295 \text{ J})$$

Endothermic

Exothermic

Ex2) Transfer of Energy Through Work

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$$\Delta E = q + w$$

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Endothermic

Exothermic

$$\Delta E = 847 \text{ J}$$

Enthalpy of Reaction (ΔH)

- The heat that is released or absorbed in a chemical reaction.

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

Heat released or absorbed in the reaction

The heat contained within the products

The heat contained within the reactants

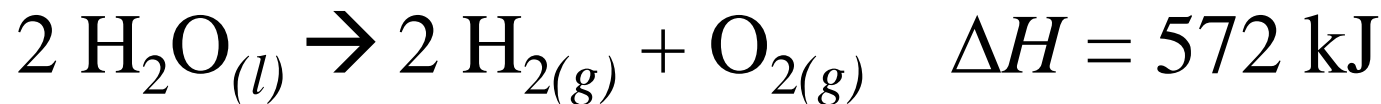
Enthalpy Change (ΔH)

Hydrogen Fuel for Your Car

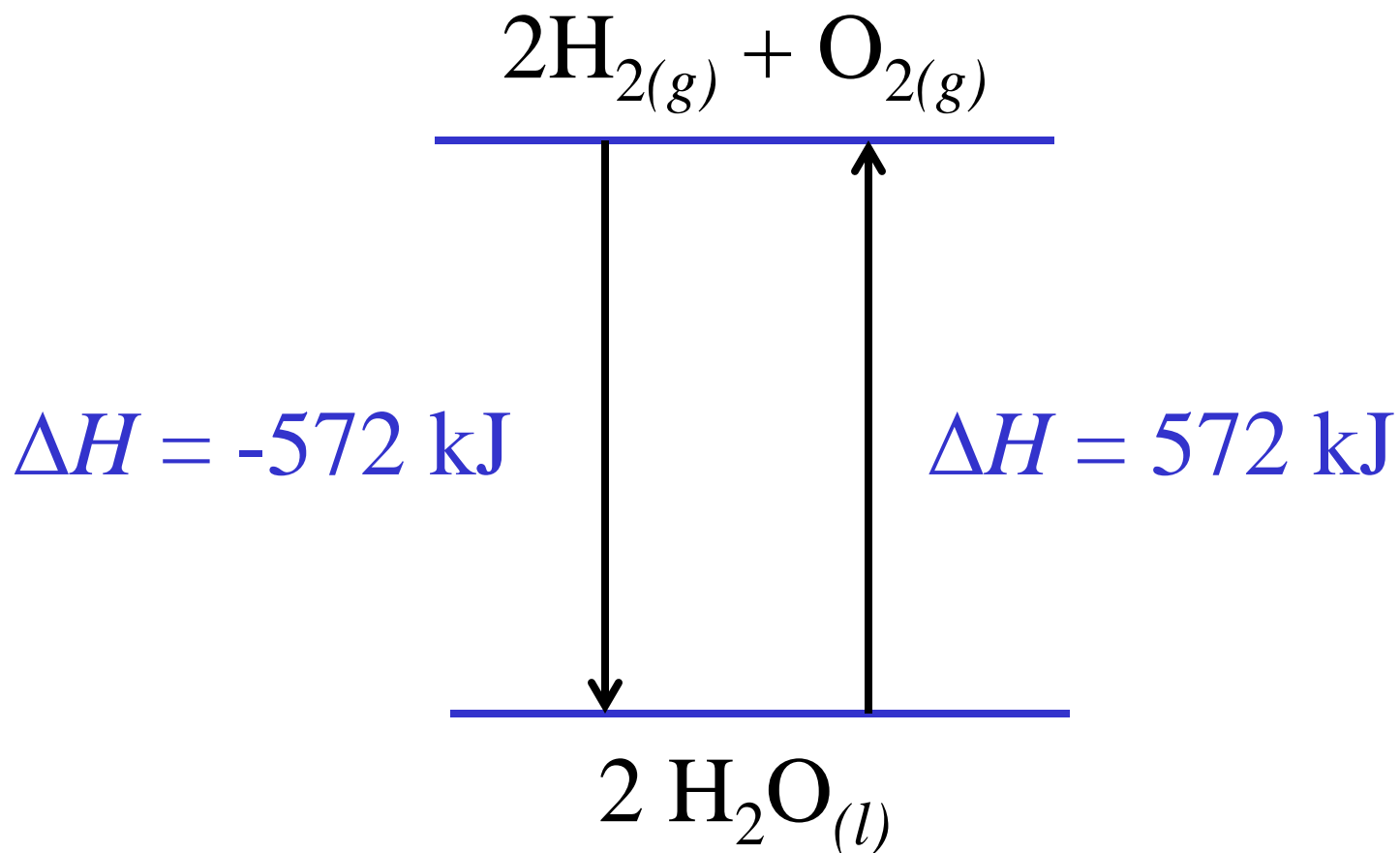
Burning Hydrogen Fuel



Making Hydrogen Gas



Enthalpy Change Diagram



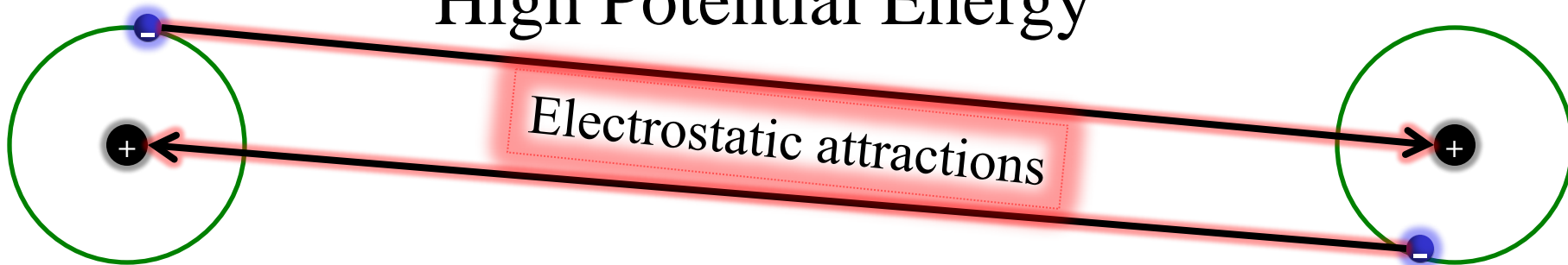
Four Methods for Finding ΔH

- 1) Calculate it using average bond enthalpies.**
- 2) Measure it using a calorimeter.
- 3) Calculate it using Hess's Law.
- 4) Calculate it using enthalpies of formation.

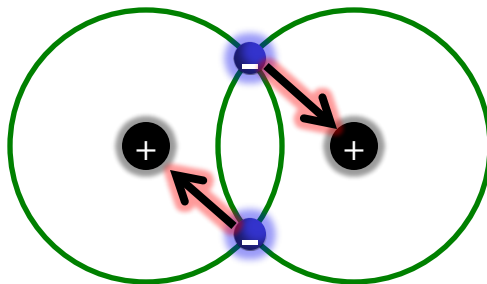
Bond Energy

- The potential energy of valence electrons decreases as they approach the nucleus of another atom.

