

6 Chemical Energy

Chapter Objectives:

- Understand potential and kinetic energy, and the first law of thermodynamics.
- Understand the concept of enthalpy, and use standard heats of formation and Hess's Law to calculate enthalpy changes.
- Learn how to use specific heat to perform calculations involving energy changes. (Section 10.11)

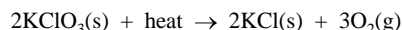
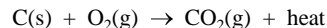
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Thermodynamics and Thermochemistry

- *Why do chemical reactions occur?* One major driving force for reactions is *stability*: Substances that are high in energy are generally less stable and more reactive, while substances that are lower in energy are generally more stable and less reactive.
- **Thermodynamics** is the study of heat and its transformations.
- **Thermochemistry** is the branch of thermodynamics that deals with the relationships between chemistry and energy.



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Energy and the First Law of Thermodynamics

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Energy, Work, and Heat

- **Energy** is the capacity to do **work** or to supply **heat**. Energy can be exchanged between objects by some combination of either heat or work:

$$\text{Energy} = \text{heat} + \text{work}$$

$$\Delta E = q + w$$



(a)



(b)



(c)

- **Work** is done when a force is exerted through a distance:

$$\text{Work} = \text{force} \times \text{distance}$$

- **Heat** is the flow of energy caused by a temperature difference.

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Kinetic and Potential Energy

- **Kinetic energy** (E_K) is the energy due to the motion of an object with mass m and velocity v :

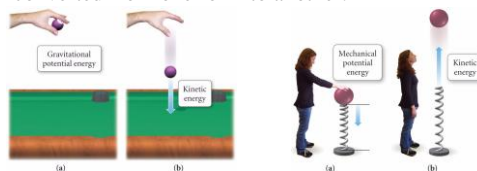
$$E_K = \frac{1}{2}mv^2$$

- **Thermal energy**, the energy associated with the temperature of an object, is a form of kinetic energy, because it arises from the vibrations of the atoms and molecules within the object.
- **Potential energy** (E_P) is energy due to position, or any other form of “stored” energy. There are several forms of potential energy:
 - Gravitational potential energy
 - Mechanical potential energy
 - Chemical potential energy (stored in chemical bonds)

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Kinetic and Potential Energy

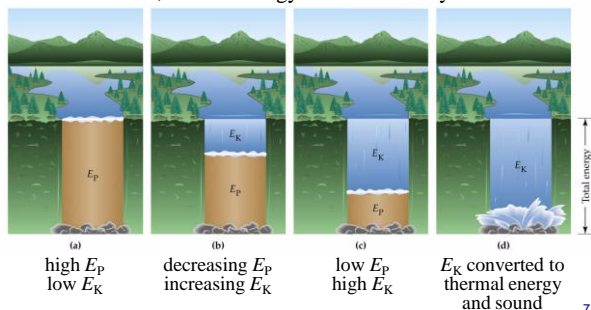
- Potential energy *increases* when things that attract each other are separated or when things that repel each other are moved closer.
- Potential energy *decreases* when things that attract each other are moved closer, or when things that repel each other are separated.
- According to the **law of conservation of energy**, energy cannot be created or destroyed, but can be converted from one form to another.



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Kinetic and Potential Energy

- Water falling in a waterfall exchanges gravitational potential energy for kinetic energy as it falls faster and faster, but the energy is never destroyed.



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Units of Energy

- The **watt (W)** is a unit of **power**, the *rate* at which energy is used:

$$1 \text{ W} = 1 \text{ J s}^{-1}$$

- Kilowatt-hours (kWh)** are the unit that is usually reported on electrical bills:

$$1 \text{ kWh} = 3.60 \times 10^6 \text{ J}$$

TABLE 6.2 Energy Uses in Various Units

| Unit | Amount Required to Raise Temperature of 1 g of Water by 1 °C | Amount Required to Light 100-W Bulb for 1 Hour | Amount Used by Human Body in Running 1 Mile (Approximate) | Amount Used by Average U.S. Citizen in 1 Day |
|---------------------|--|--|---|--|
| joule (J) | 4.18 | 3.60×10^5 | 4.2×10^5 | 9.0×10^6 |
| calorie (cal) | 1.00 | 8.60×10^4 | 1.0×10^5 | 2.2×10^6 |
| Calorie (Cal) | 0.00100 | 86.0 | 100. | 2.2×10^3 |
| kilowatt-hour (kWh) | 1.16×10^{-6} | 0.100 | 0.12 | 2.5×10^2 |

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Internal Energy, E, and State Functions

- The **internal energy (E)** of a system is the sum of all the kinetic and potential energies for every particle in the system.
- The internal energy is a **state function**, which is dependent only on the present state of the system, and not on the pathway by which it got to that state.
 - Some examples of state functions include energy (and many other thermodynamic terms), pressure, volume, altitude, distance, etc.
- An energy change in a system can occur by many **pathways** (different combinations of heat and work), but no matter what the combination, ΔE is always the same — the *amount* of the energy change does not depend on *how* the change takes place.

