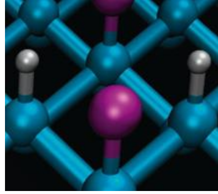


Chapter **9**

Energy and Chemistry

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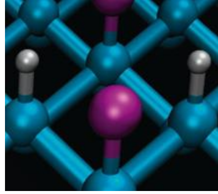
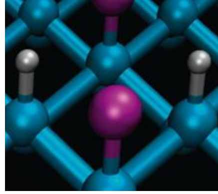


Forms of Energy

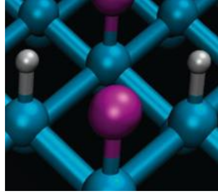
- Two broad categories of energy: Potential energy and kinetic energy
  - Potential energy: Associated with the relative position of an object
  - Kinetic energy: Associated with motion

$$\text{Kinetic energy} = \frac{1}{2}mv^2$$

Forms of Energy



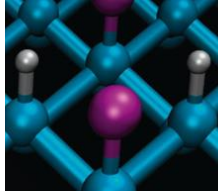
- Internal energy: The combined kinetic and potential energies of atoms and molecules that make up an object or system
- Chemical energy: Energy released or absorbed during a chemical reaction
- Other forms of energy include radiant, mechanical, thermal, electrical, and nuclear
- Thermochemistry: Study of the energetic consequences of chemistry



Heat and Work

- Heat is the flow of energy between two objects because of a difference in temperature
  - Heat flows from the warmer object to the cooler object
- Work is the transfer of energy accomplished by a force moving a mass some distance against resistance
  - Pressure-volume work or PV-work is the most common work type in chemistry
    - Releasing an inflated balloon before it is tied off illustrates an example of PV-work

Energy Units



- Joule, J, is the SI unit of energy
  - $1 \text{ Joule } = 1\,\text{Kg}\,\text{m}^2/\text{s}^2$

$$W = \text{mass} \times \text{acceleration} \times \text{distance} = \text{kg} \times \frac{\text{m}}{\text{s}^2} \times \text{m}$$

- Other energy units include the Btu and the calorie
  - 1 Btu is the energy required to raise the temperature of 1 lb of water by 1°F
    - 1 Btu = 1055 J
  - 1 calorie is the energy required to raise the temperature of 1 g of water from 14.5 to 15.5°C
    - 1 calorie = 4.184 J

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Energy Transformation and Conservation of Energy

- During energy transformation, the total energy must be conserved
  - The sum of all energy conversions and energy transfers must equal the total energy present, which must remain constant
- To account for energy transformations and conversions, the system and surroundings must be specified
  - System: The part of the universe being considered
  - Surroundings: The remainder of the universe
  - System + Surroundings = Universe
  - System and surroundings are separated by a boundary

Energy Transformation and Conservation of Energy

- For a system or surroundings, the only possible forms of energy flow are heat, *q*, and work, *w*
- The delta, Δ, means "change in" and is defined as the difference in the final and initial states

$$\Delta E = q + w$$

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

Example Problem 9.1

- If 515 J of heat is added to a gas that does 218 J of work as a result, what is the change in the energy of the system?

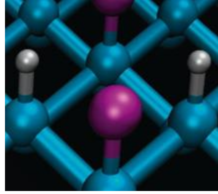
$$\Delta E = 515 J - 218 J$$

$$= 297 J$$

Energy Transformation and Conservation of Energy

- The sign resulting from the difference in the final and initial states indicates the direction of the energy flow
  - Negative values indicate that energy is being released
  - Positive values indicate that energy is being absorbed

Energy Transformation and Conservation of Energy



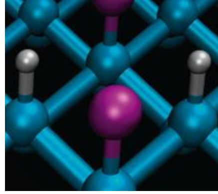
- First law of thermodynamics states that energy can be transformed from one form to another but cannot be created or destroyed

$$\Delta E_{\text{universe}} = \Delta E_{\text{surroundings}} + \Delta E_{\text{system}} = 0$$

Waste Energy

- A common way to obtain work from a system is to heat the system
- Heat flows in and is converted to work
  - It is impossible to completely convert all heat to work.
  - Heat not converted to work is considered waste energy, which may contribute to thermal pollution
    - Thermal pollution is the temperature change in a body of water from hot or cold waste streams, resulting in temperatures different from normal seasonal ranges
- The efficiency of conversion from heat to work can be expressed as a percentage
  - Increases in energy consumption can be offset by increasing energy efficiencies

