CHEMISTRY

an atoms-focused approach

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Chapter 9

Thermochemistry

Energy Changes in Chemical Reactions

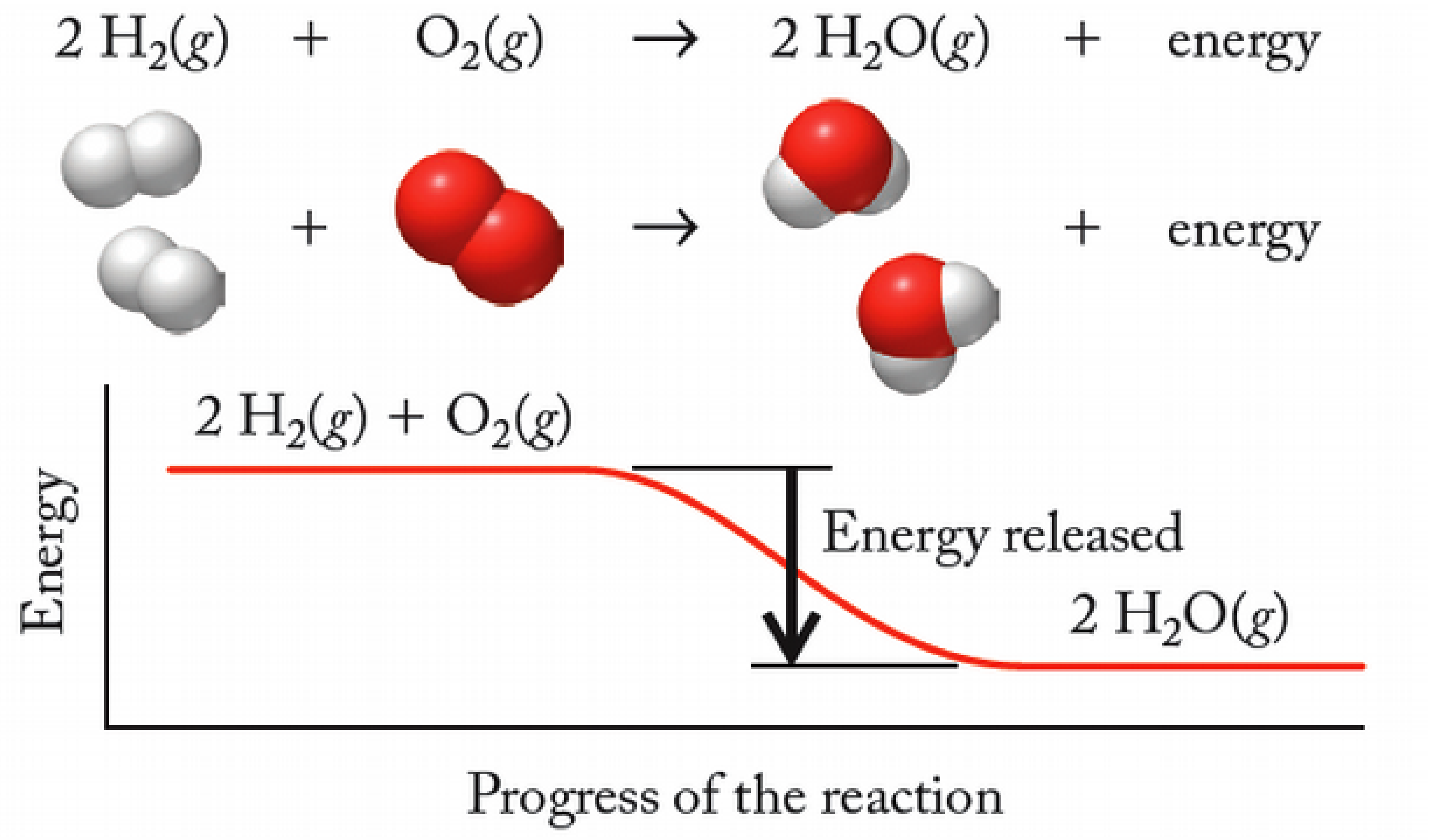
Chapter Outline

- 9.1 Energy as a Reactant or Product
- 9.2 Transferring Heat and Doing Work
- 9.3 Enthalpy and Enthalpy Changes
- 9.4 Heating Curves and Heat Capacity
- 9.5 Heats of Reaction and Calorimetry
- 9.6 Hess's Law and Standard Heats of Reactions
- 9.7 Heats of Reactions from Heats of Formation and Bond Energies
- 9.8 Applications

Definitions

- **Thermodynamics:** The study of energy and its transformation
- **Thermochemistry:** The study of the relation between chemical reactions and changes in energy
  - Thermochemical equation:
    - $2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$ + energy
- **Thermochemical Equilibrium:** A condition in which temperature is uniform throughout a material

Energy of Chemical Reactions



$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g) + \text{energy}$

First Law of Thermodynamics

- Law of Conservation of Energy:
  - Energy cannot be created or destroyed
  - It can be converted from one form to another
    - Potential energy → kinetic energy
    - Chemical energy → heat

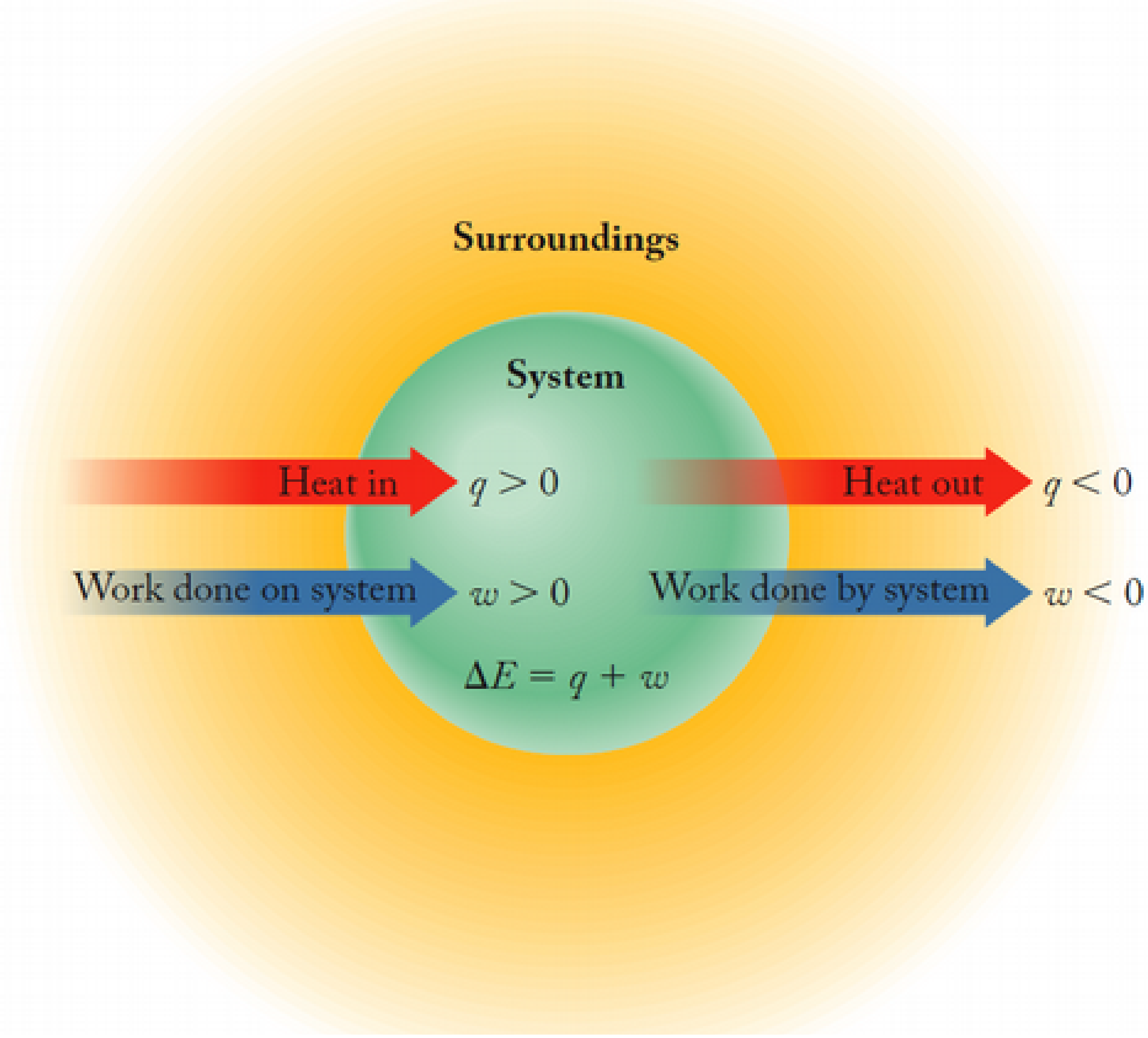
Terminology

- **System:** The part of the universe that is the focus of a thermodynamic study
    - Isolated / open / closed
- **Surroundings:** Everything in the universe that is not part of the system
- Universe = System + Surroundings

