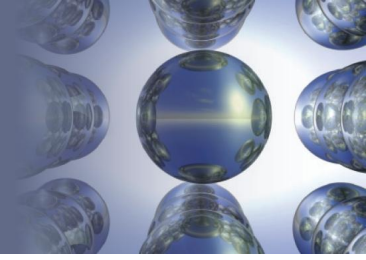


## Chapter 6

## *Thermochemistry*

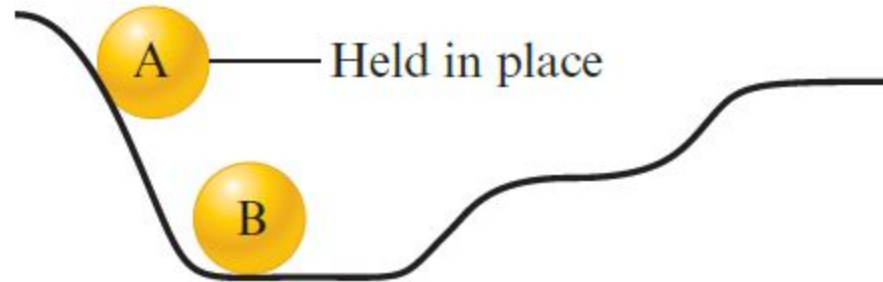
# Section 6.1

## *The Nature of Energy*



### Conversion of Energy

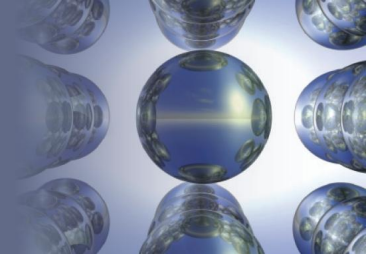
- Consider the following image:



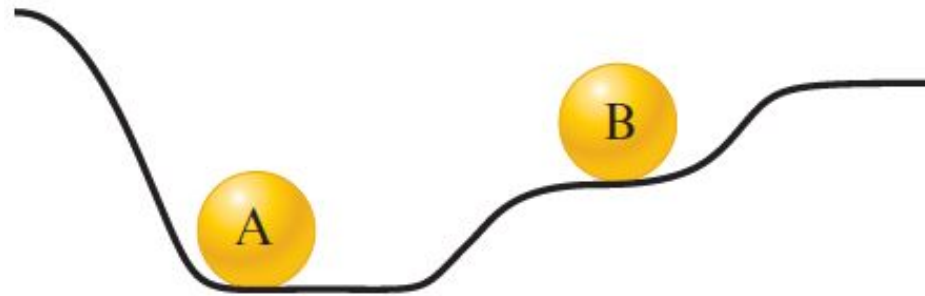
- Which ball has more potential energy?

# Section 6.1

## *The Nature of Energy*



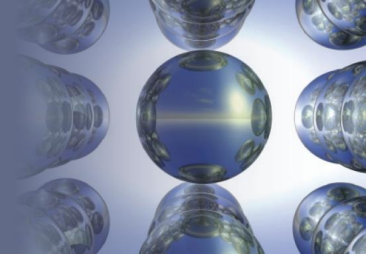
### Conversion of Energy (Continued)



- After A has rolled down the hill, the potential energy lost by A has been converted to:
  - Random motions of the components of the hill (frictional heating)
  - The increase in the potential energy of B

# Section 6.1

## *The Nature of Energy*

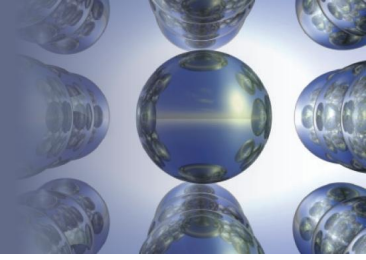


### Methods of Transferring Energy

- **Heat:** Transfer of energy between two objects due to a temperature difference
  - Temperature reflects random motion of particles in a substance
- **Work:** Force acting over a distance

# Section 6.1

## *The Nature of Energy*

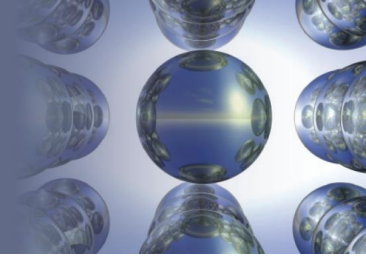


### Pathway

- Specific conditions that define the path by which energy is transferred
- Work and heat are dependent on the pathway
- Energy change is independent of the pathway

# Section 6.1

## *The Nature of Energy*

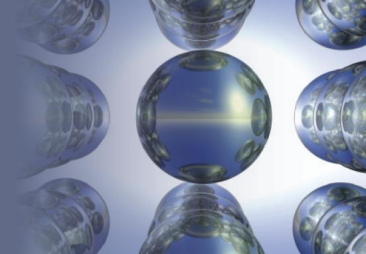


### Energy as a State Function

- **State function (state property)**: Property that does not depend in any way on the system's past or future
  - Value depends on characteristics of the present state