Heat Capacity and Calorimetry



- Calorimetry is a laboratory method for observing and measuring the flow of heat into and out of a system
- Different systems will absorb different amounts of energy based on three main factors
  - The amount of material, *m* or *n*
    - *m* is mass and *n* is number of moles
  - The type of material, as measured by *c* or C_p
    - *c* is the specific heat capacity, or specific heat, and C_p is the molar heat capacity
  - The temperature change, ΔT

Heat Capacity and Specific Heat

- The specific heat capacity, or specific heat, is a physical property of a substance that describes the amount of heat required to raise the temperature of one gram of a substance by 1°C
  - Represented by c
  - Specific heat is compound and phase specific
- The molar heat capacity is a physical property of a substance that describes the amount of heat required to raise the temperature of one mole of a substance by 1°C
  - Represented by C_p
    - The subscript p indicates constant pressure
  - Molar heat capacity is compound and phase specific

Heat Capacity and Specific Heat

- The amount of heat energy absorbed can be quantified

$$q = mc\Delta T$$

$$q = nC_p\Delta T$$

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Heat Capacity and Specific Heat

Substance	Specific Heat, *c* (J g^{-1} K^{-1})	Molar Heat Capacity, C_p (J mol^{-1} K^{-1})
Al(s)	0.900	24.3
Cu(s)	0.385	24.5
$H_2O(s)$	2.09	37.7
$H_2O(\ell)$	4.18	75.3
$H_2O(g)$	2.03	36.4

- Specific heat and molar heat capacities for some common substances

Example Problem 9.2

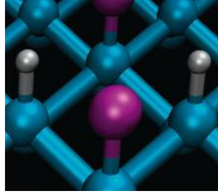
- Heating a 24.0-g aluminum can raise its temperature by 15.0°C. Find the value of *q* for the can

$$q = m \cdot C \cdot T$$

$$= 24.0 \times 0.900 \times 15.0$$

$$= 324 \text{ J}$$

Calorimetry



- Heat flow is measured using a calorimeter
- A calorimeter measures the heat evolved or absorbed by the system of interest by measuring the temperature change in the surroundings

$$q_{\text{system}} = -q_{\text{surroundings}}$$

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

Example Problem 9.4

- A glass contains 250.0 g of warm water at 78.0°C. A piece of gold at 2.30°C is placed in the water. The final temperature reached by this system is 76.9°C
  - What was the mass of gold?
  - The specific heat of water is $4.184\ \mathrm{J\,g^{-1}\,{}^{\circ}C^{-1}}$, and that of gold is $0.129\ \mathrm{J\,g^{-1}\,{}^{\circ}C^{-1}}$

$$250.0 \times 4.184 \times (78.0 - 76.9) = m \times 0.129 \times (74.6)$$

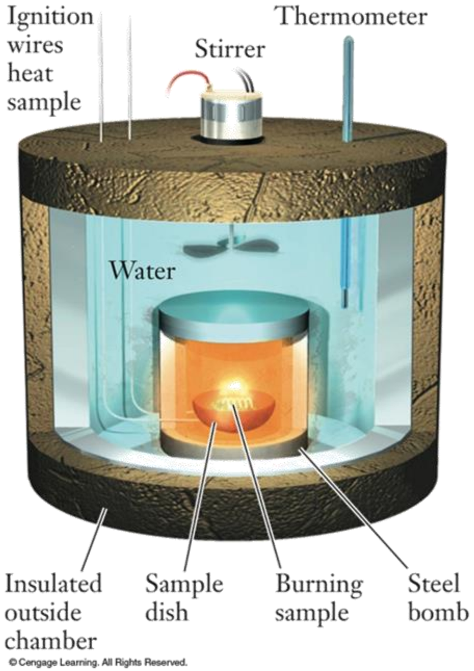
$$m = \frac{250 \times 4.184 \times 1.1}{0.129 \times 74.6} \approx 120$$

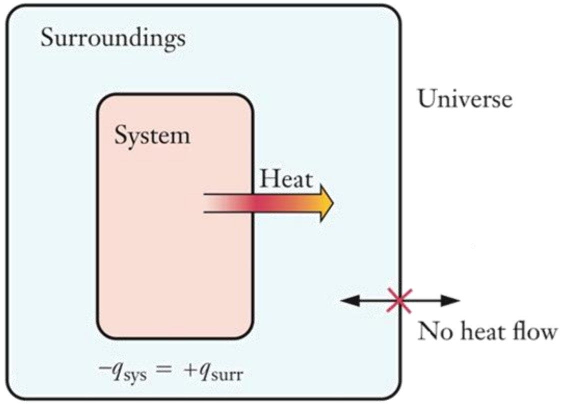
Calorimetry

- There are two steps in a calorimetric measurement
  - Calibration: The calorimeter constant, $C_{\text{calorimeter}}$, is determined by dividing the known amount of heat released in the calorimeter by the temperature change of the calorimeter
  - Actual Measurement: Heat released or absorbed in a reaction of known quantity of material is measured

$$q = C_{\text{calorimeter}} \times \Delta T$$

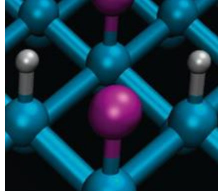
Calorimetry





- Diagram shows the standard choice of system and surroundings for a bomb calorimetry experiment

