

*Chapter 5*  
*Thermochemistry*

- Energy in reactions helps to explain why reactions occur.

*5.1 The Nature of Energy*

- Why do chemical reactions occur?
- What is energy?
- Energy is the capacity to do work or transfer heat.
- Forms of Energy - kinetic (motion) & potential (position)

*Units of Energy*

- Units of Energy  
cal, J, Cal (= kcal)
- 1 cal = 4.184 J
- 1 Cal = 1 kcal  
= 1000 cal  
= 4184 J = 4.184 kJ

*System and Surroundings*

- System is the part of the universe we are interested in studying
- Surroundings is the rest of the universe
- Identify the system and surroundings in this diagram.

*5.2 First Law of Thermodynamics*

- Law of Conservation of Energy  
Energy cannot be created or destroyed, but only converted to other forms.  
 $\Delta E = q + w$  (more later)
- Heat (q) = energy transferred because of a difference in temperature
- Work (w) = force applied to an object over a distance

*Internal Energy*

- Internal energy (E) is the sum of all the kinetic and potential energy of all parts of the system
- In what ways can energy be stored when considering matter at an atomic or molecular level?  
bonds, vibrations, rotations, molecular motion, electron motion, motion of nuclei (protons and neutrons)
- It is not possible to measure the internal energy of any system of practical interest.
- We can measure changes in internal energy:  
 $\Delta E = E_{\text{final}} - E_{\text{initial}}$
- $\Delta E > 0$  if  $E_{\text{final}} > E_{\text{initial}}$
- $\Delta E < 0$  if  $E_{\text{final}} < E_{\text{initial}}$

*Heat and Work*

- $\Delta E = q + w$
- Heat flowing from the surroundings to the system is positive (the system feels cold because it absorbs heat from your hand)
- Work done by the surroundings on the system is positive

*Heat and Temperature*

- $q < 0$  exothermic, surroundings get hot
- $q > 0$  endothermic, surroundings get cold

*State Functions*

- Value does not depend on history of the system, just its present condition
- Does the distance between Phoenix and Flagstaff depend on the route?
- Examples of state functions?
- Does the distance between San Francisco and Denver depend on how one travels from one city to another?
- $\Delta E$  is a state function
- $q$  and  $w$  are not state functions
- $\Delta E = q + w$ : If a system generates more heat, it will accomplish less work.
- State functions are given an upper case symbol

*5.3 Enthalpy*

- At constant pressure, we have  $q_p = \Delta H$ , which we call an enthalpy change, which is a state function.
- $\Delta E = \Delta H - P \Delta V$  for pressure-volume work
- $\Delta H = H_f - H_i$
- $\Delta H < 0$  exothermic
- $\Delta H > 0$  endothermic

*5.4 Enthalpies of Reaction*

- $\Delta H = H_{\text{products}} - H_{\text{reactants}}$
- $\Delta H$  is the enthalpy of reaction or heat of reaction
- $\text{H}_2(\text{g}) + \text{I}_2(\text{s}) + 53.00 \text{ kJ} \rightarrow 2\text{HI}(\text{g})$
- Thermochemical equation:  

$$\text{H}_2(\text{g}) + \text{I}_2(\text{s}) \rightarrow 2\text{HI}(\text{g}) \quad \Delta H = 53.00 \text{ kJ}$$
- $\Delta H$  is proportional to the number of moles
- What is  $\Delta H$  for this reaction if 127 g of  $\text{I}_2(\text{s})$  reacts with excess  $\text{H}_2$ ?
- Proportional to the amount of reactant consumed
- For a reaction in the reverse direction is numerically equal but opposite in sign
- Depends on the physical state of the reactants and products
  - Value changes sign with direction
  - Values depend on physical state
- Values are for the standard state: stable physical state, 1 atm, usually 25°C

### 5.5 Calorimetry

- The value of  $\Delta H$  can be determined by measuring the heat flow accompanying a reaction at constant pressure
- Apparatus to do this is called a calorimeter