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Units of Energy

- From the expression for kinetic energy it can be seen that energy has units of **kg·m²/s²** ($\text{kg m}^2 \text{s}^{-2}$)
- The SI unit of energy is the **joule (J)**:

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

[James Prescott Joule, 1818-1889]

- Since joules are fairly small units, kilojoules (kJ) are frequently used instead.
- A **calorie (cal)** is the amount of energy needed to raise the temperature of 1 g of water by 1°C.
- The nutritional unit **Calorie (Cal)** is actually a kilocalorie (kcal):

$$1 \text{ cal} = 4.184 \text{ J (exact)}$$

$$1 \text{ Cal} = 1000 \text{ cal} = 1 \text{ kcal} = 4184 \text{ J}$$

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Examples: Kinetic Energy

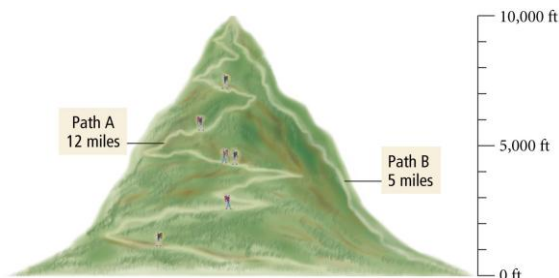
- What is the kinetic energy (in kJ) of a 2300. lb car moving at 55.0 mi/h?

Answer: 315 kJ

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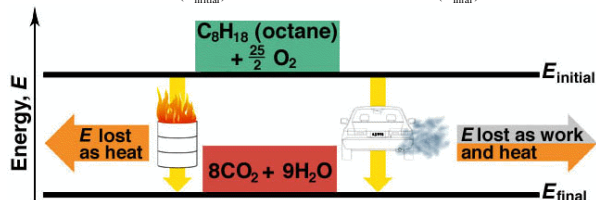
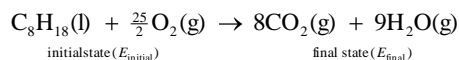
State Functions

Change in altitude is a **state function**: it only depends on the difference between the initial and final values, not on the path that the climbers take.



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State Function — A Chemical Example



- For a given change, ΔE ($q + w$) is constant, even though the specific values of q and w can vary.
- Heat and work are NOT state functions, but ΔE is.

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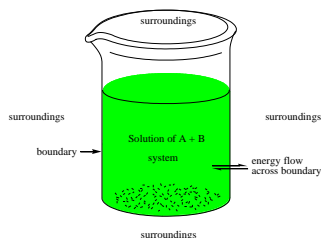
State Functions and Reversibility

- Another characteristic of state functions is their *reversibility*.
 - Climbing back down Mount Everest, your final position is now identical to your initial position, and the value of the change in altitude is 0 miles.
 - *The overall change in a state function is zero when the system returns to its original condition.*
- For a nonstate function, the overall change is *not* zero even if the path returns the system to its original condition.
 - For instance, the money spent on a trip or time expended during traveling does not reappear.

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The System and the Surroundings

- A **system** is the particular set of substances (a chemical reaction, a phase change, etc.) that we focus on in an experiment.
- The **surroundings** include everything else outside the system — the flask, the room, the building, etc.



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The System and the Surroundings

- We have an **isolated** or **closed system** when energy cannot cross the boundary in any direction.
- If the system loses energy, the surroundings gain energy, and vice versa.
 - An **exothermic** process is one where energy flows *out* of the system.
 - An **endothermic** process is one where energy flows *into* the system.

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The First Law: Conservation of Energy

- The **law of conservation of energy**, also known as the **first law of thermodynamics**, states that energy cannot be created or destroyed; it can only be converted from one form into another.
- In other words, **the total energy of the universe is a constant**.

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

- Potential and kinetic energy are interconvertible, but for a particular system the total amount of potential and kinetic energy is a constant.

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Change in Internal Energy

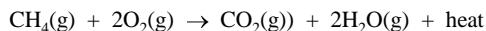
- For an isolated system, with no energy flowing in or out of the system, the internal energy is a constant.
 - **First Law of Thermodynamics (restated):** The total internal energy of an isolated system is constant.
- It is impossible to completely isolate a reaction from its surroundings, but it is possible to measure the **change** in the internal energy of the system, ΔE , as energy flows into the system from the surroundings or flows from the system into the surroundings.

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

$$\Delta E = E_{\text{products}} - E_{\text{reactants}}$$

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Energy Flow



- In this reaction, energy is released from the system to the surroundings (exothermic).
 - The reactants have a higher E than the products, so ΔE for the system is *negative*.
 - This energy is gained by the surroundings, where ΔE is positive. ($\Delta E_{\text{system}} = -\Delta E_{\text{surroundings}}$)

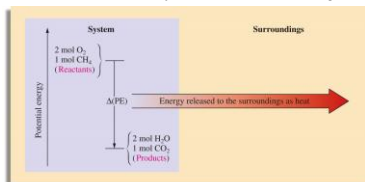
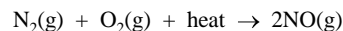


Figure 6.2

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Energy Flow



- If the reaction is reversed, energy is absorbed by the system from the surroundings.
 - The reactants have a lower E than the products, so ΔE for the system is *positive*.
 - This energy is lost by the surroundings, where ΔE is negative.