Internal Energy

- Internal Energy:
  - **State Function:** Depends only on total KE and PE of all components of the system
  - $\Delta E = E_{\text{final}} - E_{\text{initial}}$
- $\Delta E = q + w$
  - ΔE = change in system's internal energy
  - q = heat or thermal energy, w = work

Energy Flow Diagrams



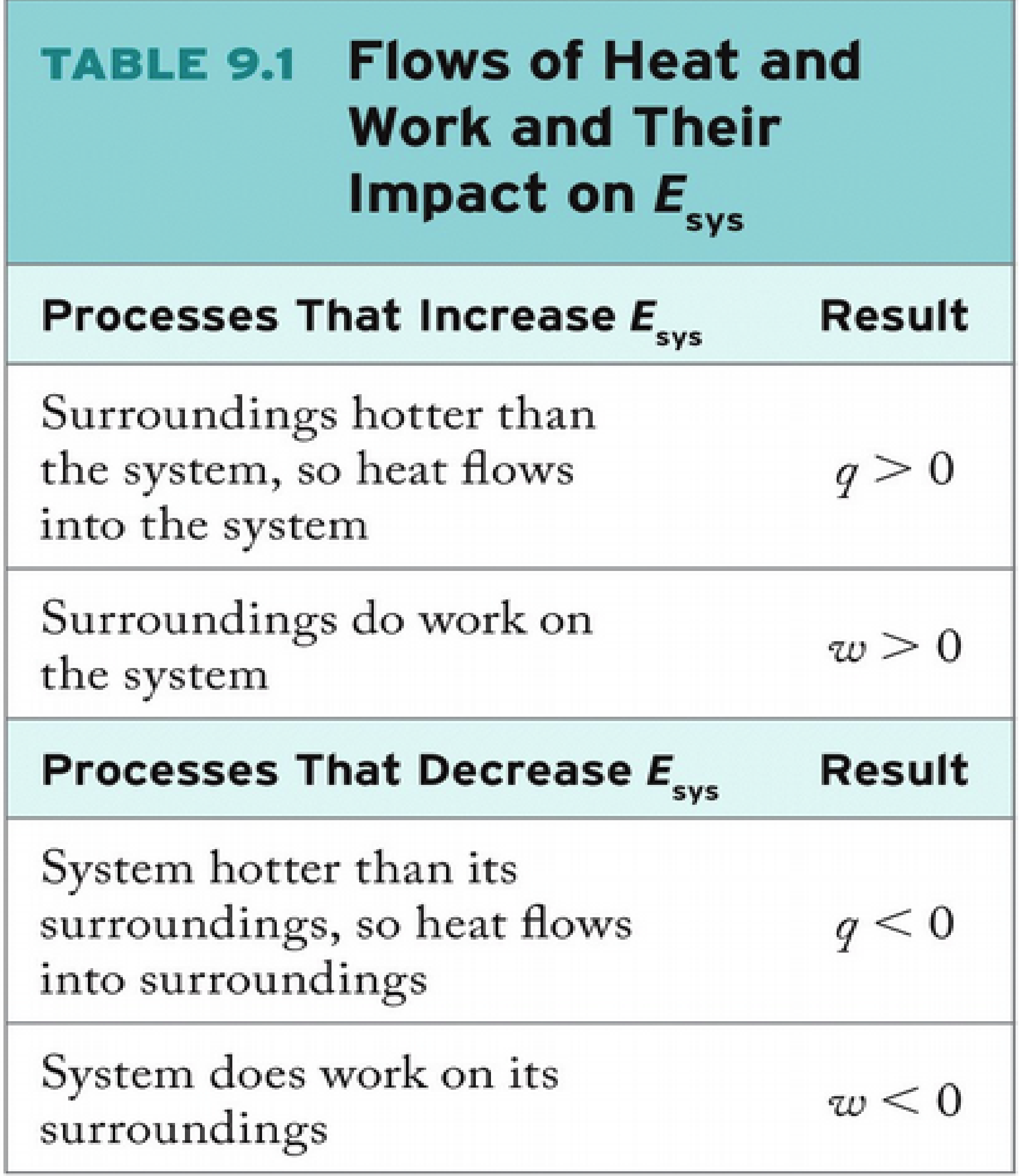
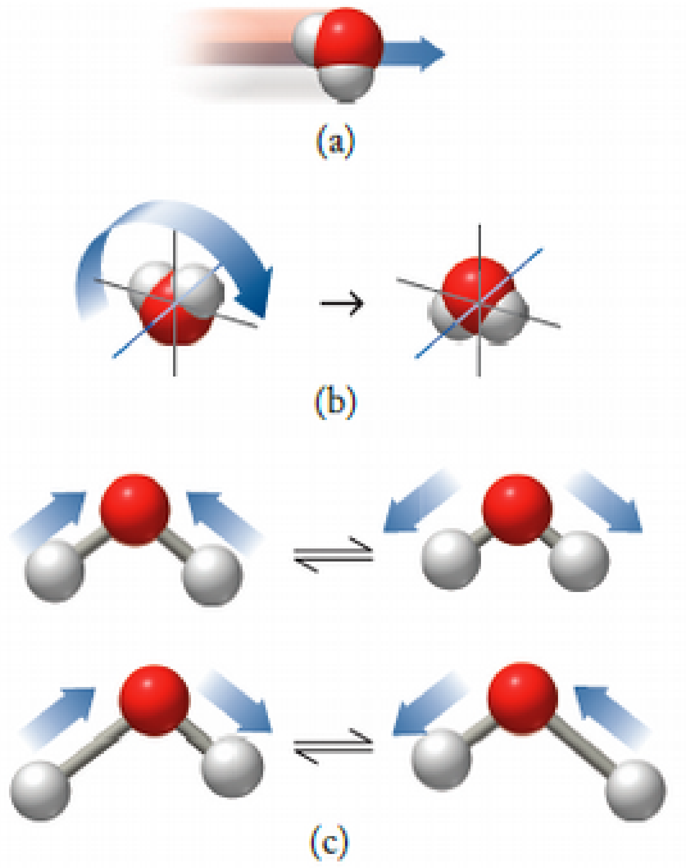


TABLE 9.1 Flows of Heat and Work and Their Impact on E_{sys}

Processes That Increase E_{sys}	**Result**
Surroundings hotter than the system, so heat flows into the system	$q > 0$
Surroundings do work on the system	$w > 0$
Processes That Decrease E_{sys}	**Result**
System hotter than its surroundings, so heat flows into surroundings	$q < 0$
System does work on its surroundings	$w < 0$

