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### Chapter 5 Thermochemistry

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# 5.1 Energy and Energy Changes

- Energy is involved in all types of physical and chemical changes
- Energy: the capacity to do work or transfer heat
- All forms of energy are either
  - Kinetic
  - Potential

Kinetic energy - energy of motion
 Defining equation

$$E_{\rm k} = \frac{1}{2}mu^2$$

- Where *m* is mass and *u* is velocity
- Thermal one form of kinetic energy associated with random motion
  - Monitor changes via changes in temperature

- **Potential energy** energy of position
  - Chemical energy is stored within structural units of chemical substances.
  - *Electrostatic energy* is energy resulting from the interaction of charged particles.
    - Dependent on charges and distance between charges (Q = charge and d = distance)
    - Defining equation

$$E_{\rm el} \propto \frac{Q_1 Q_2}{d}$$

- +  $E_{el}$ : repulsive
- –  $E_{el}$ : attractive

- Law of conservation of energy
  - Energy may be converted from one form to another.
  - The total amount of energy in the universe is constant.
  - Example
    - A chemical reaction (potential) gives off heat (thermal)

- Energy changes in chemical reactions
  - System is the part of the universe of interest.
    - Example
      - -The reactants NaOH and HCI
  - Surroundings are the rest of the universe.
    - Example
      - -When heat is given off from the reaction of NaOH and HCI, the energy is transferred from the system to the surroundings.

- Thermochemistry
  - -The study of the transfer of heat (thermal energy) in chemical reactions.
  - -*Exothermic* transfer of heat from the system to the surroundings

 $2H_2(g) + O_2(g) \rightarrow 2H_2O(/) + energy$ 

- Endothermic the transfer of heat from the surroundings to the system
  - energy + 2HgO(s)  $\rightarrow$  2Hg(/) + O<sub>2</sub>(g)

#### Comparison of Endothermic and Exothermic Processes



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• Units of Energy

### -Joule (J) is the SI unit for energy.

 The amount of energy possessed by a 2 kg mass moving at a speed of 1 m/s

$$E_{k} = \frac{1}{2}mu^{2} = \frac{1}{2}(2 \text{ kg})(1 \text{ m/s})^{2} = 1 \text{ kg} \cdot \text{m}^{2}/\text{s}^{2} = 1 \text{ J}$$

$$1 \text{ J} = 1 \text{ N} \cdot \text{m} \qquad 1 \text{ N} = 1 \text{ kg} \cdot \text{m/s}^{2}$$

$$1 \text{ kJ} = 1000 \text{ J}$$

# – Calorie (cal) - commonly used on food labels

- $-1 \text{ cal} \equiv 4.184 \text{ J}$
- -1000 cal = 1 <u>Cal</u> = 1 kcal
- -Food calories (Cal) are really 1000 calories (cal).

Nutritio Serving Size Servings Per Container	n Fa	acts ut 24 biscuits (59g/2.1 oz.) About 12		
Amount Per Serving	Cereal	Cereal with 1/2 Cup Vitamins A&D Fat Free Milk		
Calories Calories from Eat	200	240		
ioaiones nom rat	0/ 0			
Total Fat 1g*	20	any value**		
Saturated Fat 0g	0°	% <b>0</b> %		
Monounsaturated Fat 0g				
Polyunsaturated Fat 0.5	ōg			
Trans Fat 0g				
Cholesterol Omg	0	% 0%		
Sodium 5mg	0	% 3%		
Potassium 200mg	6	% 12%		
	1			

Calculate the kinetic energy of a neon atom moving at a speed of 98 m/s.

$$E_{\rm k} = \frac{1}{2}mu^2$$



$$E_{\rm k} = \frac{1}{2} (3.352 \times 10^{-26} \rm kg) (98 m/s)^2$$

$$E_{\rm k} = 1.6 \times 10^{-22} {\rm J}$$

### 5.2 Introduction to Thermodynamics

- Types of systems:
  - open (exchange of mass and energy)
  - closed (exchange of energy)
  - isolated (no exchange)







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- State functions depend only on initial and final states of the system and not on how the change was carried out.
  - Energy (E)
  - Pressure (P)
  - Volume (V)
  - Temperature (T)



# First Law of Thermodynamics

- Energy can be converted from one form to another but cannot be created or destroyed.
  - Based on the law of conservation of energy
- Internal energy (U)
  - Kinetic energy molecular motion
  - Potential energy attractive/repulsive interactions

 The change in internal energy of a system between final (f) and initial (i) states is defined as:

 $\Delta U = \Delta U_{\rm f} - \Delta U_{\rm i}$ 

- For a chemical system
  - Cannot calculate the total internal energy with any certainty
  - Can calculate the change in energy of the system experimentally

$$\Delta U = \Delta U_{(\text{products})} - \Delta U_{(\text{reactants})}$$

- Consider:

#### $S(s) + O_2(g) \rightarrow SO_2(g)$

 $\Delta U = U(\text{product}) - U(\text{reactants})$ 

= energy content of 1 mol  $SO_2(g)$  – energy content of 1 mol S(s) and 1 mol  $O_2(g)$ 

– This reaction releases heat, therefore  $\Delta U$  is negative.