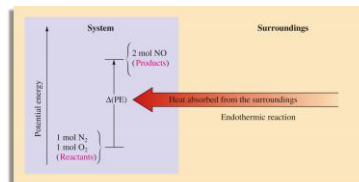


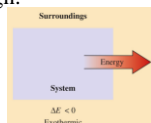
Figure 6.3

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Energy Flow: Sign Conventions

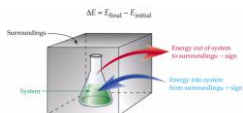
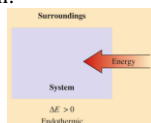
- By convention, energy changes are measured *from the point of view of the system*.
 - Any energy that flows *from* the system *to* the surroundings has a **negative** sign:

$$E_{\text{final}} < E_{\text{initial}} \\ \Delta E < 0$$



- Any energy that flows *to* the system *from* the surroundings has a **positive** sign:

$$E_{\text{final}} > E_{\text{initial}} \\ \Delta E > 0$$



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Energy Flow: Sign Conventions

- Energy exchanges between the system and surroundings take place through a combination of heat (q) and work (w):

$$\Delta E = q + w$$

- Energy going *into* the system, whether it's heat energy or work energy, has a *positive* sign, and energy *leaving* the system, whether it's heat energy or work energy, has a *negative* sign:

- q is (+) Heat is **absorbed** by the system
- q is (-) Heat is **released** by the system
- w is (+) Work is done **on** the system
- w is (-) Work is done **by** the system

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Examples: Energy Flow

- When gasoline burns in a car engine, the heat released causes the products CO_2 and H_2O to expand, which pushes the pistons outward. Excess heat is removed by the car's cooling system. If the expanding gases do 451 J of work on the pistons and the system loses 325 J to the surroundings as heat, calculate the change in energy in J, kJ, and kcal.

Answer: -776 J, -0.776 kJ, -0.185 kcal

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Work

- Work** (w) is defined as the force (F) that produces the movement of an object through a distance (d):

$$\text{Work} = \text{force} \times \text{distance}$$

$$w = F d$$

- Work also has units of J, kJ, cal, kcal, Cal, etc.
- The two most important types of chemical work are:
 - the **electrical work** done by moving charged particles (which is important in *electrochemistry*).
 - the **expansion work** done as a result of a volume change in a system, particularly from an expanding or contracting gas. This is also known as **pressure-volume work**, or **PV work**.



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Pressure-Volume Work

- When propane, C_3H_8 , is burned, 7 moles of gas are produced for every 6 moles of reactants:

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$$
- If the reaction takes place in a container with a movable piston, the greater volume of gas product will force the piston outward against the pressure of the atmosphere, thus doing work on the piston.
- Pressure-volume work** is equal to the pressure (P) times the change in volume (ΔV); the sign is negative because work is being done *by* the system (work energy is leaving the system):

$$w = -P\Delta V$$

- The units of PV work are L·atm; 1 L·atm = 101.3 J.

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Expansion Work

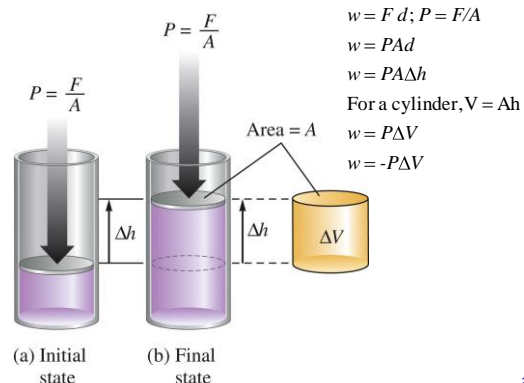


Figure 6.4

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Expansion Work

$$w = -P\Delta V$$

- If the gas expands, ΔV is positive, and the work term will have a negative sign (work energy is leaving the system).
- If the gas contracts, ΔV is negative, and the work term will have a positive sign (work energy is entering the system).
- If there is no change in volume, $\Delta V = 0$, and there is no work done. (This occurs in reactions in which there is no change in the number of moles of gas.)

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Examples: PV Work

- Calculate the work done (in kJ) during a reaction in which the volume expands from 12.0 L to 14.5 L against an external pressure of 5.00 atm.

Answer: -1.3 kJ

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Calorimetry: Measuring Heat and Work (Section 10.11)

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Heat and Temperature

- Heat and temperature are not the same thing!
 - Heat** is the exchange of thermal energy between a system and its surroundings. **Temperature** is a measure of the thermal energy of a sample.
 - A fresh cup of coffee is hotter than a swimming pool, but a swimming pool holds more heat than the coffee. If you pour a 200°F cup of coffee into a 100°F pool, the pool won't become 150°F.
- Heat flows from higher temperatures to lower temperatures, until the two regions reach the same temperature, and are at *thermal equilibrium*.
- All forms of energy can be converted quantitatively into heat, so it is possible to use heat as a measure of energy for *any* chemical or physical process.