Example Problem 9.5



- In the calibration of a calorimeter, an electrical resistance heater supplies 100.0 J of heat and a temperature increase of 0.850°C is observed. Then, 0.245 g of a particular fuel is burned in this same calorimeter and the temperature increases by 5.23°C.
  - Calculate the energy density of this fuel, which is the amount of energy liberated per gram of fuel burned

$$5.23 \times \frac{100}{0.850} \div (0.245) = 2510 \text{ J/g}$$

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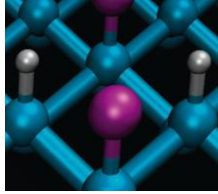

Defining Enthalpy

- Enthalpy is the heat flow under conditions of constant pressure
  - Enthalpy change can be expressed as:

$$H = E + PV$$

$$\Delta H = \Delta E + \Delta(PV)$$

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

$$\Delta H = q - P\Delta V + P\Delta V$$

$$\Delta H = q_{\mathrm{p}}$$

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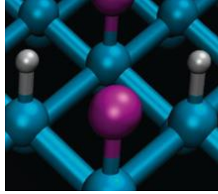
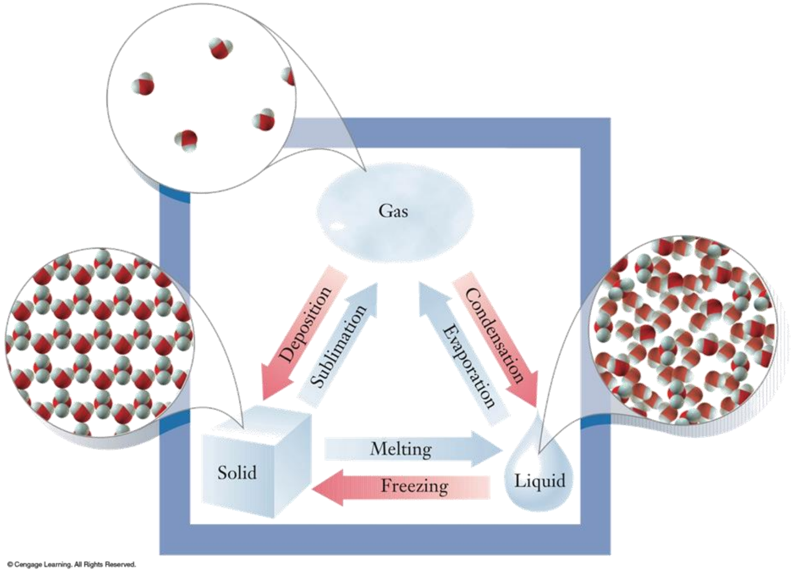
Defining Enthalpy



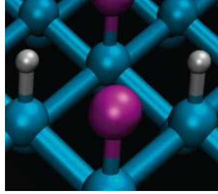
- When a system releases heat, the process is said to be exothermic
  - The value of ΔH is less than zero; the sign on ΔH is negative
- When a system absorbs heat, the process is said to be endothermic
  - The value of ΔH is greater than zero; the sign on ΔH is positive

ΔH of Phase Changes

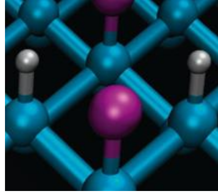
- Phase changes occur under constant pressure conditions
  - Heat flow during a phase change is an enthalpy change
  - During a phase change, temperature does not change with heat flow due to formation or breaking of intermolecular attractive forces



ΔH of Phase Changes



- Heat required to convert a liquid to a gas is the heat of vaporization, ΔH_{vap}
  - ΔH_{vap} is endothermic with a positive value
- Heat released to convert a gas to a liquid is the heat of condensation, ΔH_{cond}
  - ΔH_{cond} is exothermic with a negative value
- $\Delta H_{cond} = -\Delta H_{vap}$
  - The values of enthalpy changes in opposite directions have the same numeric values and differ only in their signs
  - The magnitude of the enthalpy change depends on the substance involved