Types of Molecular Motion

- Types of molecular motion
  a) translational
  b) rotational
  c) vibrational



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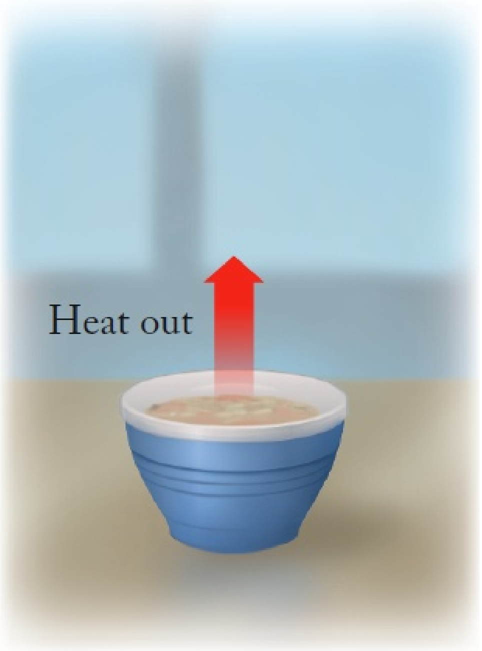
Types of Systems

(a) **Isolated system**

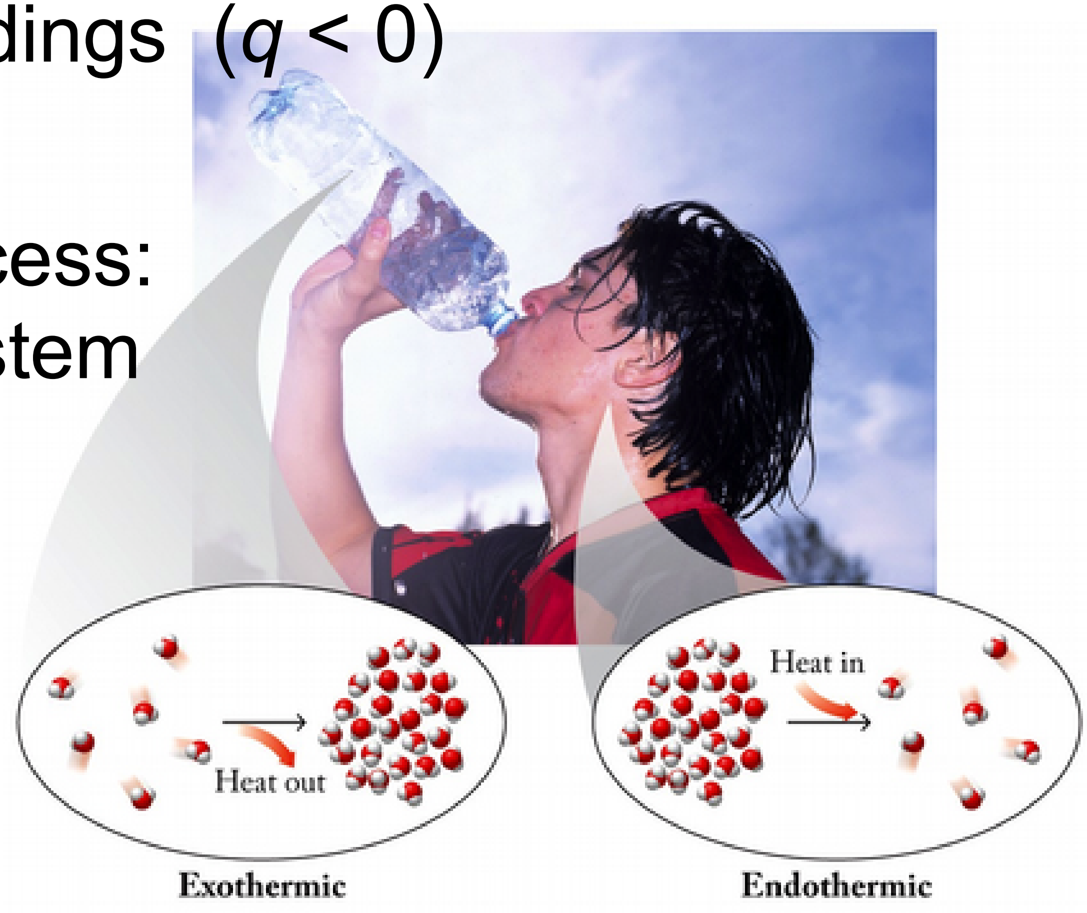


(b) **Closed system**

(c) **Open system**

Heat Flow

- **Exothermic** process: Heat flows <u>out of</u> system to surroundings ($q < 0$)
- **Endothermic** process: Heat flows <u>into</u> system from surroundings ($q > 0$)



P-*V* Work

- Work:
  - $w = -P\Delta V$

    where P = pressure, ΔV = change in volume
  - Work done by the system = energy lost by the system, $w < 0$
  - Example: Expansion of a gas

- $\Delta E = q + w$

  $= q + (-P\Delta V)$

  $= q - P\Delta V$

Units of Energy

- Energy = heat and/or work (same units!)
- Calorie (cal)
  - Amount of heat necessary to raise the temperature of 1 g of water by 1^{o}C
- Joule (J)
  - The SI unit of energy
  - 4.184 J = 1 cal
  - 101.32 J = 1 L·atm

Practice: Calculating Work

Calculate the work in L·atm and joules associated with the expansion of a gas in a cylinder from 54 L to 72 L at a constant external pressure of 18 atm.

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

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Enthalpy and Enthalpy Changes

- **Enthalpy:** $H = E + PV$
- Enthalpy change: $\Delta H = \Delta E + P\Delta V$
- ΔH = energy absorbed by reactants (endothermic), or energy given off by products (exothermic) for a reaction carried out at constant pressure

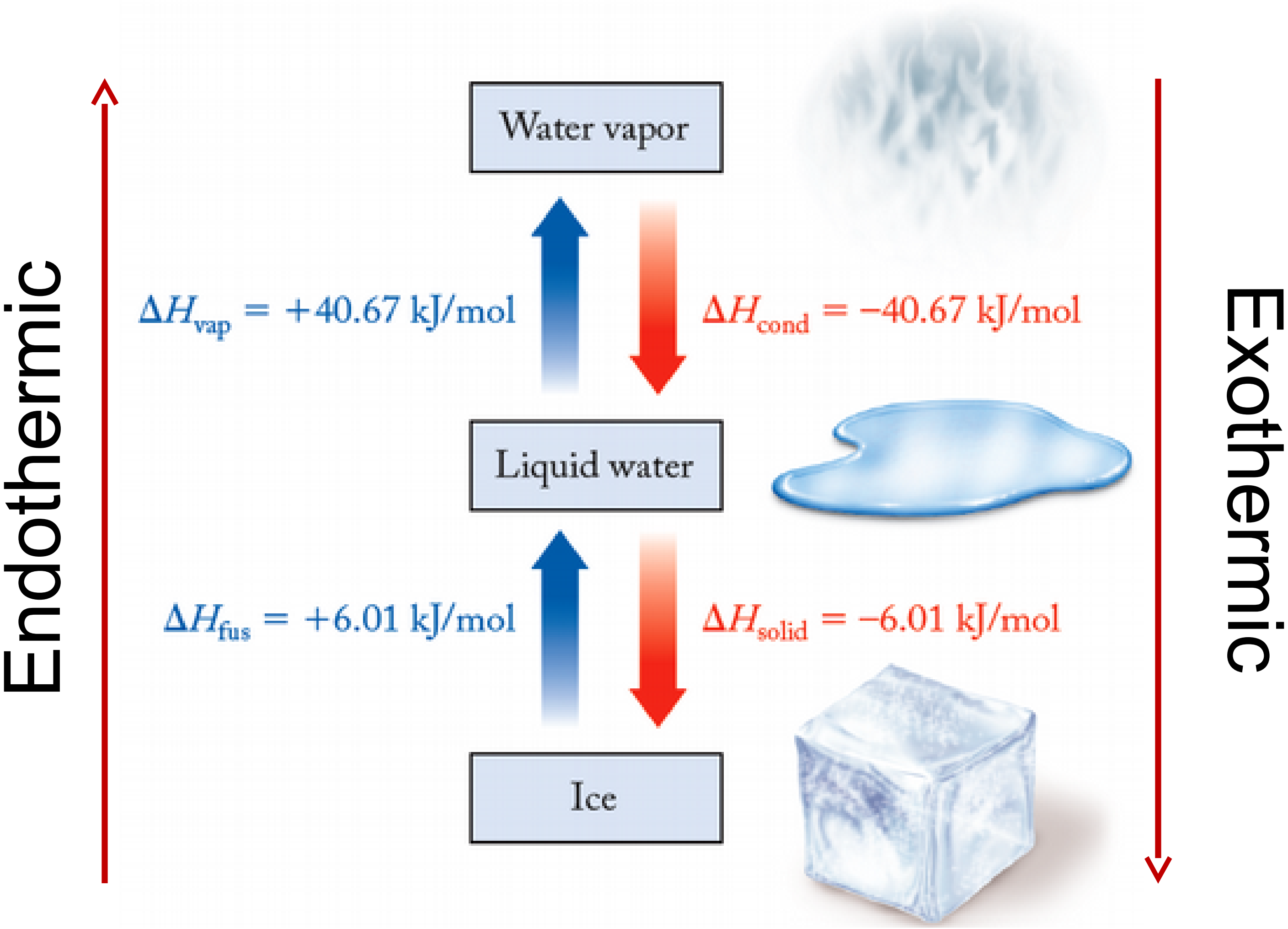
$$\Delta H = q_P = \Delta E + P\Delta V$$