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Heat Capacity

- The **thermal properties** of a substance are those that describe its ability to absorb or release heat without changing chemically.
- The **heat capacity** (C) of an object is the amount of heat (q) required to change its temperature by a given amount (ΔT):

$$C = \frac{q}{\Delta T} \quad q = C \Delta T$$

$$\Delta T = T_f - T_i$$

- Heat capacity has units of J/°C (or J/K), and is an extensive property, depending on the sample size.

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Specific Heat

- The **specific heat** (c , or **specific heat capacity**, C_s in book) of an object, is the quantity of heat required to change the temperature of *1 gram* of a substance by 1 °C (or K):

$$C_s = \frac{q}{m \Delta T} \quad q = C_s m \Delta T$$

- Specific heat has units of J/g °C, and is an *intensive* property, which is independent of the sample size.

- The **molar heat capacity** (C_m), is the quantity of heat required to change the temperature of *1 mole* of a substance by 1 °C (or K):

$$C_m = \frac{q}{\text{moles} \Delta T} \quad q = C_m \text{ moles} \Delta T$$

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Specific Heats of Some Common Substances

| Substance | Specific Heat Capacity, C_s (J g ⁻¹ °C ⁻¹) | Substance | Specific Heat Capacity, C_s (J g ⁻¹ °C ⁻¹) |
|-----------|---|---------------|---|
| Lead | 0.128 | Ethanol | 2.42 |
| Gold | 0.128 | Water (l) | 4.18 |
| Platinum | 0.133 | Water (s) | 2.03 |
| Tin | 0.228 | Carbon (s) | 0.71 |
| Silver | 0.235 | Glass (Pyrex) | 0.75 |
| Copper | 0.385 | Granite | 0.79 |
| Zinc | 0.388 | Sand | 0.84 |
| Nickel | 0.444 | | |
| Iron | 0.449 | | |
| Titanium | 0.522 | | |
| Aluminum | 0.903 | | |
| Magnesium | 1.02 | | |

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Examples: Specific Heat

- If a gold ring with a mass of 10.00 g changes in temperature from 25.00°C to 28.00°C, how much energy in joules has it absorbed? How much energy is absorbed by 10.00 g of H₂O under the same conditions?

Answer: $q_{\text{Au}} = 3.87 \text{ J}$, $q_{\text{H}_2\text{O}} = 125 \text{ J}$

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Examples: Specific Heat

- What is the specific heat of the (fictional) element dilithium if it takes 2.51 kJ to raise the temperature of 42.0 g of dilithium by 10.0°C?

Answer: 5.98 J/g°C

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Examples: Specific Heat

- What is the final temperature of a 100.0 g sample of water initially at 25.0°C after 25.1 kJ of heat energy is added? (The specific heat of water is 4.18 J/g°C.)

Answer: 85.0°C

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Constant-Volume Calorimetry: Measuring ΔE

- For any chemical reaction, the energy change is the sum of the heat and work energies:

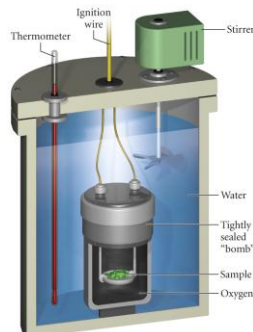
$$\Delta E_{\text{rxn}} = q + w = q - P\Delta V$$

- Under conditions of **constant volume**, $w=0$, and the energy change of the reaction is dependent only on *heat evolved at constant volume*, q_V :

$$\Delta E_{\text{rxn}} = q_V$$

- The heat change — and therefore the energy change — in a chemical reaction occurring at constant volume can be measured in a *bomb calorimeter*, in which a sample is sealed in a “bomb” surrounded by a water bath, in which the temperature change can be measured precisely.

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A Bomb Calorimeter

- The amount of heat absorbed by the water in the calorimeter is equal to the energy that is released by the reaction (but opposite in sign).

$$q_{\text{cal}} = C_{\text{cal}} \Delta T$$

$$q_{\text{rxn}} = -q_{\text{cal}}$$

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Examples: Constant-Volume Calorimetry

- When 1.010 g of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) undergoes combustion in a bomb calorimeter, the temperature rises from 24.92°C to 28.33°C . Find ΔE_{rxn} for the combustion of sucrose in kJ/mol sucrose. The heat capacity of the bomb calorimeter (determined in a separate experiment) is $4.90 \text{ kJ}/^\circ\text{C}$. (You can ignore the heat capacity of the small sample of sucrose because it is negligible compared to the heat capacity of the calorimeter)

Answer: $-5660 \text{ kJ/mol C}_{12}\text{H}_{22}\text{O}_{11}$

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Enthalpy

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Energy Changes at Constant Pressure; Enthalpy

- Most reactions are not done in sealed containers: they are carried out in open vessels at constant pressure, with the volume capable of changing freely, especially if the reactants or products of the reaction involve gases.
- In these cases, $\Delta V \neq 0$, and the energy change may be due to *both* heat transfer and *PV* work.
- In order to eliminate the contribution from *PV* work, a quantity called **enthalpy**, H , is defined as internal energy (E) plus the product of pressure and volume:

$$H = E + PV$$

- The **change in enthalpy** (ΔH) is:

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

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Enthalpy; Heats of Reaction

- By doing a little algebra, we can see the relationship between ΔH and energy:

$$\Delta E_{\text{rxn}} = q + w \quad \Delta E_{\text{rxn}} = q - P\Delta V$$

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

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

$$\Delta H = q_p$$

- Therefore, the change in enthalpy equals the *heat evolved at constant pressure, q_p* .
- The enthalpy change, ΔH , is also called the **heat of reaction** for the process. It is also a state function:

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

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Enthalpy vs. Energy

- While ΔE is a measure of the entire energy change of a system (heat and work), ΔH is a measure of only the heat exchanged at constant pressure.
- Most reactions *do* take place at constant (i.e., atmospheric) pressure, so ΔH is a good measure of energy changes in most thermodynamic systems.
- In reactions that do not involve gases, volume changes are approximately zero, and $\Delta H \approx \Delta E$.
- When the number of moles of gas doesn't change, $\Delta V = 0$, and $\Delta H = \Delta E$.
- Even in reactions in which the number of moles of gas *does* change, q_p is usually much larger than $P\Delta V$, so $\Delta H \approx \Delta E$.

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Examples: Enthalpy vs. Energy

- The reaction of nitrogen with hydrogen to make ammonia has $\Delta H = -92.2$ kJ



What is the value of ΔE (in kJ) if the reaction is carried out at a constant pressure of 40.0 atm and the volume change is -1.12 L?

Answer: -87.7 kJ

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Exothermic vs. Endothermic Processes

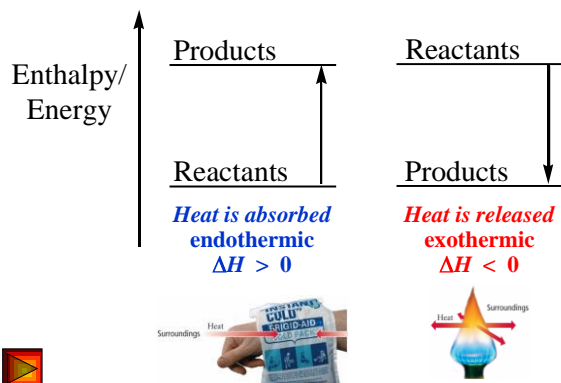
- A chemical reaction can either *release* or *absorb* heat energy:
 - An **endothermic** process **absorbs** heat energy and results in an *increase* in the enthalpy of the system (the products have *more* enthalpy than the reactants).
 - An **exothermic** process **releases** heat energy and results in a *decrease* in the enthalpy of the system (the products have *less* enthalpy than the reactants).

$$H_{\text{final}} < H_{\text{initial}} \quad \Delta H < 0 \quad \text{exothermic}$$

$$H_{\text{final}} > H_{\text{initial}} \quad \Delta H > 0 \quad \text{endothermic}$$

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Enthalpy Diagrams



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Where Does the Energy Come From?

- When an exothermic reaction occurs, the chemical potential energy that used to be stored in the chemical bonds in the reactants.
 - The higher energy bonds break and lower energy bonds form, and the system goes from a higher potential energy to a lower potential energy.
 - The energy difference is usually emitted in the form of heat or light.
- When an endothermic reaction occurs, the energy that is absorbed by the system allows new bonds with higher energies to be formed, and the potential energy of the system is raised.

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Thermochemical Equations

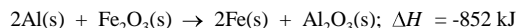
- A **thermochemical equation** is a balanced equation that also states the heat of reaction (ΔH).
- The reaction of 1 mole of N_2 and 3 moles of H_2 to form 2 moles of NH_3 releases 92.38 kJ of energy:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g); \Delta H = -92.38 \text{ kJ}$$
 - This ΔH value is true **only** when the coefficients are taken to mean the **number of actual moles** they express for that particular reaction, with the reagents in those particular physical states.
 - For other amounts of reactants or products, the energy change of the reaction can be calculated by using the ΔH term in the same way that the coefficients are used.

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Examples: Thermochemical Equations

- How much heat (in kJ) is evolved when 5.00 g of aluminum reacts with a stoichiometric amount of Fe_2O_3 in the thermite reaction? (WE 8.3)



Answer: 78.8 kJ

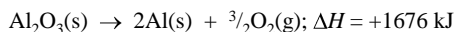
MOV: Thermite



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Examples: Thermochemical Equations

- If aluminum is produced by the thermal decomposition of bauxite (mostly Al_2O_3), how many grams of Al can form when 1.000×10^3 kJ of heat is transferred?



Answer: 32.20 g Al

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Constant-Pressure Calorimetry: Measuring ΔH

- Energy changes at **constant pressure** are measured in an insulated vessel with a stirrer, thermometer, and a loose-fitting lid that keeps the contents at atmospheric pressure. The data obtained allows us to calculate ΔH . (In undergraduate labs, this device is approximated by a coffee cup.)

