

Thermochemistry

Chapter 6

Homework

- Read Chapter 6
- Due throughout the unit
- Pg 250 75-81 odd
- Take the AP review test at the end, between pages 250-251

Nature of Energy

- **Energy (E)** is the capacity to do work or to produce heat.
- **Potential energy** is the energy of position or composition.
- **Kinetic energy** is the energy due to the motion of the object and depends on the mass of the object m and its velocity v :
 - $KE = \frac{1}{2} mv^2$.

Energy transfers

- Whenever E is transferred from one object to another, it appears as *work* (w) and/or *heat* (q).
- The way that energy transfer is divided between work and heat depends on the specific conditions called a **pathway**.
- * Regardless of the pathway, the energy or sum of heat and work will always be the same.

State function

- A **state function (state property)** refers to a property of the system that depends only on its present state, not on its pathway.
- A state function does not depend in any way on the system's past or future.
- All variables with capital letters are state functions, having more than one pathway to reach the same value.

Chemical Energy

- **Energy Flow to and from a System.**
- A **system** is what the change is occurring to.
- The **surroundings** is ANY other region relevant to the change.

Exothermic reactions

- When a reaction results in the release of heat energy to its surrounding, it is **exothermic**.
- Heat flows out of the system to the surroundings.
- In any exothermic reaction, some of the potential energy from higher energy chemical bonds is being converted to thermal energy (random KE) via heat as lower energy bonds are formed.

Endothermic

- Reactions that absorb energy from the surroundings are **endothermic**.
- Heat flows into the system from the surroundings.
- In a chemical reaction this energy is used to create higher energy bonds.
- The energy lost from one system must equal the energy gained by another

Thermodynamics

- The study of energy and its conversions is called **thermodynamics**.
- The **first law of thermodynamics** states that the *total energy of the universe is constant*.
- This is also known as the *law of conservation of energy*.
- Energy cannot be created or destroyed but can be changed from one form to another.
- $\Delta E_{\text{universe}} = \Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0$.

- **Internal energy** E of a system can be defined as the sum of the PE and KE of all particles in a system.
- When a chemical system changes, energy changes.
- Now an individual system may change in energy.
- $\Delta E = E_{\text{final}} - E_{\text{initial}} = E_{\text{products}} - E_{\text{reactants}}$

Law of Conservation of Energy

- A system may have a change in energy, but that change in energy will always be equivalent (but opposite in sign) to the change experienced by the surroundings.
- $\Delta E_{\text{universe}} = \Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0$

Heat and Work

- **Heat (q)** is the energy transfer between the system and surroundings because of a difference in temperature.
- **Work (w)** is the energy transfer when an object is moved by a force.
- $\Delta E = q + w$.
- The signs of q and w (+/-) is determined from the system's perspective.

Sign convention

- From a system's perspective
- If I am heating a system then the q value is positive. I am adding heat.
- If the system is losing heat (being cooled), q value is negative. I am removing heat.
- If work is being done on the system (it is being compressed, electrolyzed), w is positive.
- If work is being done on something else (expanding gas, reducing something) w is negative

Internal Energy Problem

- Calculate ΔE for a system undergoing an endothermic process in which 15.6 kJ of heat flows and where 1.4 kJ of work is done on the system.
- Endothermic means 15.6 kJ is a positive value or gained by the system
- Work done on the system means that value is positive.
- So $15.6 + 1.4 \text{ kJ} = 17.0 \text{ kJ}$ of work is done on the system

Units

- The joule (J) is the fundamental SI unit for energy.
- $1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2$.
- A calorie (cal) is the energy required to raise 1 gram H_2O by 1°C .
- $1 \text{ cal} = 4.184 \text{ J}$
- 1 Calories (food) = 1 kilocalorie (kcal).
- A Btu is the energy required to raise 1 pound of H_2O by 1°F .

Work

- w is often the result of a chemical reaction producing a gaseous product, resulting in $P\Delta V$ work.
- P = pressure, V = volume
- w and $P\Delta V$ have opposite signs because when the gas expands (ΔV is positive), work flows into the surroundings (w is negative).

• https://en.wikipedia.org/wiki/Four-stroke_engine?srlybrkr=814d4253

$P\Delta V$ Work

- Calculate the work associated with the expansion of a gas from 46 L to 64 L at a constant external pressure of 15 atm.
- For some reason these problems are normally done with L atm as the unit, and they give you the conversion factor $1 \text{ L atm} = 101.3 \text{ J}$.
- However, an easier conversion factor is $1 \text{ L kPa} = 1 \text{ J}$

Want to see the conversion on that?