- $\Delta H > 0$, endothermic; $\Delta H < 0$, exothermic
- Subscripts for ΔH indicate specific processes

Enthalpy Change

- **Enthalpy of fusion,** ΔH_{fus}: Energy required to convert a given amount (either in mol or g) of solid at its melting point into liquid state
- **Enthalpy of vaporization,** ΔH_{vap}: Energy required to convert a given amount (either in mol or g) of liquid at its boiling point into vapor state

Enthalpy Change



Endothermic

Water vapor

$\Delta H_{vap} = +40.67$ kJ/mol

$\Delta H_{cond} = -40.67$ kJ/mol

Liquid water

$\Delta H_{fus} = +6.01$ kJ/mol

$\Delta H_{solid} = -6.01$ kJ/mol

Ice

Exothermic

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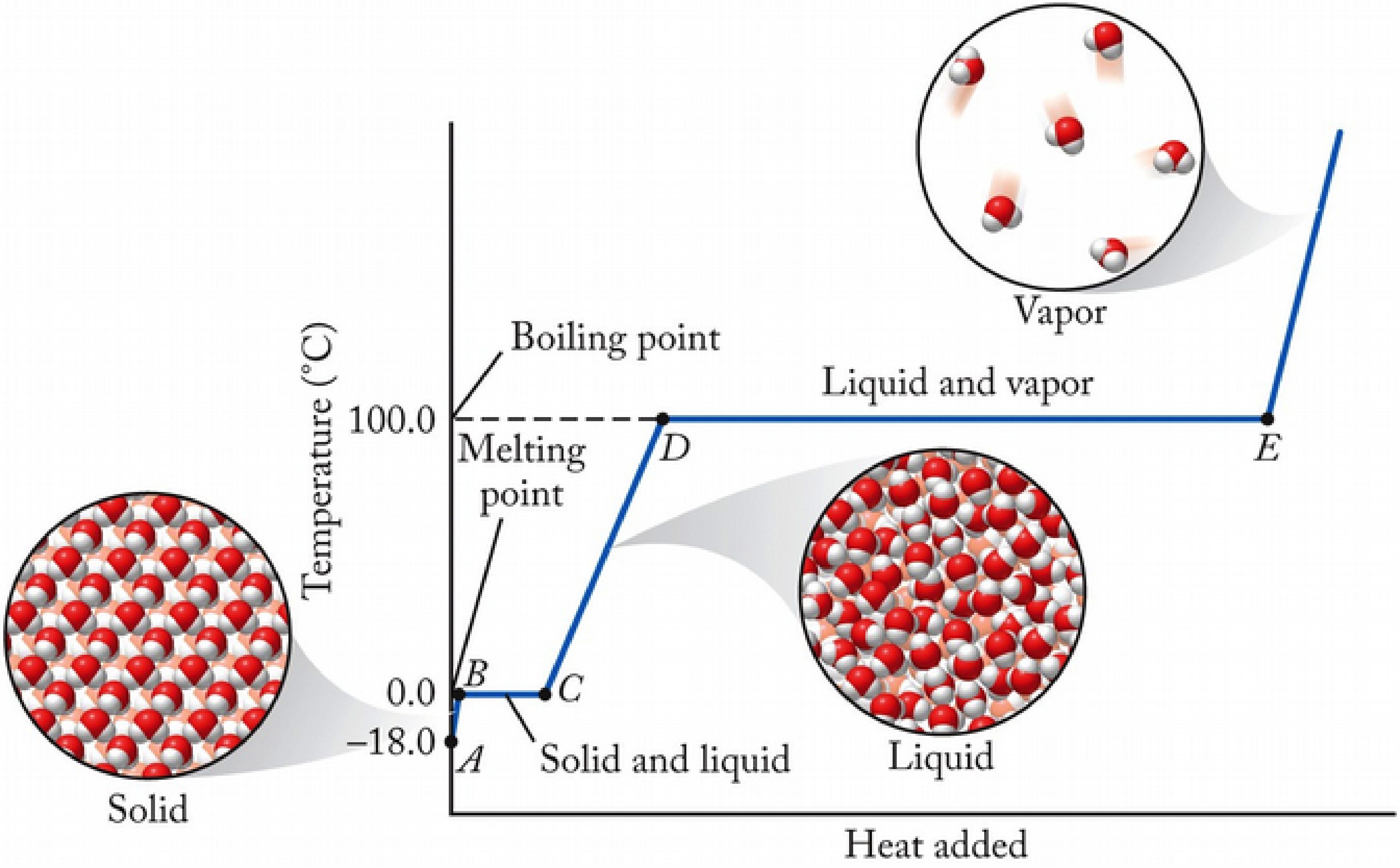
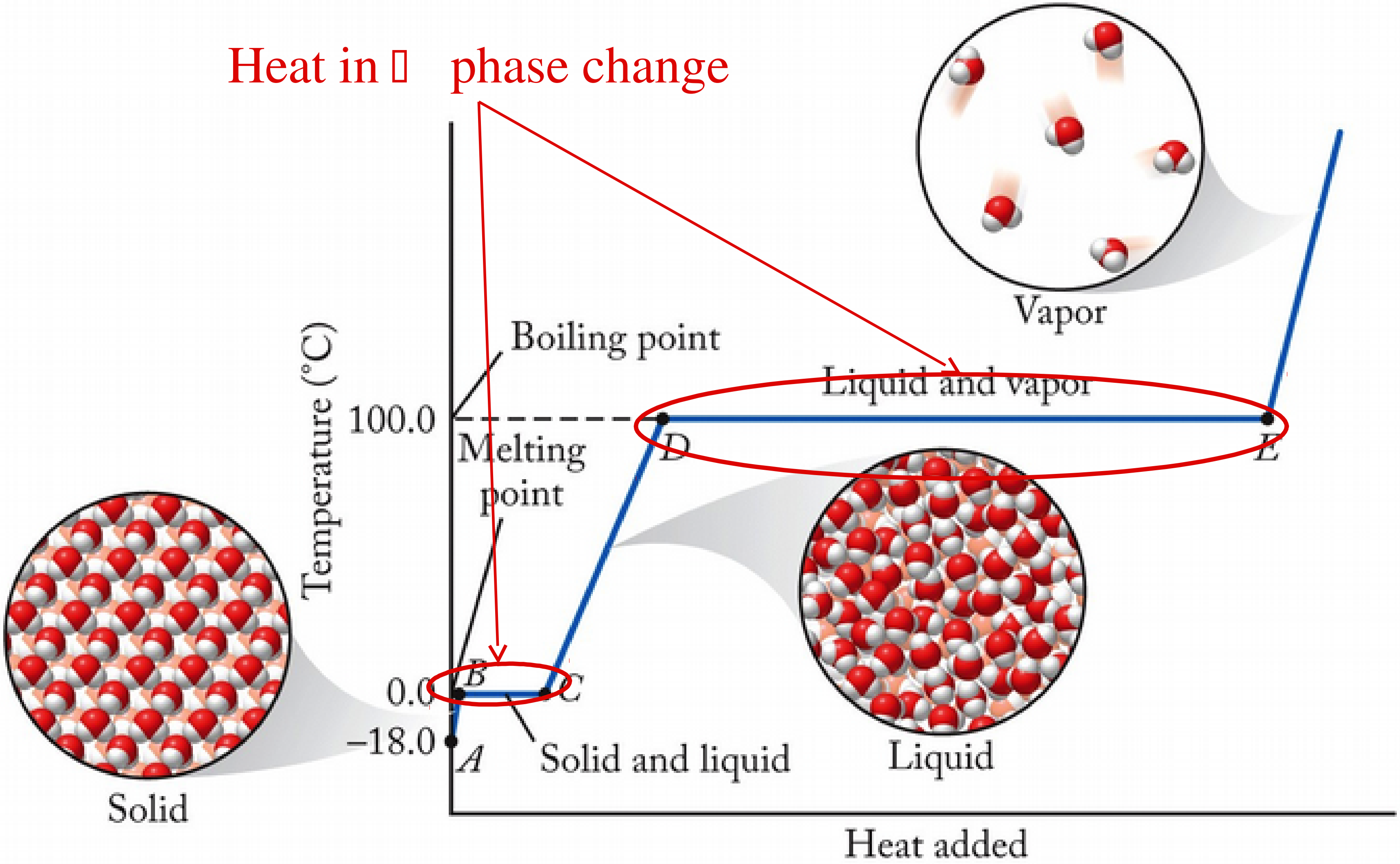
Heating Curve