# Section 6.1

## *The Nature of Energy*



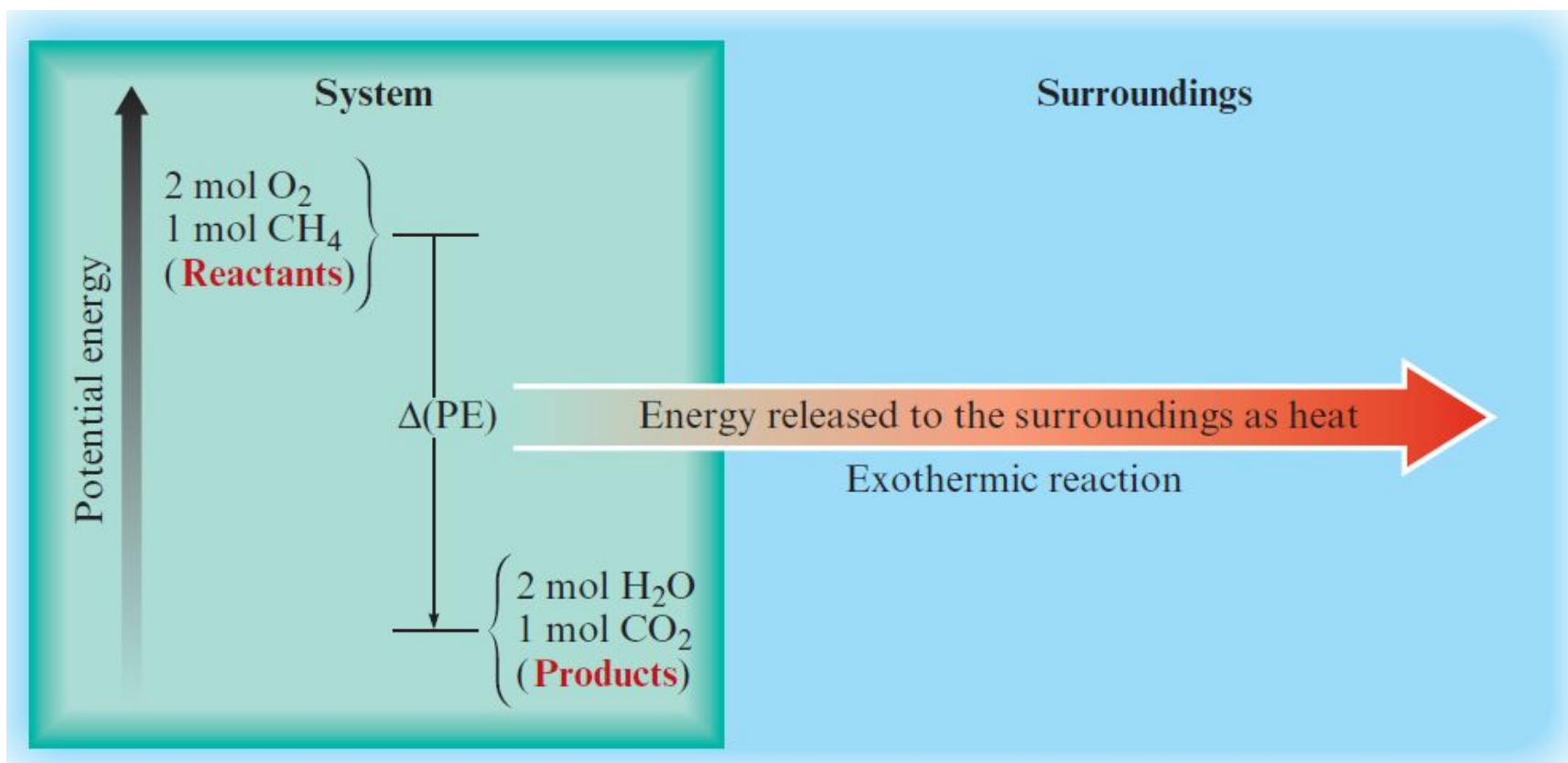
### Reaction Mechanism

- Energy gained by the surroundings must be equal to the energy lost by the system
  - Endothermic reactions result from a lowered potential energy of the reaction system
  - In exothermic reactions, potential energy stored in bonds is converted to thermal energy via heat