 When a system releases heat, some of the chemical energy is released as thermal energy to the surroundings but this does not change the total energy of the universe.

$$\Delta U_{\text{system}} + \Delta U_{\text{surroundings}} = 0$$

 When a system undergoes a change in energy, the surroundings must undergo a change in energy equal in magnitude and opposite in sign.

$$\Delta U_{\rm system} = -\Delta U_{\rm surroundings}$$

• Work and heat

$$\Delta U_{\rm sys} = q + w$$
  
where q is heat  
w is work

TABLE 5.1	Sign Conventions for Heat $(q)$ and Work $(w)$	
Process		Sign
Heat absorbed by the system (endothermic process)		q is positive
Heat released by the system (exothermic process)		q is negative
Work done on the system by the surroundings (for example, a volume decrease)		w is positive
Work done by the system on the surroundings (for example, a volume increase)		w is negative

#### Sign Conventions of *q* and *w*



Calculate the overall change in internal energy for a system that absorbs 125 J of heat and does 141 J of work on the surroundings.

> q is + (heat absorbed) w is - (work done)

$$\Delta U_{\rm sys} = q + w = (+125 \, \text{J}) + (-141 \, \text{J})$$
  
= -16 J

- Reactions carried out at constant volume
  - Pressure-volume work, *w*, done by a system is

$$w = -P\Delta V$$

- Constant volume,  $\Delta V = 0$  $\Delta U = q - P \Delta V$ 

$$q_v = \Delta U$$

#### Decomposition of NaN<sub>3</sub> at Constant Volume

$$2\text{NaN}_3(s) \longrightarrow 2\text{Na}(s) + 3\text{N}_2(g)$$



Reactions carried out at constant
 pressure

$$\Delta U = q + w$$
$$\Delta U = q_{\rho} - P\Delta V$$
$$q_{\rho} = \Delta U + P\Delta V$$

#### Decomposition of NaN<sub>3</sub> at Constant Pressure

$$2\text{NaN}_3(s) \longrightarrow 2\text{Na}(s) + 3\text{N}_2(g)$$



- Enthalpy and enthalpy changes
  - Enthalpy (*H*) is a state function defined as

$$H = U + PV$$

-At constant pressure

$$q_{\rho} = \Delta H$$

-Enthalpy of reaction

 $\Delta H = H(\text{products}) - H(\text{reactants})$ 

- $\Delta H$  is + for endothermic changes.
- $\Delta H$  is for exothermic changes.

- Thermochemical Equations
  - Equations that represent both mass and enthalpy changes

 $H_2O(s) \rightarrow H_2O(l)$   $\Delta H = + 6.01 \text{ kJ/mol}$ 

- This is an endothermic process. It requires 6.01 kJ to melt one mole of ice, H<sub>2</sub>O(s).
- The enthalpy value will change if the number of moles varies from the 1:1 reaction stoichiometry.

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

- This is an exothermic process. It releases 890.4 kJ when one mole of methane,  $CH_4$ , reacts.
- The enthalpy value will change if the number of moles varies from the 1:2:1:2 reaction stoichiometry.

#### Comparison of Endothermic and Exothermic Changes



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- Thermochemical equation guidelines
  - Always specify state of reactants and products.
  - -When multiplying an equation by a factor (n), multiply the  $\Delta H$  value by same factor.
  - -Reversing an equation changes the sign but not the magnitude of the  $\Delta H$ .