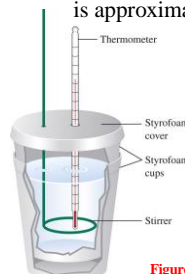


Figure 10.21

$$q_{\text{soln}} = c_{\text{soln}} m_{\text{soln}} \Delta T$$

$$q_{\text{rxn}} = -q_{\text{soln}}$$

Section 10.11

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Examples: Constant-Pressure Calorimetry

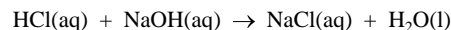
- A 25.64 g sample of a solid was heated in a test tube to 100.00 C in boiling water and carefully added to a coffee-cup calorimeter containing 50.00 g water. The water temperature increased from 25.10 C to 28.49 C. What is the specific heat capacity of the solid? (Assume all the heat is gained by the water.)

Answer: 0.387 J/g C

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Examples: Constant-Pressure Calorimetry

- The reaction of hydrochloric acid and sodium hydroxide is exothermic. The equation is



In one experiment, a student placed 50.0 mL of 1.00 M HCl at 25.50 C in a coffee cup calorimeter. To this was added 50.0 mL of 1.00 M NaOH solution also at 25.50 C. The mixture was stirred, and the temperature quickly increased to a maximum of 32.40 C. What is the energy evolved in kilojoules per mole of HCl? (Because the solutions are relatively dilute, we can assume that their specific heats are close to that of water, $4.18 \text{ J g}^{-1} \text{ C}^{-1}$, and that their densities are 1.00 g mL^{-1} .)

Answer: 57.8 kJ/mol

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Relationships Involving Enthalpy (ΔH_{rxn})

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Manipulating Thermochemical Equations

- If a chemical equation is multiplied by some factor, then ΔH_{rxn} is multiplied by the same factor.

$$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g}); \Delta H = -483.6 \text{ kJ}$$

$$4\text{H}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow 4\text{H}_2\text{O}(\text{g}); \Delta H = -967.2 \text{ kJ}$$

$$\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}); \Delta H = -241.8 \text{ kJ}$$
- If a chemical equation is reversed, the sign of ΔH_{rxn} is reversed. (This is equivalent to multiplying the equation by -1.)

$$2\text{H}_2\text{O}(\text{g}) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g}); \Delta H = +483.6 \text{ kJ}$$

$$\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}); \Delta H = +241.8 \text{ kJ}$$

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Examples: Thermochemical Equations

1. Given the following thermochemical equation



What is the ΔH_{rxn} for the reactions shown below?

- $2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}); \Delta H = +92.38 \text{ kJ}$
- $2\text{N}_2(\text{g}) + 6\text{H}_2(\text{g}) \rightarrow 4\text{NH}_3(\text{g}); \Delta H = -184.8 \text{ kJ}$
- $\frac{1}{2}\text{N}_2(\text{g}) + \frac{3}{2}\text{H}_2(\text{g}) \rightarrow \text{NH}_3(\text{g}); \Delta H = -46.19 \text{ kJ}$
- $4\text{NH}_3(\text{g}) \rightarrow 2\text{N}_2(\text{g}) + 6\text{H}_2(\text{g}); \Delta H = +184.8 \text{ kJ}$
- $6\text{NH}_3(\text{g}) \rightarrow 3\text{N}_2(\text{g}) + 9\text{H}_2(\text{g}); \Delta H = +277.1 \text{ kJ}$
- $2\text{NH}_3(\text{aq}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}); \Delta H = \text{no relation!}$

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Two Paths to CO_2

- We can imagine two paths leading from 1 mole of carbon and oxygen (O_2) to 1 mole of carbon dioxide:

One-Step Path:

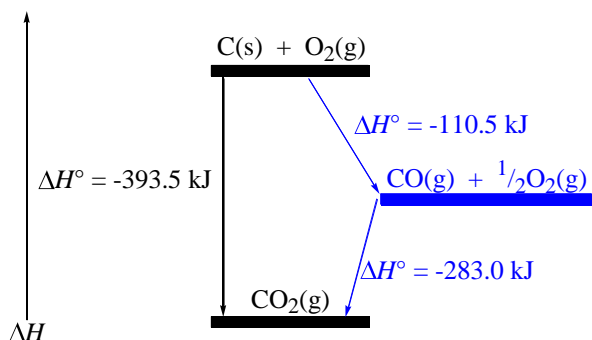


Two-Step Path:



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Enthalpy Diagram for the Formation of CO_2



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Hess's Law

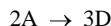
- Since ΔH is a state function, the path which leads from the starting materials to the products should be irrelevant to the overall energy change.
- This is generalized into **Hess's Law**: if a reaction can be expressed as the sum of a series of steps, then ΔH for the overall reaction is the sum of the ΔH° 's of the individual steps.

$$\begin{array}{l} \text{A} + \text{B} \rightarrow \text{C}; \Delta H = -100 \text{ kJ} \\ \text{C} \rightarrow \text{D}; \Delta H = +30 \text{ kJ} \\ \hline \text{A} + \text{B} \rightarrow \text{D}; \Delta H = -70 \text{ kJ} \end{array}$$
- We can use this property to determine the ΔH° 's of reactions which are difficult to measure directly, by writing the reaction as the sum of reactions with known ΔH° 's.