# Section 6.1

## *The Nature of Energy*

**Figure 6.2** - Energy Diagram for the Combustion of Methane

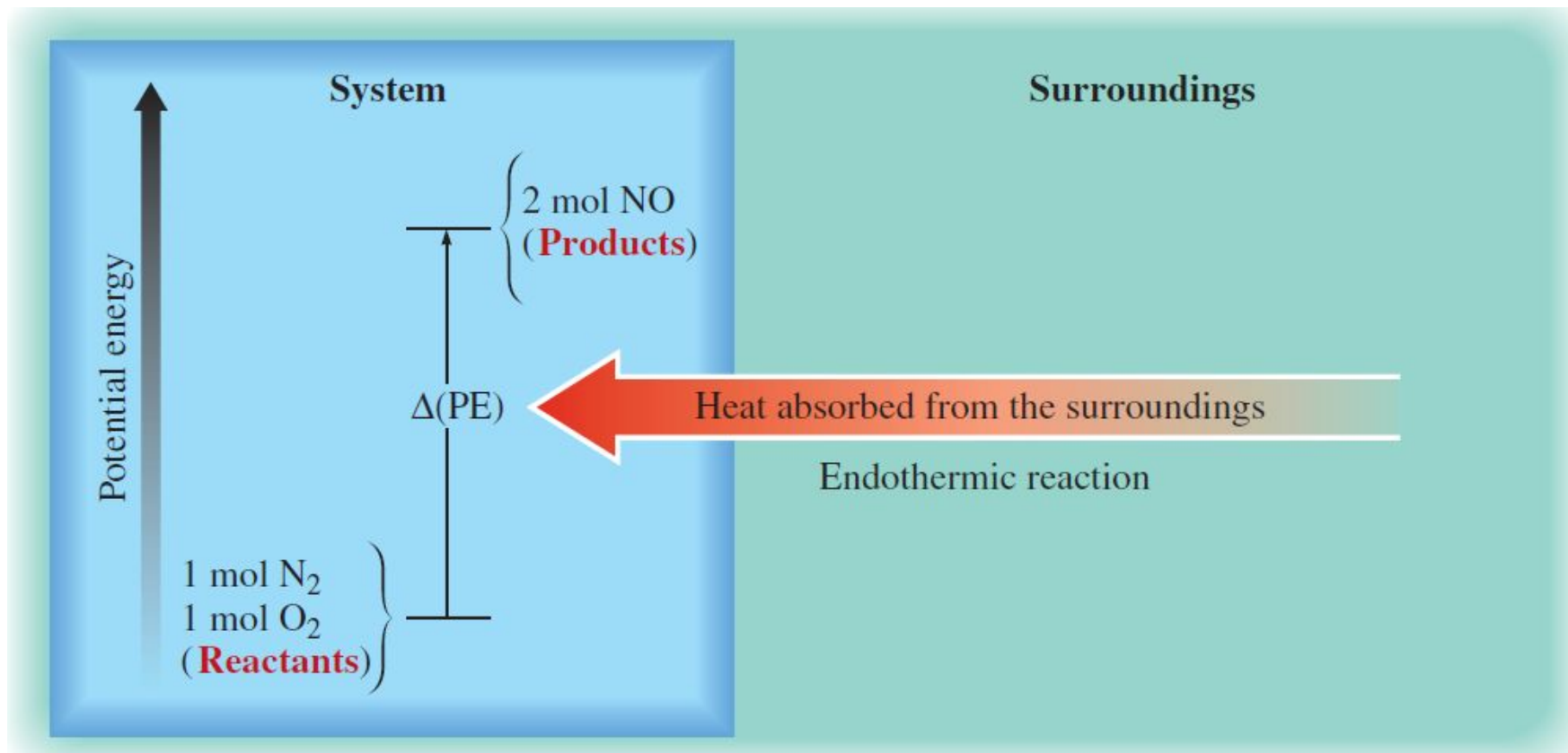




# Section 6.1

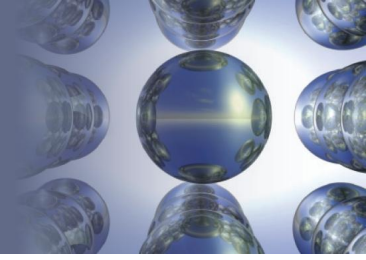
## *The Nature of Energy*

**Figure 6.3** - Energy Diagram for the Formation of Nitric Oxide



# Section 6.1

## *The Nature of Energy*

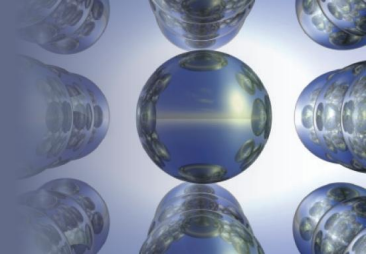


### Thermodynamics

- Study of energy and its interconversions
- **First law of thermodynamics:** Energy of the universe is constant
  - Known as the law of conservation of energy

## Section 6.2

# *Enthalpy and Calorimetry*



## Enthalpy ( $H$ )

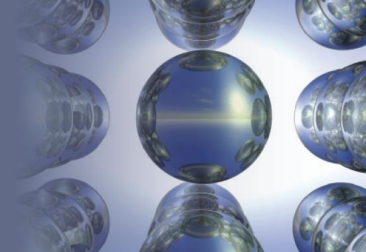
- A state function that is defined as:

$$H = E + PV$$

- $E$  - Internal energy of the system
- $P$  - Pressure of the system
- $V$  - Volume of the system