Given the following equation,

$$C_6H_{12}O_{6(s)}$$
 + 6 $O_{2(g)}$  → 6 $CO_{2(g)}$  + 6 $H_2O_{(l)}$   
 $\Delta H = -2803$  kJ/mol

calculate the energy released when 45.00 g of glucose is burned in oxygen.

$$45.00 \text{ g } \text{C}_{6}\text{H}_{12}\text{O}_{6} \times \frac{1 \text{ mol } \text{C}_{6}\text{H}_{12}\text{O}_{6}}{180.2 \text{ g } \text{C}_{6}\text{H}_{12}\text{O}_{6}} \times \frac{2803 \text{ kJ}}{1 \text{ mol } \text{C}_{6}\text{H}_{12}\text{O}_{6}} = 700.0 \text{ kJ}$$

# 5.4 Calorimetry

- Calorimetry is the measurement of heat changes
- Specific heat (s) the amount of heat required to raise the temp of 1 g of a substance by 1°C.
  - Units: J/g °C
  - Relation to amount of heat (q)

$$q = ms\Delta T$$

where q is heat, m is mass, s is specific heat and  $\Delta T$  = change in temp ( $\Delta T = T_{\text{final}} - T_{\text{initial}}$ )

TABLE 5.2	Specific Heat Values of Some Common Substances		
Substance	Specific Heat (J/g·°C)		
Al(s)	0.900		
Au(s)	0.129		
C (graphite)	0.720		
C (diamond)	0.502		
Cu(s)	0.385		
Fe(s)	0.444		
Hg(l)	0.139		
$H_2O(l)$	4.184		
$C_2H_5OH(l)$ (etha	nol) 2.46		

- Heat capacity (C) the amount of heat required to raise the temp of an object by 1°C.
  - Units: J/°C
  - Relation to amount of heat (q)

$$q = C\Delta T$$

where *q* is heat, *m* is mass, *C* is heat capacity and  $\Delta T$  = change in temp ( $\Delta T = T_{\text{final}} - T_{\text{initial}}$ ) Calculate the amount of energy required to heat 95.0 grams of water from 22.5°C to 95.5°C.

$$q = ms\Delta T$$

 $\Delta T = T_{\text{final}} - T_{\text{initial}} = 95.5 \text{ °C} - 22.5 \text{ °C}$  $\Delta T = 73.0 \text{ °C}$ 

 $q = (95.0 \text{ g}) (4.184 \text{ J/g}^{\circ}\text{C}) (73.0^{\circ}\text{C})$ 

 $q = 2.90 \times 10^4 \text{ J} \text{ or } 29.0 \text{ kJ}$ 

Constant-pressure calorimetry

$$q_{\rm sys} = -ms\Delta T$$

#### - System: reactants and products

$$q_{\rm sys} = -q_{\rm surr}$$

$$q_{\rm surr} = ms\Delta T$$

- Surroundings: water
- Used to measure
  - Specific heats
  - $\Delta H$  values



### **TABLE 5.3**Heats of Some Typical Reactions and Physical Processes Measured<br/>at Constant Pressure

Type of Reaction	Example	$\Delta H$ (kJ/mol)
Heat of neutralization	$HCl(aq) + NaOH(aq) \longrightarrow H_2O(l) + NaCl(aq)$	-56.2
Heat of ionization	$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$	+56.2
Heat of fusion	$H_2O(s) \longrightarrow H_2O(l)$	+6.01
Heat of vaporization	$H_2O(l) \longrightarrow H_2O(g)$	+44.0*

\*Measured at 25°C. At 100°C. the value is +40.79 kJ.

A metal pellet with a mass of 85.00 grams at an original temperature of 92.5°C is dropped into a calorimeter with 150.00 grams of water at an original temperature of 23.1°C. The final temperature of the water and the pellet is 26.8°C. Calculate the heat capacity and the specific heat for the metal.

 $q_{\text{water}} = ms \Delta T$ 

- = (150.00 g) (4.184 J/g°C) (3.7°C)
- = 2300 J (water gained energy)
- = -2300 J (pellet released energy)

Heat capacity of pellet:  $q = C \Delta T$ 

 $C = q/\Delta T$ = -2300 J/-65.7°C = 35 J/°C Specific heat of pellet: J/g°C

$$s = \frac{35 \text{ J/}^{\text{O}}\text{C}}{85.00 \text{ g}} = 0.41 \text{ J/g}^{\text{O}}\text{C}$$

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- Constant-volume calorimetry
  - Isolated system

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

$$q_{\rm sys} = -q_{\rm surr}$$

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

$$q_{\rm rxn} = -C_{\rm cal}\Delta T$$

– Measures  $\Delta U$ 



#### bomb calorimeter

- Typical procedure used in a bomb calorimeter
  - Known amount of sample placed in steel container and then filled with oxygen gas
  - Steel chamber submerged in known amount of water
  - Sample ignited electrically
  - Temperature increase of water is determined

A snack chip with a mass of 2.36 g was burned in a bomb calorimeter. The heat capacity of the calorimeter 38.57 kJ/°C. During the combustion the water temp rose by 2.70°C. Calculate the energy in kJ/g for the chip.

$$q_{rxn} = -C_{cal} \Delta T$$
  
= -(38.57 kJ/°C) (2.70°C)  
= - 104 kJ

### Energy content is a positive quantity. = 104 kJ/2.36 g = 44.1 kJ/g

### Food Calories: 10.5 Cal/g

### 5.5 Hess's Law

- Hess's Law: The change in enthalpy that occurs when reactants are converted to products is the same whether the reaction occurs in one step or a series of steps.
- Used for calculating enthalpy for a reaction that cannot be determined directly.