ΔH of Phase Changes

Standard molar enthalpies and temperatures for phase changes of water

Phases change	Fusion	Freezing	vaporization	Condensation
Transition Temperature	0°C	0°C	100°C	100°C
Δ*H* (J/mol)	6009.5	−6009.5	40,700	−40,700

- Standard molar enthalpies and temperatures for phase changes of water

ΔH of Phase Changes

- The value of ΔH for a phase change is compound specific and has units of kJ/mol
  - The heat flow can be calculated using the number of moles of substance, n, and the value of the enthalpy change

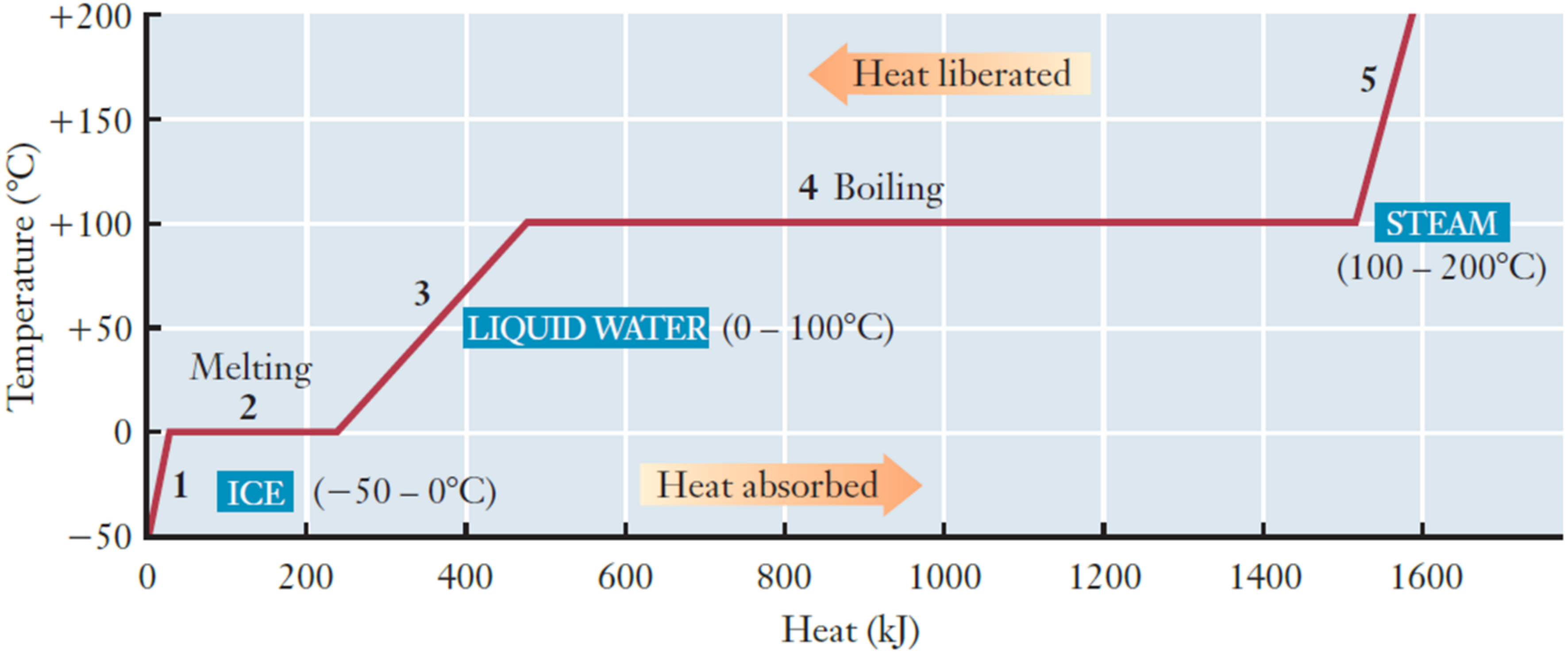
$$\Delta H = n \times \Delta H_{\text{phase change}}$$

Example Problem 9.6

- Calculate the enthalpy change when 245 g of ice melts

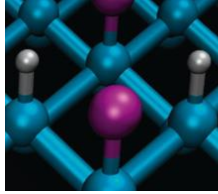
$$\frac{245g}{18g/mol} \times 6009.5\ J/mol = 81786\ J$$

ΔH of Phase Changes



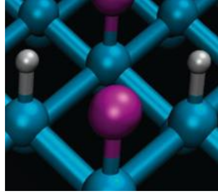
- Heat curve for the heating of 500-g ice at −50°C to 200°C