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Examples: Hess's Law

2. Calculate the value of ΔH° for the hypothetical reaction



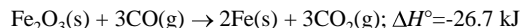
Use the following equations to determine the value of ΔH° . (sim. to Ex. 6.8)



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Examples: Hess's Law

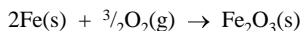
4. Carbon monoxide is often used in metallurgy to remove oxygen from metal oxides and thereby give the free metal. The thermochemical equation for the reaction of CO with iron(III) oxide, Fe_2O_3 , is



Use this equation and the equation for the combustion of carbon monoxide,



to calculate the value of ΔH° for the following reaction.



Answer: -822.3 kJ

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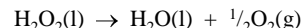
Thermodynamic Standard States

- The enthalpy change is the amount of heat released or absorbed when reactants are converted to products at the same temperature and in the molar amounts represented by coefficients in the balanced equation. The physical states must also be specified, since a substance in the gas phase has a different heat content from one in the liquid phase.
- In order to compare thermodynamic measurements from different reactions, a set of conditions called the **thermodynamic standard state** is defined: *the most stable form of a substance at 1 atm pressure and 25 °C, 1 M for all substances in solution.*
- When ΔH is measured with all substances in their standard states, it is called the **standard enthalpy (heat) of reaction, ΔH°** .

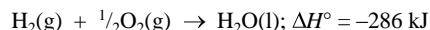
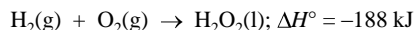
65

Examples: Hess's Law

3. Hydrogen peroxide, H_2O_2 , decomposes into water and oxygen by the following equation.



Use the following equations to determine the value of ΔH° for the decomposition of hydrogen peroxide. (sim. to example on p. 314)

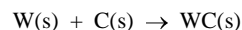


Answer: -98 kJ

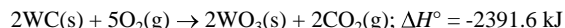
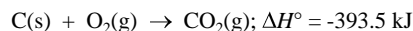
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Examples: Hess's Law

5. Use Hess's law to calculate the value of ΔH° for the reaction of tungsten with carbon:



Use the following thermochemical equations:



Answer: -38.0 kJ

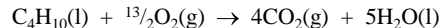
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Some Important Types of Enthalpy Change

- Heat of fusion (ΔH_{fus})** — enthalpy change when 1 mole of a substance melts.

$$\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{l}); \Delta H = 6.01 \text{ kJ/mol at } 0 \text{ }^\circ\text{C}$$
- Heat of vaporization (ΔH_{vap})** — enthalpy change when 1 mole of a substance vaporizes.

$$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g}); \Delta H = 40.7 \text{ kJ/mol at } 100 \text{ }^\circ\text{C}$$
- Heat of sublimation (ΔH_{subl})** — enthalpy change when 1 mole of a substance *sublimes* (converts directly from the solid phase to the vapor phase).
- Heat of combustion (ΔH_c)** — enthalpy change when 1 mole of a substance combines with O_2 in a combustion reaction.



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Standard Enthalpy of Formation (ΔH_f°)

- The **standard enthalpy (heat) of formation, ΔH_f°** , is the enthalpy change for the formation of 1 mole of a substance in its standard state *from its constituent elements* in their standard states.
- The most stable form of any element in its standard state has $\Delta H_f^\circ = 0$ kJ. This establishes a baseline from which to calculate the ΔH_f° for other compounds.
- The elements must be in their *standard states* at 25°C. That is, elements which are diatomic must be in the diatomic form; physical states must be reasonable for that element at 25°C, etc.
- In most cases, ΔH_f° for a compound is negative (i.e., a compound is usually more stable than its elements.)

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Standard Enthalpies of Formation

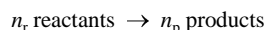
| Formula | ΔH_f° (kJ/mol) | Formula | ΔH_f° (kJ/mol) | Formula | ΔH_f° (kJ/mol) |
|-----------------------------------|-----------------------------|--|-----------------------------|-------------------------------------|-----------------------------|
| Bromine | | C ₂ H ₅ OH(l) | -277.6 | Nitrogen | |
| Br ₂ (g) | 111.9 | C ₃ H ₆ (g) | -103.85 | N ₂ (g) | 0 |
| Br ₂ (l) | 0 | C ₃ H ₈ O(l, acetone) | -248.4 | NH ₃ (g) | -45.9 |
| HBr(g) | -36.3 | C ₃ H ₇ O(l, isopropanol) | -318.1 | NH ₄ NO ₃ (s) | -365.6 |
| Calcium | | C ₄ H ₄ (l) | 49.1 | NO(g) | 91.3 |
| Ca(s) | 0 | C ₆ H ₁₂ O ₆ (s, glucose) | -1273.3 | N ₂ O(g) | 81.6 |
| CaO(s) | -634.9 | C ₁₂ H ₂₂ O ₁₁ (s, sucrose) | -2226.1 | Oxygen | |
| CaCO ₃ (s) | -1207.6 | Chlorine | | O ₂ (g) | 0 |
| Carbon | | Cl ₂ (g) | 121.3 | O ₃ (g) | 142.7 |
| C(s, graphite) | 0 | Cl ₂ (g) | 0 | H ₂ O(g) | -241.8 |
| C(s, diamond) | 1.88 | HCl(g) | -92.3 | H ₂ O(l) | -285.8 |
| CO(g) | -110.5 | Fluorine | | Sodium | |
| CO ₂ (g) | -393.5 | F ₂ (g) | 79.38 | Na(s) | 0 |
| CH ₄ (g) | -74.6 | F ₂ (g) | 0 | Na(g) | 107.5 |
| CH ₃ OH(l) | -238.6 | HF(g) | -273.3 | NaCl(s) | -411.2 |
| C ₂ H ₂ (g) | 227.4 | Hydrogen | | Na ₂ CO ₃ (s) | -1130.7 |
| C ₂ H ₄ (g) | 52.4 | H ₂ (g) | 218.0 | NaHCO ₃ (s) | -950.8 |
| C ₂ H ₆ (g) | -84.68 | H ₂ (g) | 0 | | |