# Section 6.2

## *Enthalpy and Calorimetry*



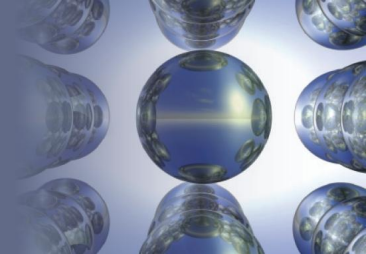
### Enthalpy and $PV$ Work

- At constant pressure,  $\Delta H = q$
- For a chemical reaction, the enthalpy change is given by the following equation:

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

# Section 6.2

## *Enthalpy and Calorimetry*

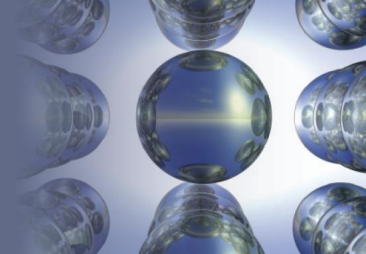


### Enthalpy and $PV$ Work (Continued)

- When  $H_{\text{products}} > H_{\text{reactants}}$ ,  $\Delta H$  is positive
  - Heat is absorbed by the system
  - Reaction is endothermic
- When  $H_{\text{products}} < H_{\text{reactants}}$ ,  $\Delta H$  is negative
  - Decrease in enthalpy is achieved by generation of heat
  - Reaction is exothermic

## Section 6.2

### *Enthalpy and Calorimetry*

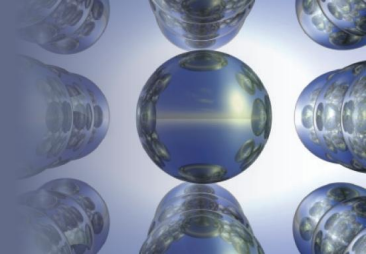


**Answer in notes, compare with partner**

- When 1 mole of methane ( $\text{CH}_4$ ) is burned at constant pressure, 890 kJ of energy is released as heat
  - Calculate  $\Delta H$  for a process in which a 5.8-g sample of methane is burned at constant pressure

## Section 6.2

# *Enthalpy and Calorimetry*

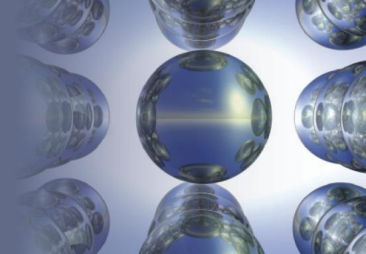


### Interactive Example 6.4 - Solution

- Where are we going?
  - To calculate  $\Delta H$
- What do we know?
  - $q_p = \Delta H = -890 \text{ kJ/mol CH}_4$
  - Mass = 5.8 g  $\text{CH}_4$
  - Molar mass  $\text{CH}_4 = 16.04 \text{ g}$

## Section 6.2

# Enthalpy and Calorimetry



### Interactive Example 6.4 - Solution (Continued 1)

- How do we get there?
  - What are the moles of  $\text{CH}_4$  burned?

$$5.8 \cancel{\text{ g CH}_4} \times \frac{1 \text{ mol CH}_4}{16.04 \cancel{\text{ g CH}_4}} = 0.36 \text{ mol CH}_4$$

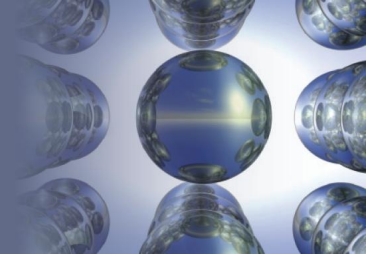
- What is  $\Delta H$ ?

$$\Delta H = 0.36 \cancel{\text{ mol CH}_4} \times \frac{-890 \text{ kJ}}{\cancel{\text{ mol CH}_4}} = -320 \text{ kJ}$$



## Section 6.2

# *Enthalpy and Calorimetry*



### Interactive Example 6.4 - Solution (Continued 2)

- Thus, when a 5.8-g sample of  $\text{CH}_4$  is burned at constant pressure,

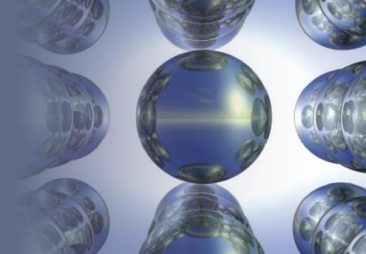
$$\Delta H = \text{heat flow} = -320 \text{ kJ}$$