Heat of Reaction



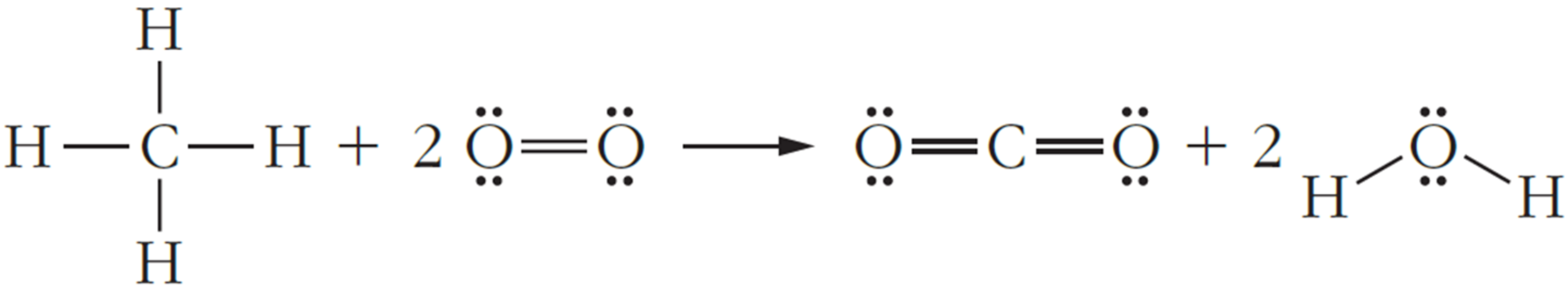
- Enthalpy changes can be calculated for chemical reactions in addition to temperature changes and phase transitions
    - Enthalpy change is commonly referred to as the heat of reaction

Bonds and Energy



- Enthalpy change for a reaction can be estimated using bond energies
- During a chemical reaction, reactant bonds are broken and product bonds are formed
  - Breaking bonds requires energy
  - Making bonds releases energy
- If the energy released in forming new bonds is greater than the energy required to break the original bonds, then the overall reaction should be exothermic
- If the energy needed for bond breaking is greater than that released in bond making, then the reaction will be endothermic

Bonds and Energy



$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

- Combustion of methane breaks $4\,C{-}H$ bonds and $2\,O{=}O$ bonds
  - $2\,C{=}O$ bonds and $4\,O{-}H$ bonds are formed

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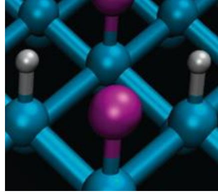
Bonds and Energy



- The accuracy of enthalpy changes calculated from tabulated bond energies is not very good
  - The bond energies used are averages
  - Bond energy method is used to estimate enthalpy changes for reactions involving compounds with no available thermochemical data
- A thermochemical equation summarizes the overall energetics for a chemical reaction
  - The sign on the ΔH indicates whether the reaction is endothermic or exothermic

$$\mathrm{CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell)}$$

$$\Delta H = -890.4 \text{ kJ}$$

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Bonds and Energy

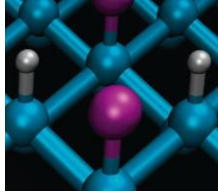
- The combustion of methane is an exothermic reaction and releases 890.4 kJ of heat energy when 1 mole of methane reacts with 2 moles of oxygen

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell)$$
$$\Delta H = -890.4 \text{ kJ}$$

- For thermochemical equations, if the stoichiometric coefficients are multiplied by some factor, the heat of reaction must also be multiplied by the same factor

$$2CH_4(g) + 4O_2(g) \longrightarrow 2CO_2(g) + 4H_2O(\ell)$$
$$\Delta H = -1780.8 \text{ kJ}$$

Heats of Reaction for Some Specific Reactions



- Some classes of chemical reactions are given their own labels for heats of reactions
  - Heats of combustion, ΔH_{comb}
  - Heats of neutralization, ΔH_{neut}
  - Heats of formation, ΔH_f°, is the heat of reaction for formation of substances

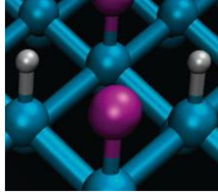
$$C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g)$$

  - Fractional coefficients are allowed for formation reactions because only one mole of product can be formed