- $\text{Pa} = 1 \text{ N}/\text{m}^2$
- $1 \text{ kPa} = .001 \text{ N}/\text{m}^2$ ($1 \text{ N} / 10 \text{ cm}^2$)
- $\frac{0.001 \text{ N}}{1 \text{ m}^2} \times \frac{1 \text{ m}}{1 \text{ m}} = \frac{.001 \text{ N} \cdot \text{m}}{1 \text{ m}^3} \times \frac{1 \text{ m}^3}{1000 \text{ L}} = \frac{1 \text{ N} \cdot \text{m}}{\text{L}}$
- A $\text{N} \cdot \text{m}$ is a joule
- So $1 \text{ kPa} = 1 \text{ J} / \text{L}$
- Therefore $\text{kPa} \cdot \text{L} = 1 \text{ J}$

Snippet of the AP equation sheet

$K_{\text{equilibrium}} = \frac{1}{2} m^{-2}$ Molarity, M = moles of solute per liter of solution $A = ebc$	Gas constant, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ $= 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$ $= 62.36 \text{ L Torr mol}^{-1} \text{ K}^{-1}$ $760 \text{ mm Hg} = 760 \text{ Torr}$ STP = 273.15 K and 1.0 atm Ideal gas at STP = 22.4 L mol ⁻¹
THERMODYNAMICS/ELECTROCHEMISTRY $q = m\Delta T$ $\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$ $\Delta H^\circ = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{reactants}}$ $\Delta G^\circ = \sum \Delta G^\circ_{\text{products}} - \sum \Delta G^\circ_{\text{reactants}}$ $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ $= -RT \ln K$ $= -nFE^\circ$ $I = \frac{q}{t}$ $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q$	q = heat m = mass c = specific heat capacity T = temperature S° = standard entropy H° = standard enthalpy G° = standard Gibbs free energy n = number of moles E° = standard reduction potential I = current (amperes) q = charge (coulombs) t = time (seconds) Q = reaction quotient Faraday's constant, $F = 96,485 \text{ coulombs per mole of electrons}$ $1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$

Internal Energy Heat and Work

- A hot air balloon is being inflated to its full extent by heating the air inside it. In the final stages of this process, the volume of the balloon changes from $4.00 \times 10^6 \text{ L}$ to $4.50 \times 10^6 \text{ L}$ by the addition of $1.3 \times 10^8 \text{ J}$ of energy as heat. Assuming that the balloon expands against a constant pressure of 1.0 atm, calculate ΔE for the process (To convert between L atm and J, use $1 \text{ L atm} = 101.3 \text{ J}$.)

Enthalpy

- Enthalpy is a measure of the total energy of a system.
- Enthalpy is a state function (the pathway does not matter) with the symbol H .
- $H = E + PV$
- E is the internal energy of the system, P is the pressure of the system, and V is the volume of the system.

Heat at Constant Pressure

- The change in enthalpy of a system has no easily interpreted meaning **except at constant pressure, where $\Delta H = \text{heat}$** .
- $\Delta H = H_{\text{products}} - H_{\text{reactants}}$
- At constant pressure...
 - Exothermic means ΔH is negative.**
 - Endothermic means ΔH is positive.**

Enthalpy

- When 1 mole of methane is burned at constant pressure, 890 kJ of energy is released as heat. Calculate the energy released for a process in which a 5.8 g sample of methane is burned at constant pressure.

Calorimetry

- The device used experimentally to determine the heat associated with a chemical reaction is called a **calorimeter**.
- Calorimetry** is the science of measuring heat.
- Heat capacity** is the amount of heat required to raise an object's temperature one degree.
 - * $C = \frac{\text{heat absorbed}}{\text{increase in temperature}}$

Heat Capacity

Specific heat capacity is the energy required to raise the temperature of one gram of a substance by one degree Celsius.

units are $\text{J}/^\circ\text{C}\cdot\text{g}$ or $\text{J}/\text{K}\cdot\text{g}$.

Molar heat capacity is the energy required to raise the temperature of one mole of a substance one degree Celsius.

units are $\text{J}/^\circ\text{C}\cdot\text{mol}$ or $\text{J}/\text{K}\cdot\text{mol}$.

The equation

- The symbol for heat energy is q (J)
- Molar heat capacity is C (J/mol K)
- Temperature is T , change in temperature is ΔT (K)
- ΔT is calculated by final temp-initial temp ($T_f - T_i$)
- The symbol for number of particles is n (mol)
- $q = n C \Delta T$
- $q = n C (T_f - T_i)$

-----Or-----

- The symbol for heat energy is q (J)
- specific heat capacity is c (J/ g K)
- Temperature is T , change in temperature is ΔT (K)
- ΔT is calculated by final temp-initial temp ($T_f - T_i$)
- The symbol for mass m (g)
- $q = m c \Delta T$
- $q = m c (T_f - T_i)$

Heat Capacity

- Some common values are found in Table 6.1, p 251.
- * The higher the value, the longer it takes to heat an object and the longer it takes for that same object to cool.

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

- Sign convention
- Losing energy means the value is negative.
- Gaining energy means the value is positive.
- **The absolute value of the energy transferred will be the same.**
- However, losing will be negative, gaining will be positive

Constant-Pressure Calorimetry I

- 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 Na_2SO_4 solution at 25°C in a calorimeter, the white solid BaSO_4 forms and the temperature of the mixture increases to 28.1°C . Assuming that the calorimeter absorbs only a negligible quantity of heat, that the specific heat capacity of the solution is $4.18 \text{ J}/^\circ\text{C}\cdot\text{g}$, and that the density of the final solution is 1.0 g/mL , calculate the enthalpy change per mole of BaSO_4 formed.

Constant-Pressure Calorimetry II

- One piece of copper jewelry placed at 100°C has exactly twice the mass of another piece, which is at 40°C . They are placed inside a calorimeter whose heat capacity is negligible. What is the final temperature inside the calorimeter?