High Potential Energy



Low Potential Energy



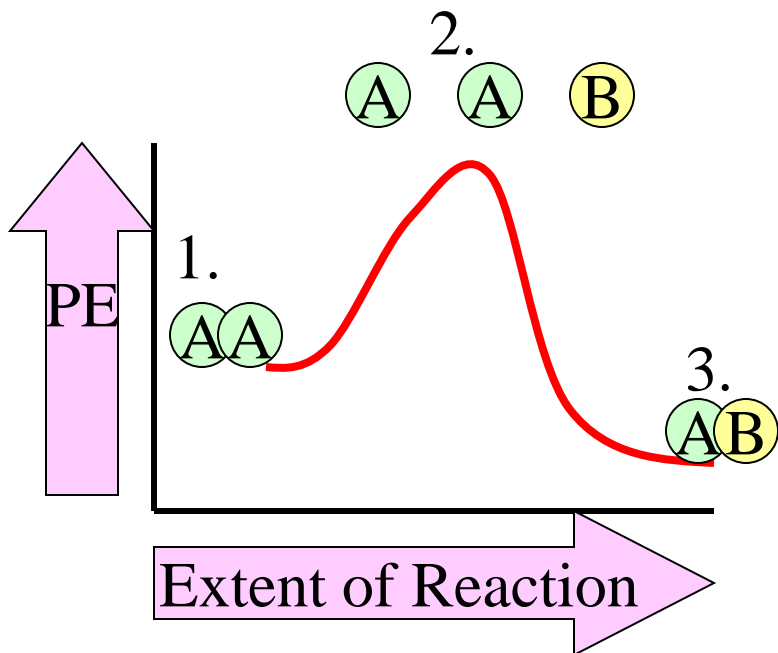
Bond Enthalpy

- Energy is always released during the formation of a bond.
 - Potential energy decreases as the atoms move closer together.
- The same amount of energy must be added in order to break that specific bond.
 - Potential energy increases as the atoms move away from one another.

ΔH from Bond Enthalpies

$$\Delta H = \sum BE_{(\text{bonds broken})} - \sum BE_{(\text{bonds formed})}$$

BE = Bond Enthalpy – the amount of energy required to break a bond, which is equal to the amount of energy released when that same bond is formed.



1 to 2: In order to break the A-A bond, a certain amount of energy must be absorbed.

2 to 1: If an A-A bond forms, the same amount of energy is released.

2 to 3: If an A-B bond is formed, a different amount of energy is released.

ΔH from Bond Enthalpies

$$\Delta H = \sum BE_{(\text{bonds broken})} - \sum BE_{(\text{bonds formed})}$$

Exothermic Process

- More energy is released during the formation of bonds in the products than is required to break the bonds in the reactants.
- The products are at a lower potential energy than the reactants.

ΔH from Bond Enthalpies

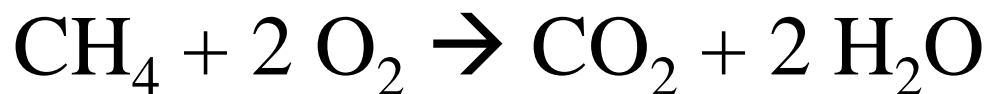
$$\Delta H = \sum BE_{(\text{bonds broken})} - \sum BE_{(\text{bonds formed})}$$

Endothermic Process

- Less energy is released during the formation of bonds in the products than is required to break the bonds in the reactants.
- The products are at a higher potential energy than the reactants.

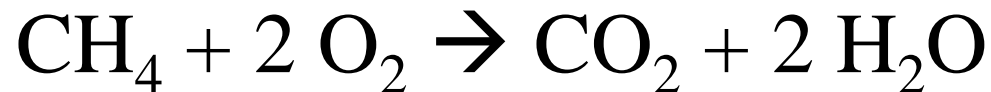
Ex1) ΔH from Bond Enthalpies

Ex1) Calculate the enthalpy change for the following reaction using the table of values.



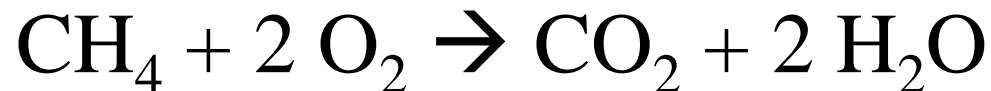
Bond	Average Bond Enthalpy
C – H	413 kJ/mol
O = O	495 kJ/mol
C – O	358 kJ/mol
C = O	799 kJ/mol
O – H	467 kJ/mol

Ex1) ΔH from Bond Enthalpies (cont.)