Heats of Reaction for Some Specific Reactions

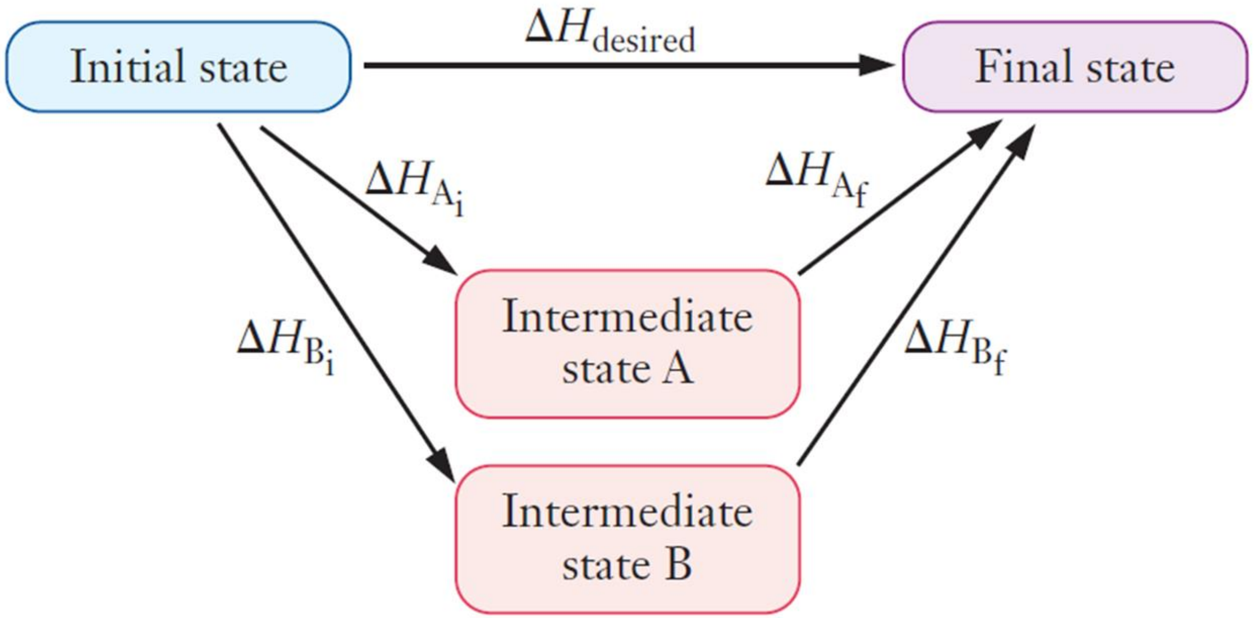
- A formation reaction is the chemical reaction by which one mole of a compound is formed from its elements in their standard states
- The standard state is the most stable form of an element at room temperature, 25°C, and pressure, 1 atm
- $\Delta H°$ = 0 for an element in its standard state

Hess’s Law and Heats of Reaction



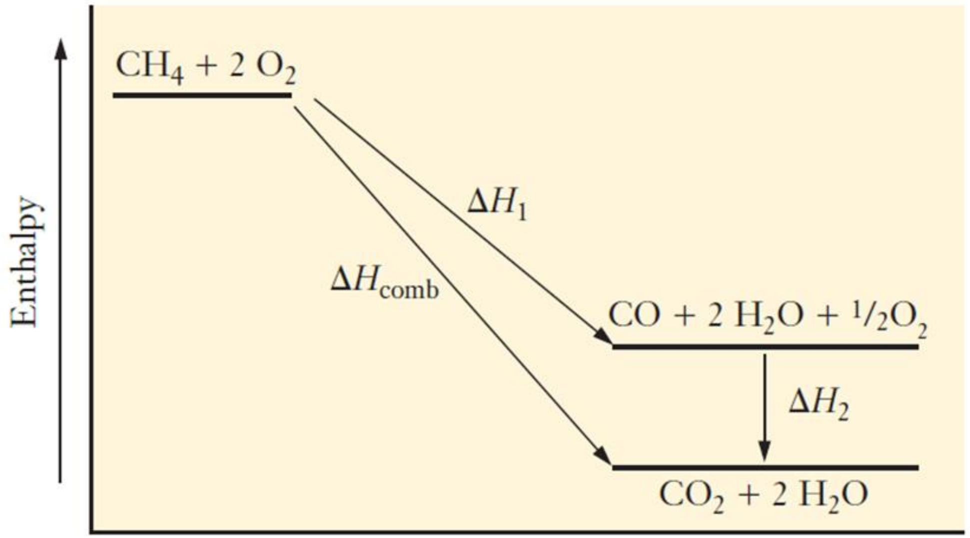
- Direct calorimetric determinations of some reactions may be too difficult or dangerous to perform
  - Indirect method is needed to obtain heats of reaction
- Hess’s law: Enthalpy change for any process is independent of the particular way the process is carried out
  - Enthalpy is a state function
    - A state function is a variable whose value depends only on the state of the system and not its history