- In using stepwise reactions to determine an overall reaction
  - Remember the rules for manipulating equations.
  - -Add the  $\Delta H$  values for each step together after proper manipulation to obtain the overall enthalpy for the desired reaction.

Given the following equations:

$$\begin{array}{ll} \mathsf{H}_{3}\mathsf{BO}_{3}(aq) & \rightarrow \mathsf{HBO}_{2}(aq) & + \ \mathsf{H}_{2}\mathsf{O}(l) \\ \mathsf{H}_{2}\mathsf{B}_{4}\mathsf{O}_{7}(aq) & + \ \mathsf{H}_{2}\mathsf{O}(l) & \rightarrow 4 \ \mathsf{HBO}_{2}(aq) \\ \mathsf{H}_{2}\mathsf{B}_{4}\mathsf{O}_{7}(aq) & \rightarrow 2 \ \mathsf{B}_{2}\mathsf{O}_{3}(s) & + \ \mathsf{H}_{2}\mathsf{O}(l) \end{array}$$

 $\Delta H_{\rm rxn} = -0.02 \text{ kJ}$  $\Delta H_{\rm rxn} = -11.3 \text{ kJ}$  $\Delta H_{\rm rxn} = 17.5 \text{ kJ}$ 

Find the  $\Delta H$  for this overall reaction.

 $2H_3BO_3(aq) \rightarrow B_2O_3(s) + 3H_2O(l)$ 

$$2H_3BO_{3(aq)} \rightarrow 2HBO_{2(aq)} + 2H_2O_{(l)}$$
 x 2  
 $\Delta H_{rxn} = 2(-0.02 \text{ kJ}) = -0.04 \text{ kJ}$ 

2HBO<sub>2(aq)</sub> →1/2H<sub>2</sub>B<sub>4</sub>O<sub>7(aq)</sub> + 1/2H<sub>2</sub>O<sub>(/)</sub> reverse, ÷2  
$$\Delta H_{rxn}$$
 = +11.3 kJ/2 = 5.65 kJ

1/2H<sub>2</sub>B<sub>4</sub>O<sub>7(aq)</sub> → B<sub>2</sub>O<sub>3(s)</sub>+ 1/2H<sub>2</sub>O<sub>(/)</sub> ÷ 2  

$$\Delta H_{rxn} = 17.5 \text{ kJ/2} = 8.75 \text{ kJ}$$

$$2H_{3}BO_{3}(aq) \rightarrow B_{2}O_{3}(s) + 3H_{2}O(l)$$
$$\Delta H_{rxn} = 14.36 \text{ kJ}$$

# 5.6 Standard Enthalpies of Formation

- Standard enthalpy of formation
  - Symbol:  $\Delta H_{\rm f}^{\circ}$
  - The enthalpy change that results when 1 mole of a compound is formed from its elements in their standard states.
    - △H<sub>f</sub>° for an element in its standard state is defined as zero.
  - Standard state: 1 atm, 25°C
  - Values found in reference tables
  - Used to calculate the  $\Delta H^{\circ}_{rxn}$

Defining equation for enthalpy of reaction:

$$\Delta H^{\circ}_{rxn} = \Sigma n \Delta H^{\circ}_{f} (products) - \Sigma m \Delta H^{\circ}_{f} (reactants)$$

where  $\Sigma$  denotes summation *n* and *m* are the coefficients in the balanced equation Calculate the  $\Delta H^{\circ}_{rxn}$  for the following reaction from the table of standard values.

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

 $\Delta H_{\rm rxn}^{\circ} = \Sigma n \Delta H_{\rm f}^{\circ}_{\rm (products)} - \Sigma m \Delta H_{\rm f}^{\circ}_{\rm (reactants)}$ 

= [1(-393.5) + 2(-285.8)] - [1(-74.8) + 2(0)]

= -890.3 kJ/mol (exothermic)

# Key Points

- Energy and energy types
- Law of conservation of energy
- Energy associated with reactions
- System and surroundings
- Exothermic and endothermic
- Thermochemistry
- Systems open, closed, isolated

# Key Points

- First law of thermodynamics
- Enthalpy (heat of formation; heat of reaction)
- State function
- Calorimetry
- Specific heat
- Hess's law
- Calculations involving enthalpy, specific heat, energy