- Reality check

- In this case, a 5.8-g sample of  $\text{CH}_4$  is burned
  - Since this amount is smaller than 1 mole, less than 890 kJ will be released as heat

## Section 6.2

### *Enthalpy and Calorimetry*

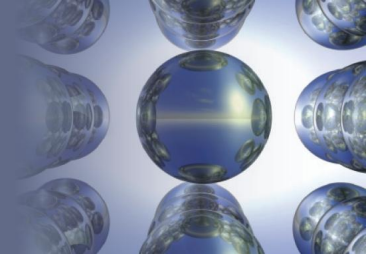


#### Interactive Example 6.5 - Constant-Pressure Calorimetry

- When 1.00 L of 1.00 M  $\text{Ba}(\text{NO}_3)_2$  solution at 25.0°C is mixed with 1.00 L of 1.00 M  $\text{Na}_2\text{SO}_4$  solution at 25.0°C in a calorimeter, the white solid  $\text{BaSO}_4$  forms, and the temperature of the mixture increases to 28.1°C
- Calculate the enthalpy change per mole of  $\text{BaSO}_4$  formed

## Section 6.2

# *Enthalpy and Calorimetry*

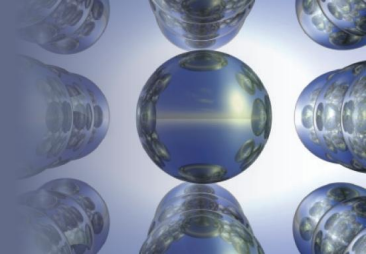


## Interactive Example 6.5 - Constant-Pressure Calorimetry (Continued)

- Assume that:
  - The calorimeter absorbs only a negligible quantity of heat
  - The specific heat capacity of the solution is  $4.18 \text{ J/ } ^\circ\text{C} \cdot \text{g}$
  - The density of the final solution is  $1.0 \text{ g/mL}$

## Section 6.2

# Enthalpy and Calorimetry

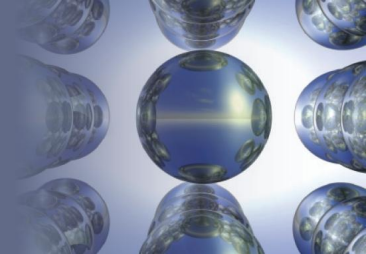


### Interactive Example 6.5 - Solution

- Where are we going?
  - To calculate  $\Delta H$  per mole of  $\text{BaSO}_4$  formed
- What do we know?
  - 1.00 L of 1.00 M  $\text{Ba}(\text{NO}_3)_2$
  - 1.00 L of 1.00 M  $\text{Na}_2\text{SO}_4$
  - $T_{\text{initial}} = 25.0^\circ\text{C}$  and  $T_{\text{final}} = 28.1^\circ\text{C}$
  - Heat capacity of solution =  $4.18 \text{ J}/^\circ\text{C} \cdot \text{g}$
  - Density of final solution =  $1.0 \text{ g/mL}$

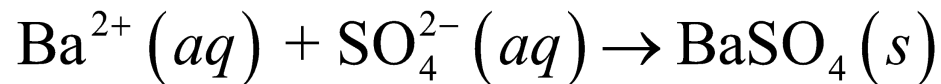
## Section 6.2

# *Enthalpy and Calorimetry*



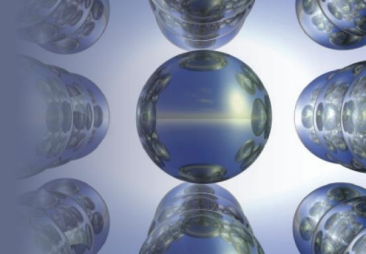
### Interactive Example 6.5 - Solution (Continued 1)

- What do we need?
  - Net ionic equation for the reaction
    - The ions present before any reaction occurs are  $\text{Ba}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{Na}^+$ , and  $\text{SO}_4^{2-}$
    - The  $\text{Na}^+$  and  $\text{NO}_3^-$  ions are spectator ions, since  $\text{NaNO}_3$  is very soluble in water and will not precipitate under these conditions
    - The net ionic equation for the reaction is:



## Section 6.2

# *Enthalpy and Calorimetry*

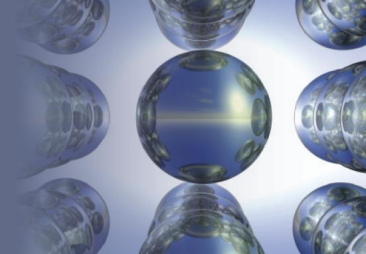


### Interactive Example 6.5 - Solution (Continued 2)

- How do we get there?
  - What is  $\Delta H$ ?
    - Since the temperature increases, formation of solid  $\text{BaSO}_4$  must be exothermic
    - $\Delta H$  is negative
    - Heat evolved by the reaction
      - = heat absorbed by the solution
      - = specific heat capacity  $\times$  mass of solution  $\times$  increase in temperature

## Section 6.2

### *Enthalpy and Calorimetry*



#### Interactive Example 6.5 - Solution (Continued 3)

- What is the mass of the final solution?

$$\text{Mass of solution} = 2.00 \cancel{\text{ L}} \times \frac{1000 \cancel{\text{ mL}}}{1 \cancel{\text{ L}}} \times \frac{1.0 \text{ g}}{\cancel{\text{ mL}}} = 2.0 \times 10^3 \text{ g}$$

- What is the temperature increase?