Hess’s Law



- Conceptual diagram representing Hess’s law
  - Enthalpy is a state function, so any convenient path can be used to calculate the enthalpy change

Hess's Law



- Enthalpy diagram for the combustion of methane
  - CH_4 is converted to CO, then the CO is converted to CO_2
  - ΔH for each step is used to calculate the ΔH for the overall reaction
  - ΔH will be the same for both paths

Example Problem 9.7

$$S(s) + \frac{3}{2}O_2(g) \rightarrow SO_3(g)$$

- Given the thermochemical information below, determine the heat for this reaction

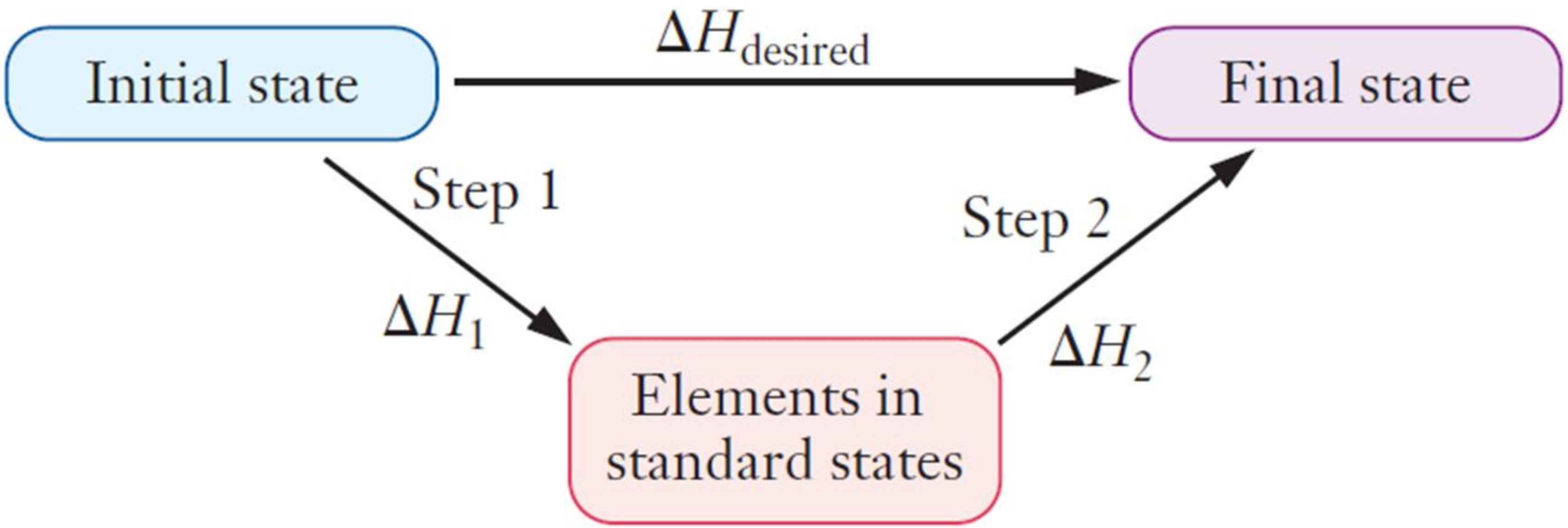
$$S(s) + O_2(g) \rightarrow SO_2(g) \qquad \Delta H^\circ = -296.8 \text{ kJ}$$

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g) \qquad \Delta H^\circ = -197.0 \text{ kJ}$$

$$\Delta H = \Delta H_1^\circ + \frac{1}{2}\Delta H_2^\circ = -395.3$$

Example Problem 9.7

Formation Reactions and Hess's Law



- Conceptual diagram showing how to use tabulated enthalpies of formation to calculate the enthalpy change for a chemical reaction

Formation Reactions and Hess's Law

- The enthalpy change for a reaction can be calculated using Hess's law and heats of formation

$$\Delta H^\circ = \sum_i v_i \Delta H_f^\circ(\text{products})_i - \sum_j v_j \Delta H_f^\circ(\text{reactants})_j$$

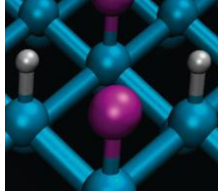
Example Problem 9.9

- Ethanol, C_2H_5OH, is used to introduce oxygen into some blends of gasoline
  - It has a heat of combustion of 1366.8 kJ/mol
    - What is the heat of formation of ethanol?