Heating Curve

Heat in phase change

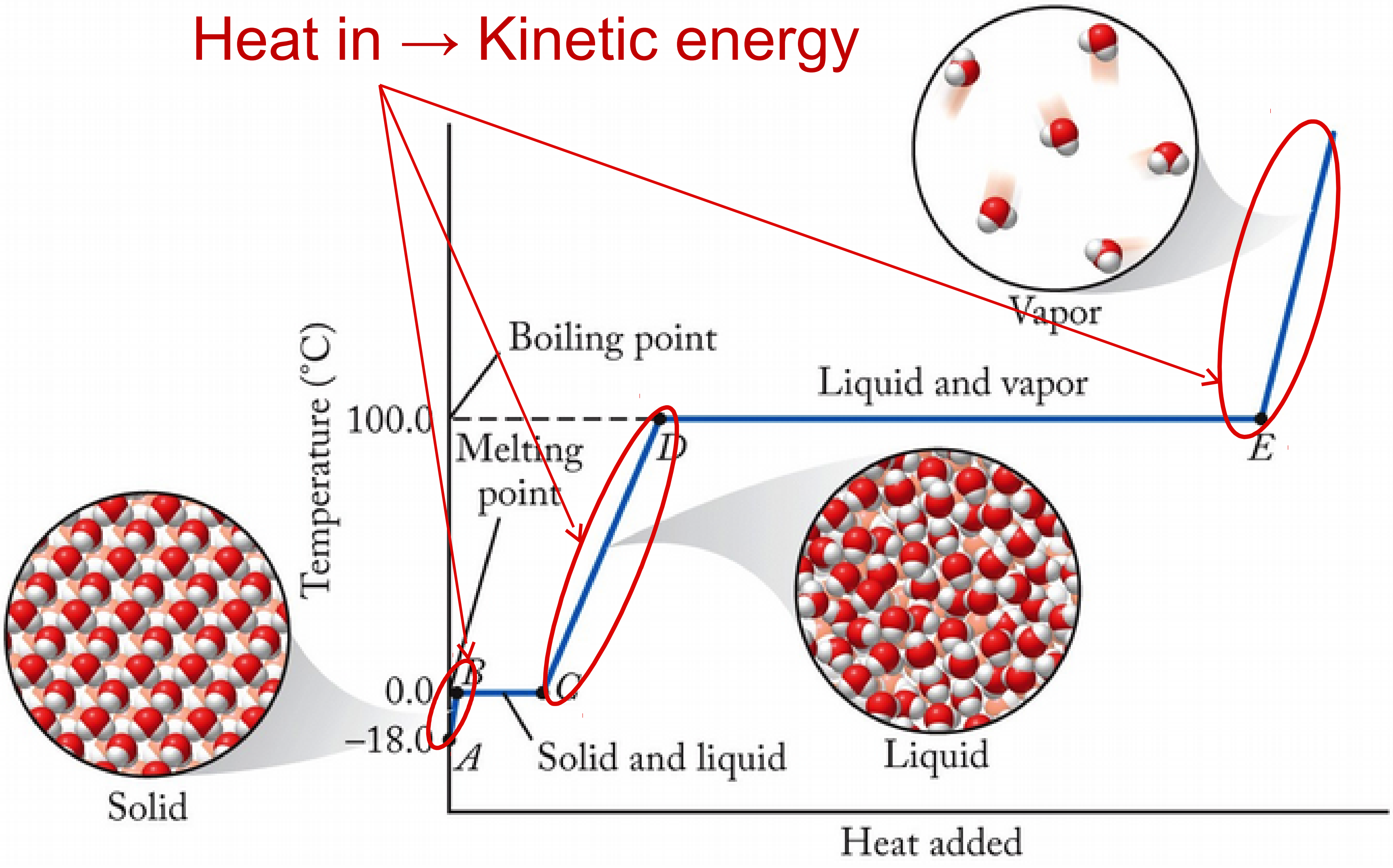


Heat Capacities

- **Heat capacity (C_p)**
  - Quantity of energy needed to raise the temperature of an object by 1°C (at constant P)
- **Molar heat capacity (c_p)**
  - Quantity of energy required to raise the temperature of 1 mol of a substance by 1°C
  - $q = nc_p\Delta T$ (c_p = J / (mol·°C))
- **Specific heat (c_s)**
  - Quantity of energy required to raise the temperature of 1 g of a substance by 1°C (at constant P)
  - $q = mc_s\Delta T$ (c_s = J / (g·°C))