Appendix 4 on pages A19 through A21 lists thermodynamic properties of more substances.

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Determining ΔH° from ΔH_f°

- The standard enthalpy of reaction can be calculated by subtracting the sum of the heats of formation of all reactants from the sum of the heats of formation of all products, with each ΔH_f° multiplied by the appropriate coefficient in the balanced equation:



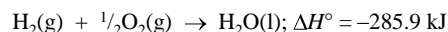
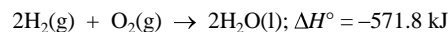
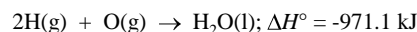
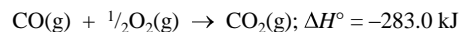
$$\Delta H_{\text{rxn}}^\circ = \sum n_p \Delta H_f^\circ (\text{products}) - \sum n_r \Delta H_f^\circ (\text{reactants})$$

- This process is really an application of Hess's Law.
- Thus, to calculate the ΔH° for any reaction, we write the balanced equation, and look up the ΔH_f° 's of all of the reactants and products.

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Examples: Standard Heats of Formation

6. Do the following reactions represent a ΔH_f° equation?



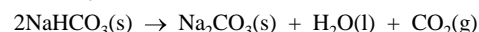
70

Examples: Standard Heats of Formation

7. What equation must be used to represent the formation of NaHCO₃(s) when we want to include its value of ΔH_f° ?

Examples: Standard Heats of Formation

8. Some chefs keep baking soda, NaHCO₃, handy to put out grease fires. When thrown on the fire, baking soda partly smothers the fire and the heat decomposes it to give CO₂, which further smothers the flame. The equation for the decomposition of NaHCO₃ is



Use the ΔH_f° data in Appendix 4 to calculate the ΔH° for this reaction in kilojoules.

Answer: 91.6 kJ

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Examples: Standard Heats of Formation

9. Use the ΔH_f° data in Appendix 4 to calculate ΔH for the combustion of ethanol, $C_2H_5OH(l)$, at $25^\circ C$.

Answer: -1234.8 kJ

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Examples: Standard Heats of Formation

10. Use the ΔH_f° data in Appendix 4 to calculate the *standard heat of vaporization* of water.

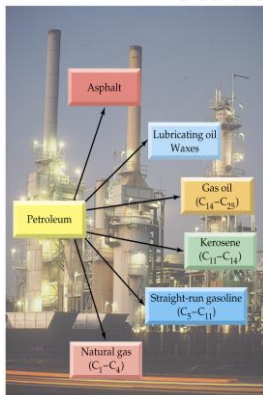
Answer: +44.0 kJ

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**Fuels**

- Most common fuels (except for H_2) are organic compounds whose energy is ultimately derived from the Sun through the conversion of CO_2 and water into glucose by the process of photosynthesis in plants (and some bacteria).
- Coal, natural gas, and petroleum are collectively known as **fossil fuels**, the remains of organisms which have been decaying for millions of years.
 - Coal, which is primarily of vegetable origin, is mainly graphite-like carbon compounds, and can be burned without much refinement.
 - Petroleum is a viscous liquid mixture of hydrocarbons primarily of marine origins.

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Petroleum Refining

- Petroleum is refined primarily by *distillation* — the separation of a complex mixture of compounds by differences in boiling points:
 - gasoline (30-200 C), C_5-C_{11}
 - kerosene (175-300 C), $C_{11}-C_{14}$
 - gas oil (275-400 C), $C_{14}-C_{25}$
 - lubricating oils are high bp compounds with a large number of carbon atoms
 - asphalt is the residual tar that remains after the distillation process

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Fuel Consumption

- Most energy in the U.S. is derived from fossil fuels.

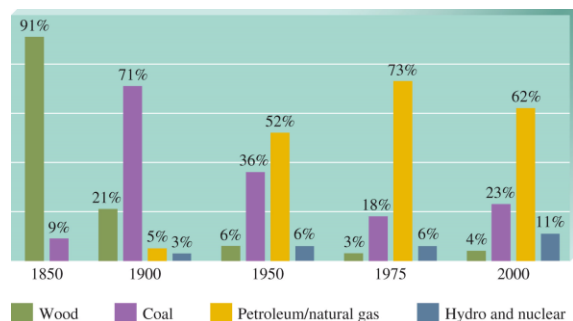


Figure 6.9

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