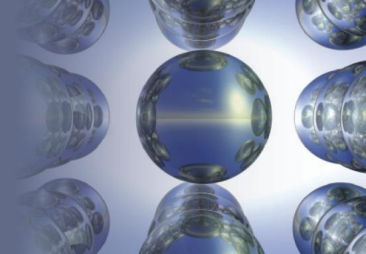
$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 28.1^\circ\text{C} - 25.0^\circ\text{C} = 3.1^\circ\text{C}$$

- How much heat is evolved by the reaction?

$$\text{Heat evolved} = (4.18 \text{ J}/^\circ\text{C} \cdot \text{g})(2.0 \times 10^3 \text{ g})(3.1^\circ\text{C}) = 2.6 \times 10^4 \text{ J}$$

## Section 6.2

# Enthalpy and Calorimetry



### Interactive Example 6.5 - Solution (Continued 4)

- Thus,

$$q = q_P = \Delta H = -2.6 \times 10^4 \text{ J}$$

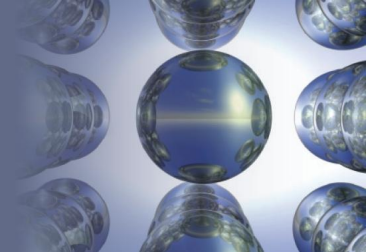
- What is  $\Delta H$  per mole of  $\text{BaSO}_4$  formed?
  - Since 1.0 L of 1.0 M  $\text{Ba}(\text{NO}_3)_2$  contains 1 mole of  $\text{Ba}^{2+}$  ions and 1.0 L of 1.0 M  $\text{Na}_2\text{SO}_4$  contains 1.0 mole of  $\text{SO}_4^{2-}$  ions, 1.0 mole of solid  $\text{BaSO}_4$  is formed in this experiment
  - Thus the enthalpy change per mole of  $\text{BaSO}_4$  formed is

$$\Delta H = -2.6 \times 10^4 \text{ J/mol} = -26 \text{ kJ/mol}$$



## Section 6.3

### *Hess's Law*

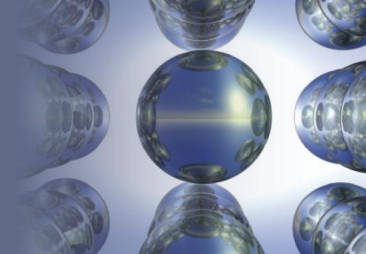


## Hess's Law

- In going from a particular set of reactants to a particular set of products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps

## Section 6.3

### *Hess's Law*

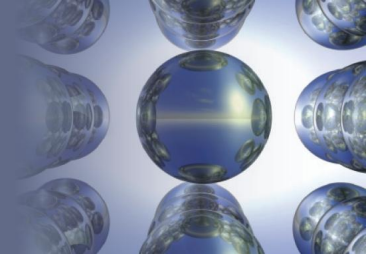


## Problem-Solving Strategy - Hess's Law

- Work backward from the required reaction
- Reverse any reactions as needed to give the required reactants and products
- Multiply reactions to give the correct numbers of reactants and products

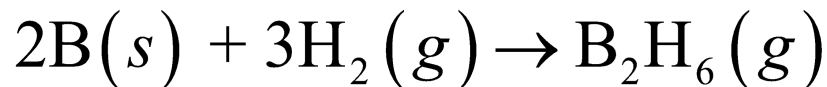
## Section 6.3

### *Hess's Law*



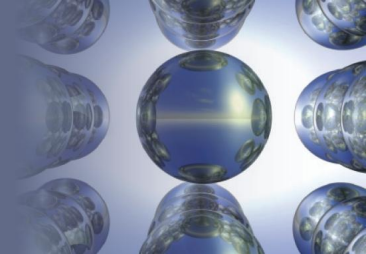
**Write in your notes, next slide will ask the question.**

- Diborane ( $B_2H_6$ ) is a highly reactive boron hydride that was once considered as a possible rocket fuel for the U.S. space program
  - Calculate  $\Delta H$  for the synthesis of diborane from its elements, according to the following equation:



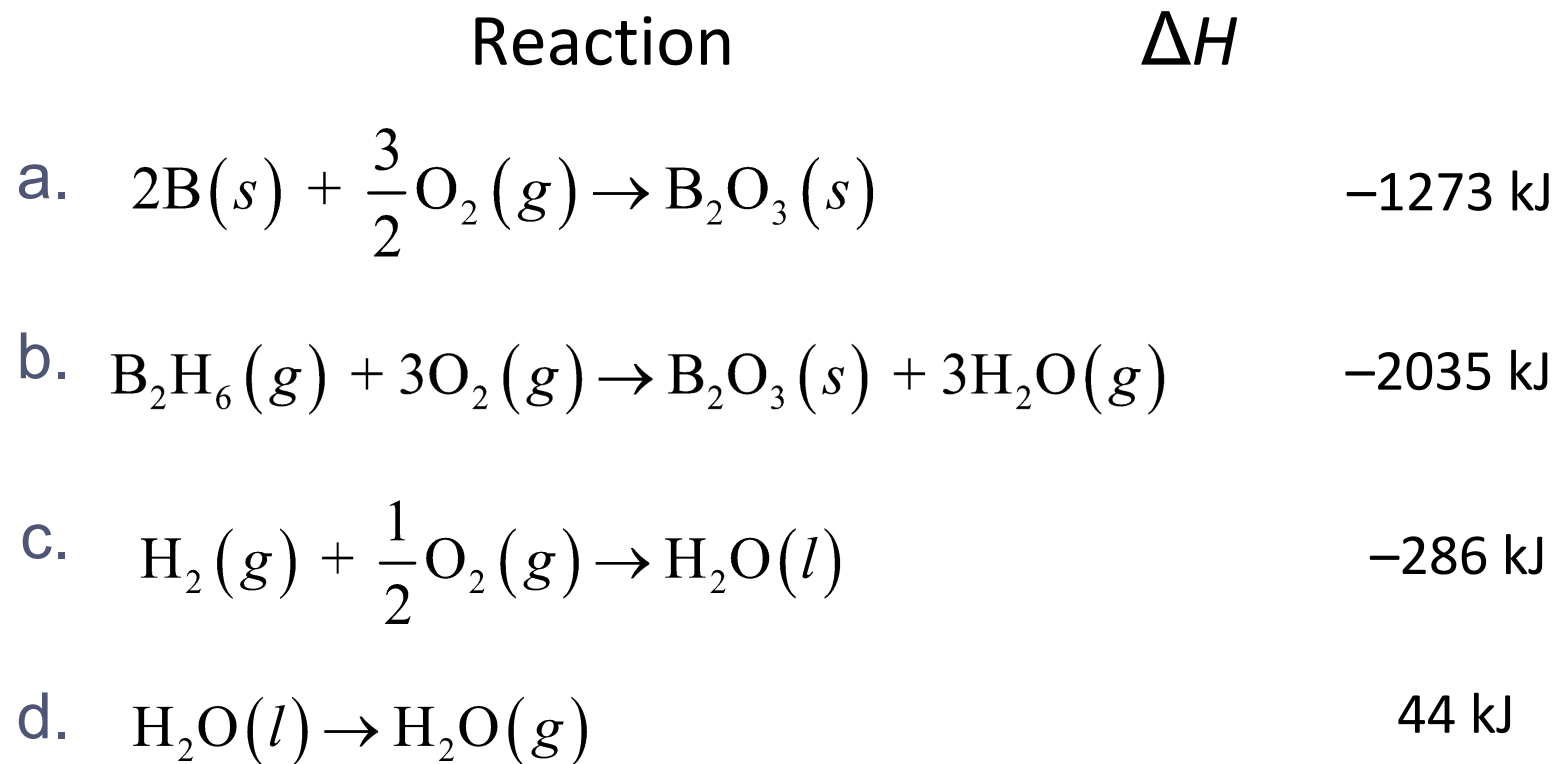
## Section 6.3

### Hess's Law



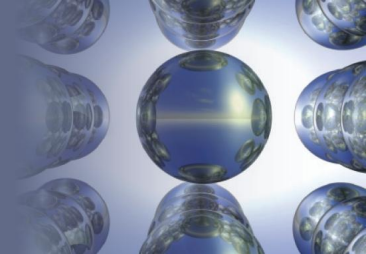
Answer in your notes, compare with partner

- Use the following data:



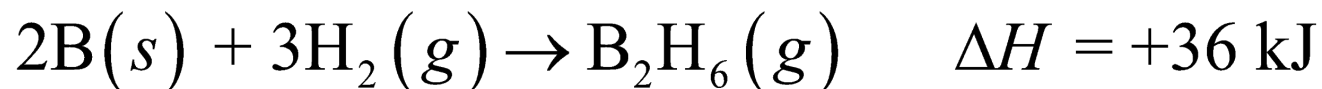
## Section 6.3

### *Hess's Law*



## Interactive Example 6.8 - Solution (Continued 6)

- This gives the reaction required by the problem

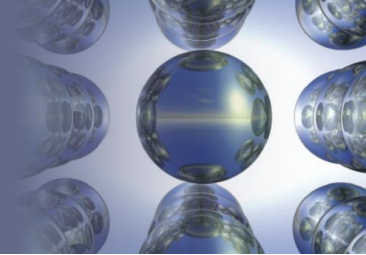


- **Conclusion**

- $\Delta H$  for the synthesis of 1 mole of diborane from the elements is +36 kJ