Heating Curve

Heat in → Kinetic energy



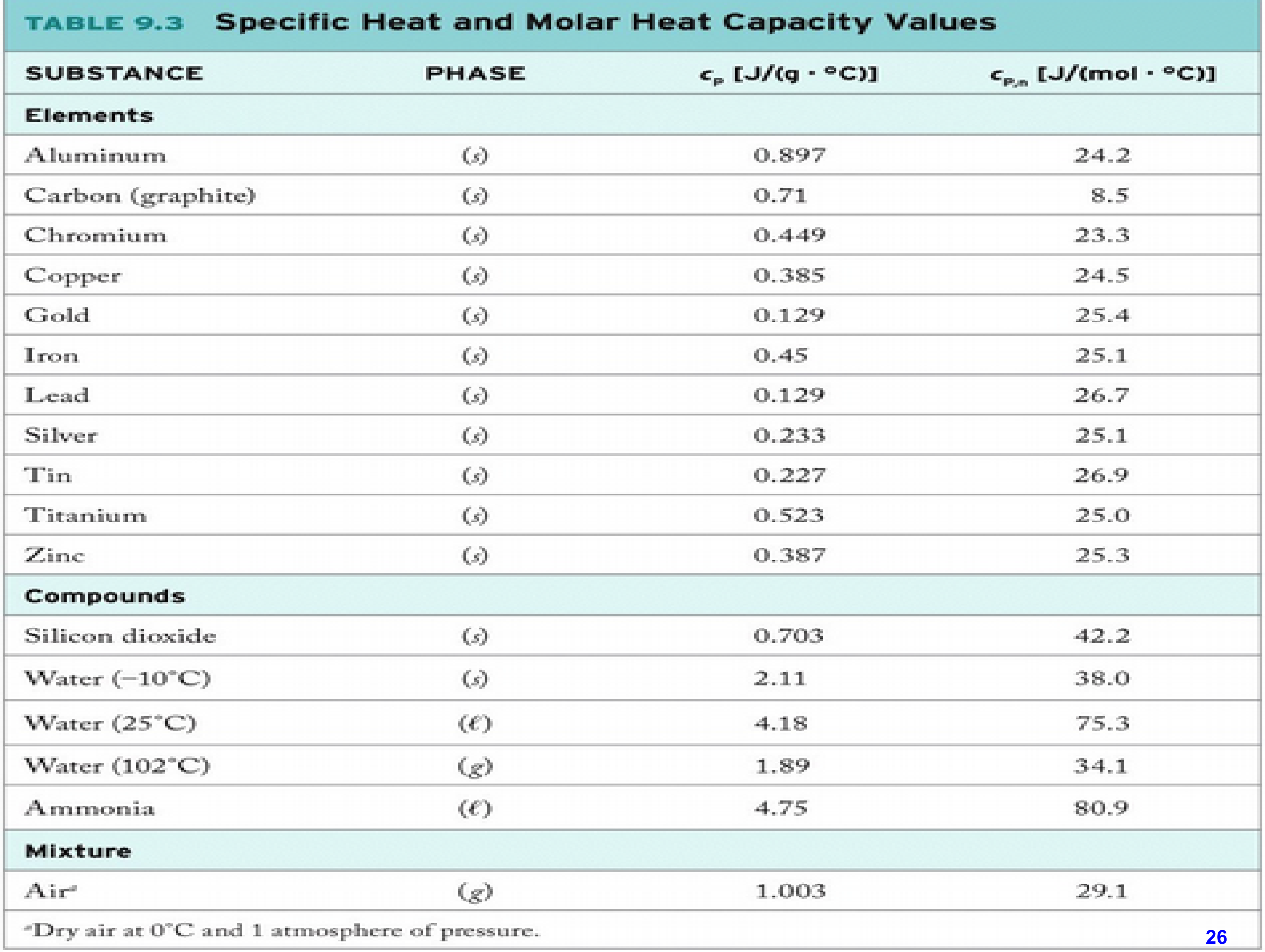


TABLE 9.3 Specific Heat and Molar Heat Capacity Values

SUBSTANCE	PHASE	c_p [J/(g · °C)]	$c_{p,n}$ [J/(mol · °C)]
Elements			
Aluminum	(*s*)	0.897	24.2
Carbon (graphite)	(*s*)	0.71	8.5
Chromium	(*s*)	0.449	23.3
Copper	(*s*)	0.385	24.5
Gold	(*s*)	0.129	25.4
Iron	(*s*)	0.45	25.1
Lead	(*s*)	0.129	26.7
Silver	(*s*)	0.233	25.1
Tin	(*s*)	0.227	26.9
Titanium	(*s*)	0.523	25.0
Zinc	(*s*)	0.387	25.3
Compounds			
Silicon dioxide	(*s*)	0.703	42.2
Water (−10°C)	(*s*)	2.11	38.0
Water (25°C)	(*ℓ*)	4.18	75.3
Water (102°C)	(*g*)	1.89	34.1
Ammonia	(*ℓ*)	4.75	80.9
Mixture			
Air[a]	(*g*)	1.003	29.1

[a] Dry air at 0°C and 1 atmosphere of pressure.

Heat Transfer Calculations

- Transfer of heat between systems
- Calculated based on the first law of thermodynamics

$$q_{\text{lost}} = -q_{\text{gained}}$$

Cooling Curves

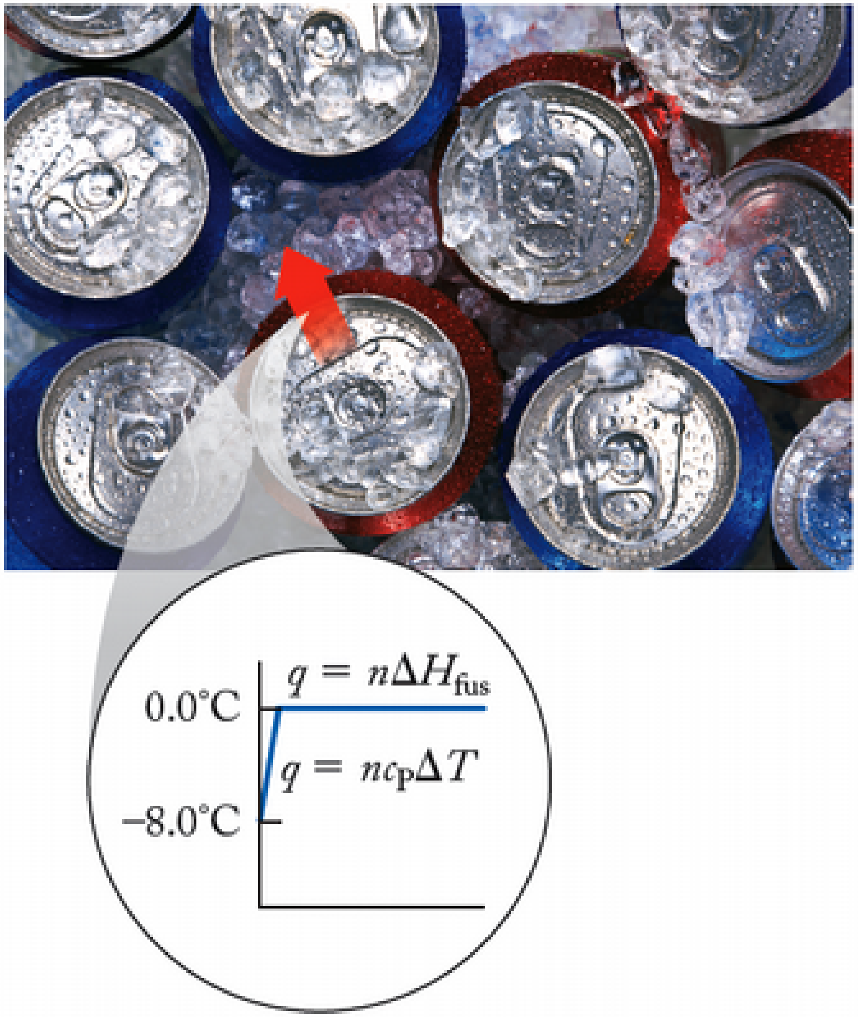
Heat transfer: Ice
@ -8.0°C to water
@ 0.0 °C

1. Temp change:

   $$q_1 = nc_p\Delta T$$

2. Phase change:

   $$q_2 = n\Delta H_{fus}$$



Practice: Specific Heat Capacity

During a strenuous workout, a student generates 2000 kJ of heat energy. What mass of water would have to evaporate from the student’s skin to dissipate this much heat?

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

Practice: Final Temperature

You heated 500 mL chicken broth to 99°C, which is too hot to consume. How many mL of cold chicken broth (12°C) must you add to the hot broth to get the temperature of the mixture down 37°C? (assume c_{broth} = 4.184 J/g$^{\text{o}}$C, D = 1.0 g/mL)

- Collect and Organize
- Analyze:
- Solve:
- Think about It:

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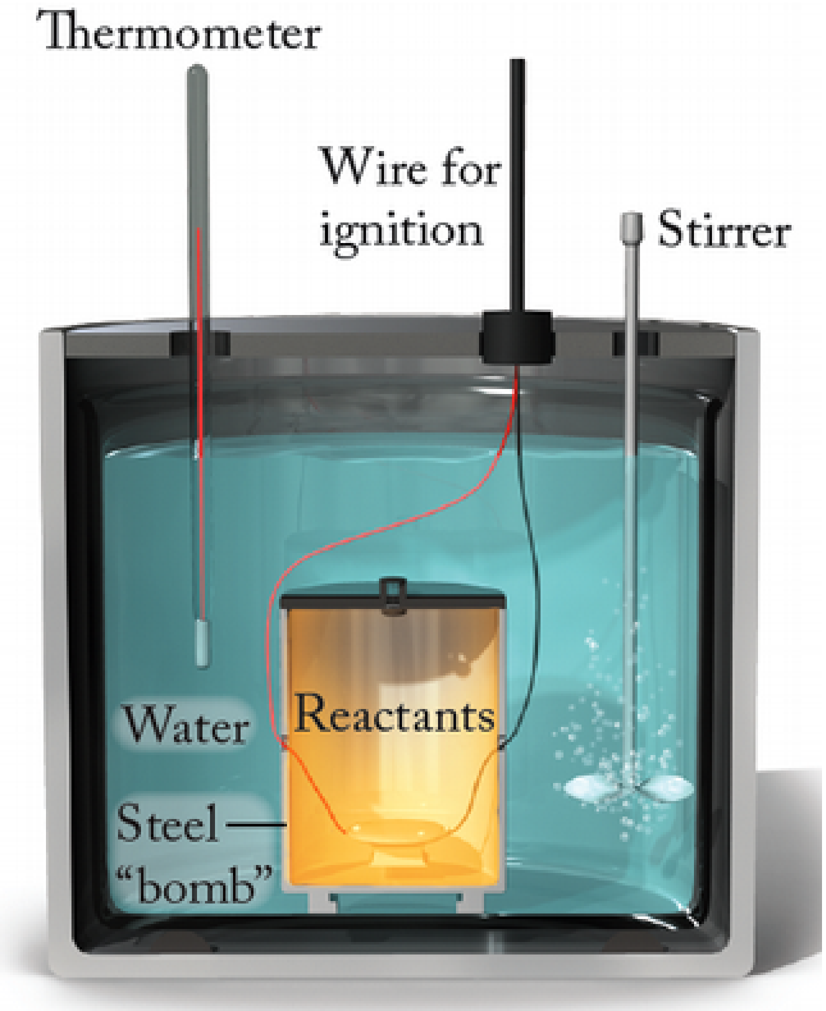
Calorimetry

- **Calorimetry**
  - Experimental measurement of heat transferred during a physical change or chemical change
- **Calorimeter**
  - Device used to measure the absorption or release of heat by a physical change or chemical process
  - Closed system! $-q_{\text{system}} = q_{\text{calorimeter}}$

Heat of Reaction

- Bomb calorimeter:
  - Constant-volume device used to measure the energy released during a combustion reaction
  - Heat produced by reaction = heat gained by calorimeter
  - $q_{cal} = C_{cal}\Delta T = -\Delta H_{rxn}$



Practice: Heat of Reaction

When 25 mL of 0.100 M reactant A are added to 25 mL of 0.100 M reactant B in a coffee cup calorimeter at 18.5°C, the temperature of the mixture increases to 25.0°C. If the densities of the two solutions are 1.00 g/mL, what is the ΔH per mol of A reacted? Assume the heat capacity of the calorimeter is 0 J/°C.

$$\mathrm{A}(aq) + \mathrm{B}(aq) \rightarrow \text{products}$$

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

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Hess's Law

- Hess's Law of Constant Heat of Summation:
  - The $\Delta H^\circ_{\text{rxn}}$ for a reaction that is the sum of two or more reactions is equal to the sum of the $\Delta H^\circ_{\text{rxn}}$ values of the constituent reactions.

1. $CH_4(g) + H_2O(g) \rightarrow \cancel{CO}(g) + 3\cancel{H_2}(g) \qquad \Delta H_1$
2. $\cancel{CO}(g) + \cancel{3H_2}(g) + H_2O(g) \rightarrow 4H_2(g) + CO_2(g) \qquad \Delta H_2$

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3. $CH_4(g) + 2H_2O(g) \rightarrow 4H_2(g) + CO_2(g) \qquad \Delta H_3$

$$\Delta H_3 = \Delta H_1 + \Delta H_2$$

Calculations Using Hess's Law

1. If a reactioni s reversed, ΔH sign changes.

$$N_2(g) + O_2(g) \rightarrow 2NO(g) \qquad \Delta H = 180\ \text{kJ}$$

$$2NO(g) \rightarrow N_2(g) + O_2(g) \qquad \Delta H = -180\ \text{kJ}$$

2. If the coefficients of a reaction are multiplied by an integer, ΔH is multiplied by the same integer.

$$6NO(g) \rightarrow 3N_2(g) + 3O_2(g) \qquad \Delta H = 3(-180\ \text{kJ})$$

$$\Delta H = -540\ \text{kJ}$$

Practice: Using Hess's Law

Using the following data, calculate the ΔH_{rxn} for the following reaction.

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

	ΔH_{rxn}
$H_2(g) + 1/2O_2(g) \rightarrow H_2O(\ell)$	-285.8 kJ
$C_2H_4(g) + 3O_2(g) \rightarrow 2H_2O(\ell) + 2CO_2(g)$	-1411 kJ
$C_2H_6(g) + 7/2O_2(g) \rightarrow 3H_2O(\ell) + 2CO_2(g)$	-1560 kJ

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

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Enthalpy of Formation, ΔH_f^o

- The **standard enthalpy of formation**, ΔH_f^o
  - The enthalpy change for the process of forming 1 mol of a substance from its constituent elements in their ***standard states****
  - e.g., formation reaction for NO:
    - $\frac{1}{2}\, N_2(g) \; + \; \frac{1}{2}\, O_2(g) \; \rightarrow \; NO(g)$
    - $\Delta H_{rxn} = \Delta H_f^o\,(NO)$
- (*The standard state of an element is its most stable form under 1atm pressure and 25°C.)

Standard Enthalpy of Reactions

- **Standard enthalpy of reaction** ($\Delta H^\circ_{\mathrm{rxn}}$)
  - Enthalpy change associated with a reaction that takes place under standard conditions
  - Also called standard heat of reaction
- Calculated from ΔH_f° (see Appendix 4)
  - $\Delta \mathrm{H}^\circ_{\mathrm{rxn}} = \Sigma n_p \Delta H_f^\circ$(products) 📫 💧 $n_r \Delta H_f^\circ$(reactants)

Methods of Determining $\Delta H^\circ_{\text{rxn}}$

1. From calorimetry experiments:
   - $\Delta H^\circ_{\text{rxn}} = -\,C_{\text{cal}}\Delta T$
2. From enthalpies of formation:
   - $\Delta H^\circ_{\text{rxn}} = \Sigma n_{\text{p}}\Delta H_{\text{f}}^\circ(\text{products}) - \Sigma n_{\text{r}}\Delta H_{\text{f}}^\circ(\text{reactants})$
   - $\Delta H_{\text{f}}^\circ$ values listed in Appendix 4.
3. Using Hess’s law (Section 9.6)

Practice: Using $\Delta H_\mathrm{f}^\circ$ to find $\Delta H_\mathrm{rxn}^\circ$