$$C_2H_5OH + 3O_2 \rightleftharpoons 2CO_2 + 3H_2O \quad \Delta H = -1366.8\ kJ/mol$$

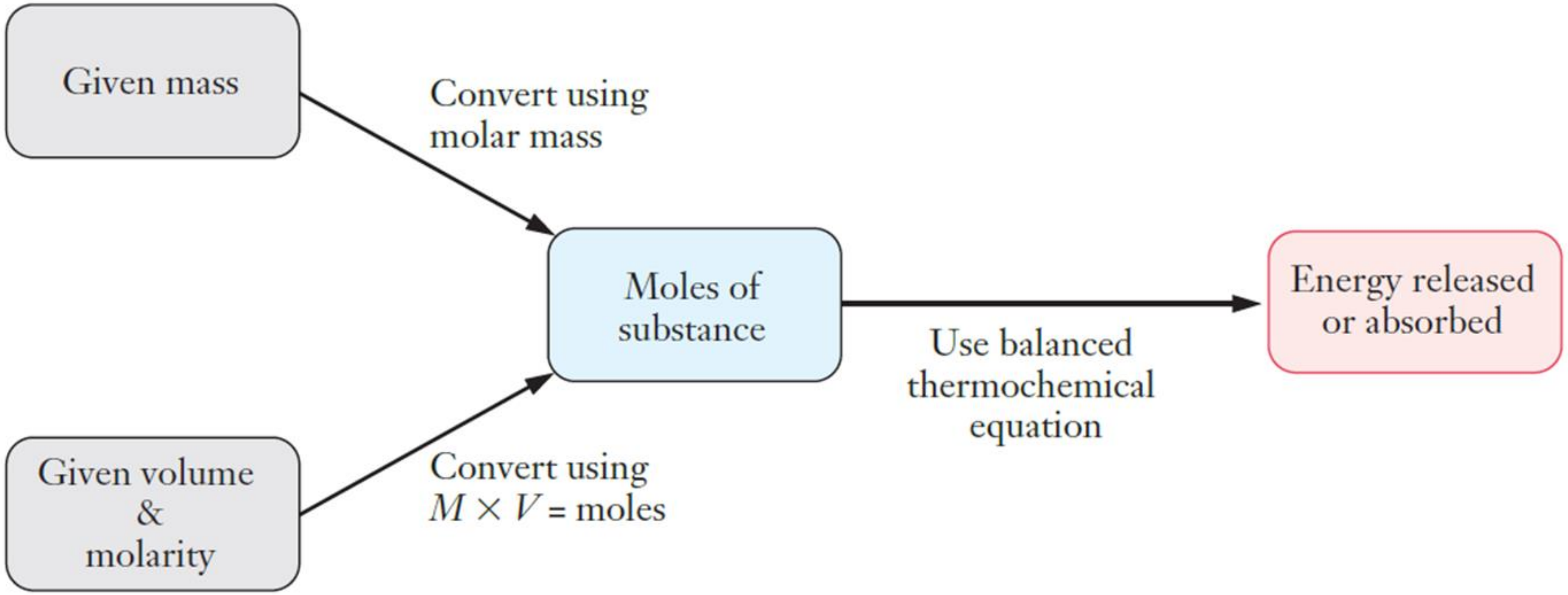
$$2C + 3H_2 + \frac{1}{2}O_2 \rightleftharpoons C_2H_5OH$$

Energy and Stoichiometry



- Thermochemical equation allows for the stoichiometric treatment of energy
  - For an exothermic reaction, energy is treated as a product
  - For an endothermic reaction, energy is treated as a reactant
- The thermochemical equation is used to convert between the number of moles of a reactant or product and the amount of energy released or absorbed
  - The stated value of ΔH for a thermochemical equation corresponds to the reaction taken place exactly as written, with the indicated numbers of moles of each substance reacting

Energy and Stoichiometry



- Flow chart detailing the sequence of steps needed to calculate the amount of energy released or absorbed when a chemical reaction is carried out using a given amount of material

Example Problem 9.10

- An engine generates 15.7 g of nitric oxide gas during a laboratory test
  - How much heat was absorbed in producing this NO?

$$N_2(g) + O_2(g) \rightarrow 2NO(g) \qquad \Delta H^\circ = 180.5\text{ kJ}$$

$$\frac{15.7\,\cancel{g}}{30\,g/mol} \times \frac{1}{2} \times 180.5\,kJ = 47.2\,kJ$$