## Section 6.4

# Standard Enthalpies of Formation



## Problem-Solving Strategy - Enthalpy Calculations

(Continued)

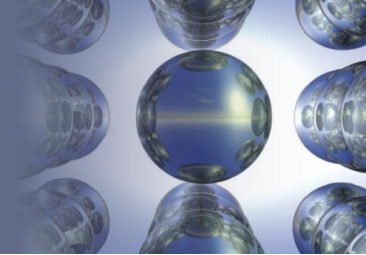
- Change in enthalpy for a given reaction can be calculated from the enthalpies of formation of the reactants and products:

$$\Delta H^{\circ}_{\text{reaction}} = \sum n_{\text{p}} \Delta H^{\circ}_{\text{f}} (\text{products}) - \sum n_{\text{r}} \Delta H^{\circ}_{\text{f}} (\text{reactants})$$

- Elements in their standard states are not included in the  $\Delta H_{\text{reaction}}$  calculations

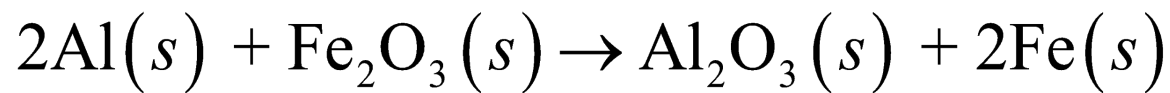
## Section 6.4

### *Standard Enthalpies of Formation*



**Answer in your notes, using the table in Appendix 4 (Page A19), then compare with partner**

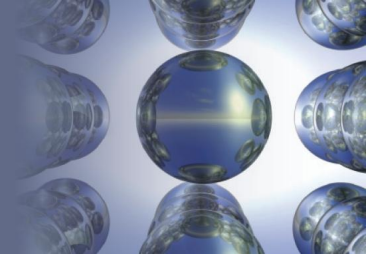
- Using enthalpies of formation, calculate the standard change in enthalpy for the thermite reaction:



- This reaction occurs when a mixture of powdered aluminum and iron(III) oxide is ignited with a magnesium fuse

## Section 6.4

# Standard Enthalpies of Formation



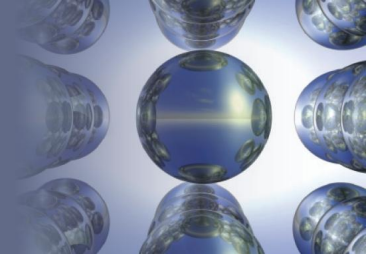
### Interactive Example 6.10 - Solution

- Where are we going?
  - To calculate  $\Delta H$  for the reaction
- What do we know?
  - $\Delta H_f^\circ$  for  $\text{Fe}_2\text{O}_3(s) = -826 \text{ kJ/mol}$
  - $\Delta H_f^\circ$  for  $\text{Al}_2\text{O}_3(s) = -1676 \text{ kJ/mol}$
  - $\Delta H_f^\circ$  for  $\text{Al}(s) = \Delta H_f^\circ$  for  $\text{Fe}(s) = 0$



## Section 6.4

# Standard Enthalpies of Formation



### Interactive Example 6.10 - Solution (Continued 1)

- What do we need?
  - We use the following equation:

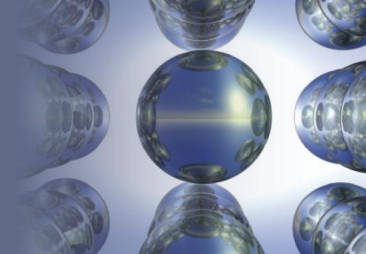
$$\Delta H^\circ = \sum n_p \Delta H^\circ_f (\text{products}) - \sum n_r \Delta H^\circ_f (\text{reactants})$$

- How do we get there?

$$\begin{aligned}\Delta H^\circ_{\text{reaction}} &= \Delta H^\circ_f \text{ for } \text{Al}_2\text{O}_3 (s) - \Delta H^\circ_f \text{ for } \text{Fe}_2\text{O}_3 (s) \\ &= -1676 \text{ kJ} - (-826 \text{ kJ}) = -850 \text{ kJ}\end{aligned}$$

## Section 6.4

# *Standard Enthalpies of Formation*



### Interactive Example 6.10 - Solution (Continued 2)

- This reaction is so highly exothermic that the iron produced is initially molten
  - Used as a lecture demonstration
  - Used in welding massive steel objects such as ships' propellers