Use Table 9.4 to calculate an approximate enthalpy of reaction for

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$$

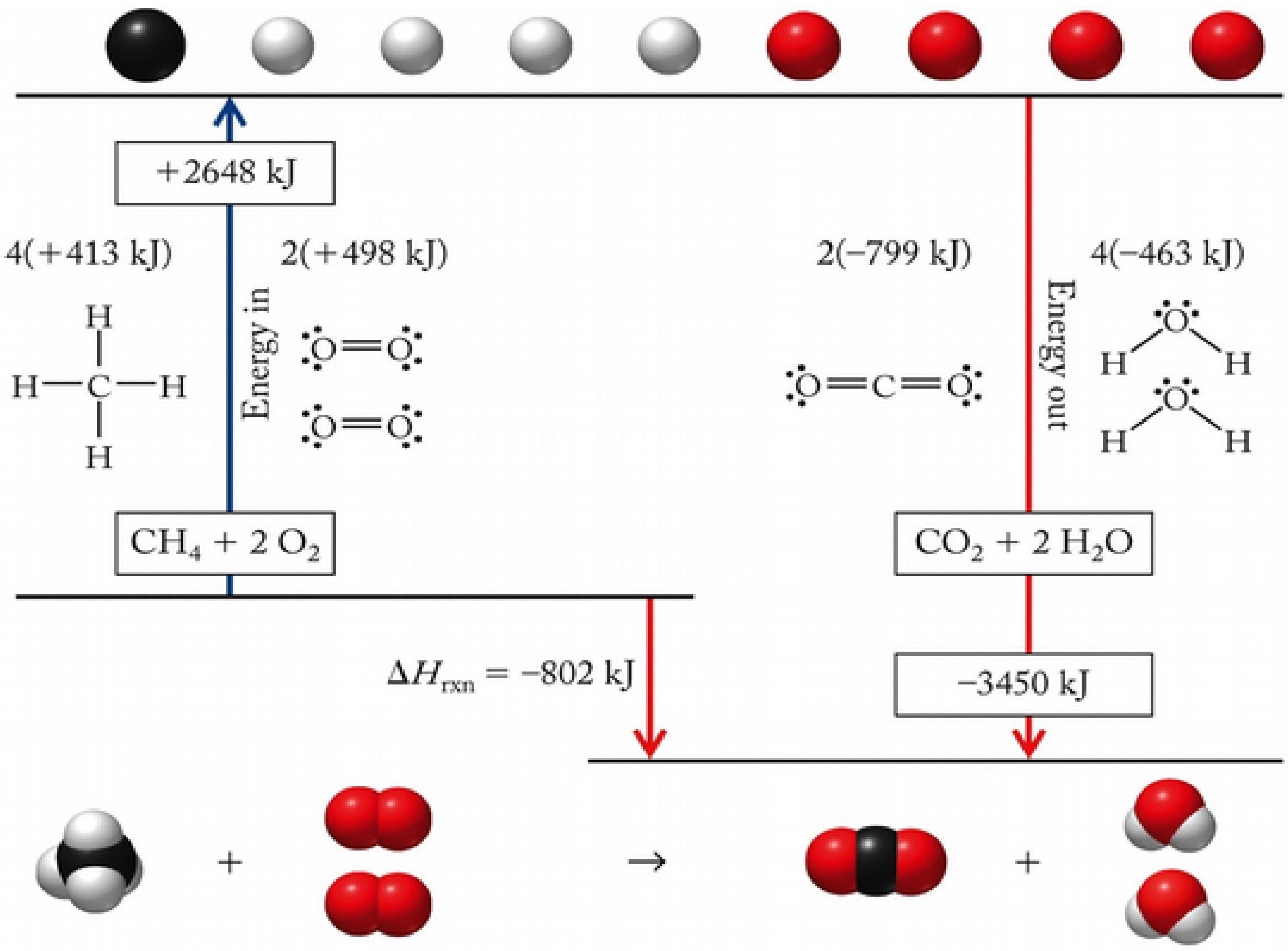
- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

Bond Energies

- **Bond Energy:** Enthalpy change that occurs when 1 mol of bonds in the gas phase are broken

- Bond energy is also a measure of the bond strength. The larger the bond energy, the stronger the bond.

Bond Energies



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Fuel Values

- **Fuel value** = Energy released during complete combustion of 1 g of a substance
  - $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$
  - $\Delta H^\circ_{\text{comb}} = -802.3$ kJ/mol
  - Fuel value = (802.3 kJ/mol)·(1 mol/16.04 g)
  - = 50.02 kJ/g
- **Fuel density** = Energy released during complete combustion of 1 L of a liquid fuel

Fuel Values

Substance	MW (g/mol)	Fuel Value (kJ/g)
CH_4, methane	16.04	54.0
C_3H_8, propane	44.09	50.3
C_5H_{12}, pentane	72.14	48.8
C_9H_{20}, avg. gasoline compound	128.25	47.4
$C_{14}H_{30}$, avg. diesel compound	198.37	44.8

Food Values

- Quantity of energy produced when a material consumed by an organism for sustenance is burned completely
  - Determined by bomb calorimetry
  - Nutritional calorie = 1 kcal = 4.184 kJ

Food Category	Food Value (Cal or kcal/g)	Food Value (kJ/g)
Proteins	4.0	16.7
Carbohydrates	4.0	16.7
Fats	9.0	37.7

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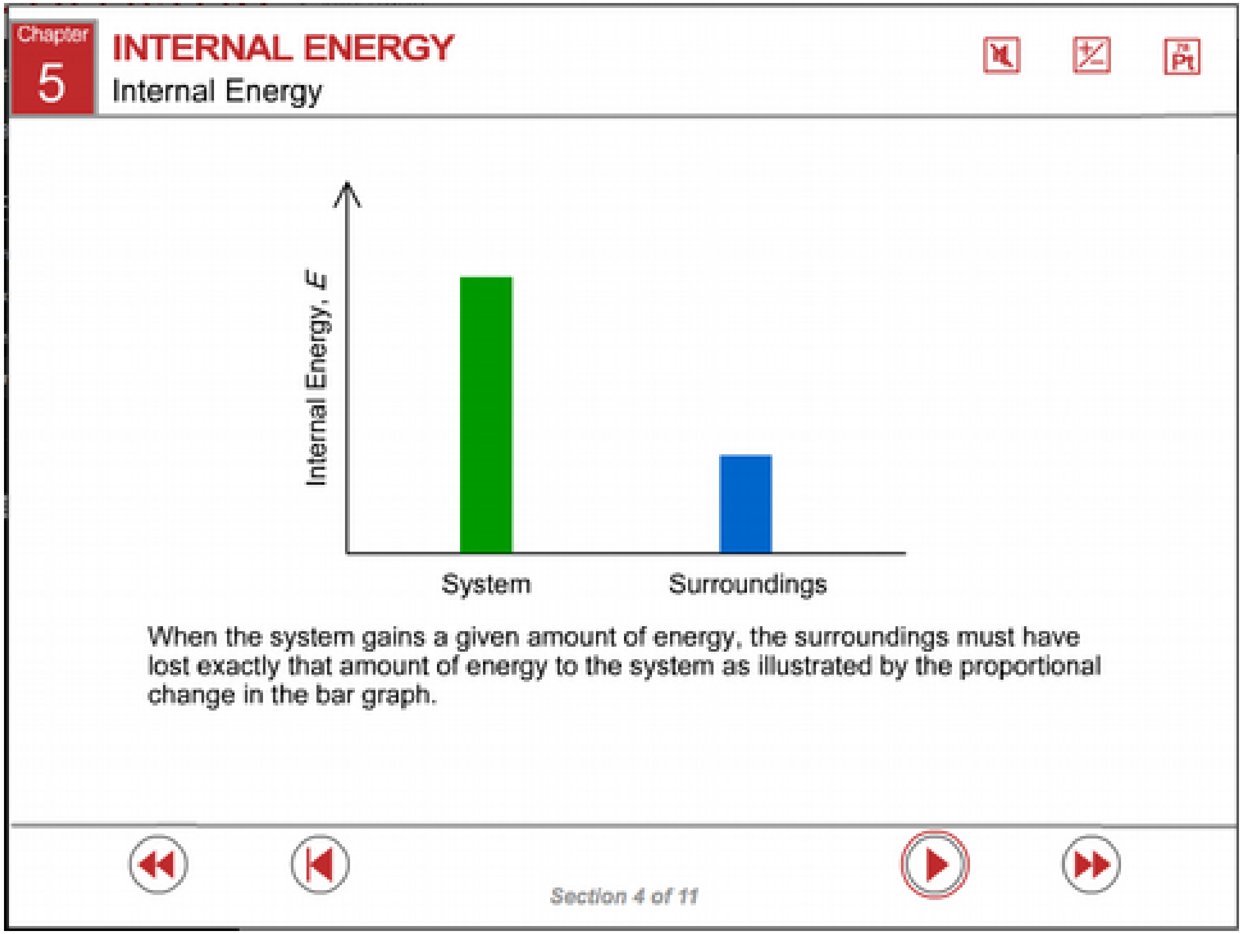

INTERNAL ENERGY

Internal Energy

When the system gains a given amount of energy, the surroundings must have lost exactly that amount of energy to the system as illustrated by the proportional change in the bar graph.

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This concludes the Lecture PowerPoint presentation for Chapter 9

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