$$\Delta H = \sum BE_{(\text{bonds broken})} - \sum BE_{(\text{bonds formed})}$$

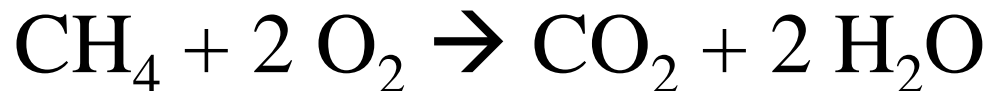
Ex1) ΔH from Bond Enthalpies (cont.)



$$\Delta H = \Sigma BE_{\text{(bonds broken)}} - \Sigma BE_{\text{(bonds formed)}}$$

$$\Delta H = [4(\text{BE}_{\text{C-H}}) + 2(\text{BE}_{\text{O=O}})] - [2(\text{BE}_{\text{C=O}}) + 4(\text{BE}_{\text{O-H}})]$$

Ex1) ΔH from Bond Enthalpies (cont.)



$$\Delta H = \Sigma BE_{(\text{bonds broken})} - \Sigma BE_{(\text{bonds formed})}$$

$$\Delta H = [4(\text{BE}_{\text{C-H}}) + 2(\text{BE}_{\text{O=O}})] - [2(\text{BE}_{\text{C=O}}) + 4(\text{BE}_{\text{O-H}})]$$

$$\Delta H = [4(413) + 2(495)] - [2(799) + 4(467)]$$

$$\Delta H = 2642 \text{ kJ/mol} - 3466 \text{ kJ/mol}$$

$$\Delta H = - 824 \text{ kJ/mol}$$

Ex2) ΔH from Bond Enthalpies

Ex2) Calculate the average bond energy in an H – H bond.



Bond	Average Bond Enthalpy
O = O	495 kJ/mol
O – H	467 kJ/mol

Ex2) ΔH from Bond Enthalpies (cont.)



$$\Delta H = \sum BE_{(\text{bonds broken})} - \sum BE_{(\text{bonds formed})}$$

Ex2) ΔH from Bond Enthalpies (cont.)



$$\Delta H = \Sigma BE_{(\text{bonds broken})} - \Sigma BE_{(\text{bonds formed})}$$

$$\Delta H = \left[2(BE_{\text{H-H}}) + (BE_{\text{O=O}}) \right] - 4(BE_{\text{O-H}})$$

Ex2) ΔH from Bond Enthalpies (cont.)



$$\Delta H = \Sigma BE_{(\text{bonds broken})} - \Sigma BE_{(\text{bonds formed})}$$

$$\Delta H = [2(BE_{\text{H-H}}) + (BE_{\text{O=O}})] - 4(BE_{\text{O-H}})$$

$$2(BE_{\text{H-H}}) = - [(BE_{\text{O=O}}) - 4(BE_{\text{O-H}}) - \Delta H]$$

Ex2) ΔH from Bond Enthalpies (cont.)



$$\Delta H = \sum BE_{(\text{bonds broken})} - \sum BE_{(\text{bonds formed})}$$

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$$2(BE_{\text{H-H}}) = -(BE_{\text{O=O}}) + 4(BE_{\text{O-H}}) + \Delta H$$

Ex2) ΔH from Bond Enthalpies (cont.)



$$\Delta H = \Sigma BE_{(\text{bonds broken})} - \Sigma BE_{(\text{bonds formed})}$$

$$\Delta H = [2(BE_{\text{H-H}}) + (BE_{\text{O=O}})] - 4(BE_{\text{O-H}})$$

$$2(BE_{\text{H-H}}) = - [(BE_{\text{O=O}}) - 4(BE_{\text{O-H}}) - \Delta H]$$

$$2(BE_{\text{H-H}}) = -(BE_{\text{O=O}}) + 4(BE_{\text{O-H}}) + \Delta H$$

$$2(BE_{\text{H-H}}) = -495 \text{ kJ/mol} + 4(467 \text{ kJ/mol}) - 572 \text{ kJ/mol}$$

$$BE_{\text{H-H}} = \frac{801 \text{ kJ/mol}}{2} = 401 \text{ kJ/mol}$$