#### *Heat Capacity/Specific Heat*

- Heat capacity = amount of heat that can be absorbed by a sample of material for a given temperature increase; units =  $J/^\circ C$
- Molar heat capacity = amount of heat that can be absorbed by 1 mole of material when its temperature increases by  $1^\circ C$ ; units =  $J/mol\ ^\circ C$
- Specific Heat Capacity or Specific Heat = amount of heat that can be absorbed by 1 gram of material when its temperature increases by  $1^\circ C$ ; units =  $J/g\ ^\circ C$
- Which holds more heat when exposed to  $120^\circ F$  sunlight -- a wood or an iron bench (both at the same temperature)?
- Which has the higher heat capacity?
- Which holds more heat - pie filling or pie crust?

#### *Calorimetric Measurements*

- $\Delta T = T_f - T_i$
- $q = n C_m \Delta T$
- $q = m \text{ sp.ht. } \Delta T$
- Conservation of energy:  
heat gained + heat lost = 0
- 150.0 g Zn at  $79.5^\circ C$  added to 250.0 g  $H_2O$  at  $25.0^\circ C$ . What is the final temperature of the mixture?
- Specific heats: Zn 0.377,  $H_2O$  4.184  $J/g\ ^\circ C$

#### *Enthalpy Change and Changes of Physical State*

- If temperature changes involve changes of physical state as well, we must also calculate how much heat is involved in the change of state.
- Various processes to change physical state are reversible; the amount of heat required to go one direction must be recovered going the opposite direction
- $\Delta H = \Sigma \Delta H$  for phase changes +  $\Sigma n C_m \Delta T$

### 5.6 Hess's Law

- Does the energy change in a reaction depend on the number of steps in the reaction?
- $H_2(g) + I_2(s) \rightarrow 2HI(g) \quad \Delta H = 53.00 \text{ kJ}$   
 $I_2(s) \rightarrow I_2(g) \quad \Delta H = 62.44 \text{ kJ}$   
 $H_2(g) + I_2(g) \rightarrow 2HI(g) \quad \Delta H = -9.44 \text{ kJ}$
- How are these reactions related?
- Hess's Law:  $\Delta H_{\text{sum of steps}} = \Sigma \Delta H_{\text{steps}}$   
 Enthalpy change independent of path

*Application of Hess's Law*

- How can we use known values of  $\Delta H^\circ$  to calculate unknown values for other reactions?
- $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} \quad \Delta H^\circ = -393.5 \text{ kJ}$   
 $2\text{C(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{CO(g)} \quad \Delta H^\circ = -221.0 \text{ kJ}$
- What is  $\Delta H^\circ$  for the following reaction?  
 $2\text{CO(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)} \quad \Delta H^\circ = ?$
- What is  $\Delta H^\circ$  for the following reaction?  
 $\text{C(s)} + \text{CO}_2\text{(g)} \rightarrow 2\text{CO(g)} \quad \Delta H^\circ = ?$

*5.7 Enthalpies of Formation*

- $\Delta H^\circ_f = \Delta H^\circ$  for formation of 1 mole of a substance from the stable form of its elements at 1 atm and 25°C
- Generally given only for the standard state
- $\Delta H^\circ_f = 0$  for a stable element
- Which of these have  $\Delta H^\circ_f = 0$  ?
  - CO, Cu, Br<sub>2</sub>, Cl, O<sub>2</sub>, O<sub>3</sub>, O<sub>2</sub>(s), P<sub>4</sub>

*Heats of Formation**An application of Hess's Law*

- Heats of formation involve decomposition of reactants into elements, then formation of products from the elements
- $\Delta H^\circ_{\text{rxn}} = \sum \Delta H^\circ_{\text{f,products}} - \sum \Delta H^\circ_{\text{f,reactants}}$
- Calculate values of  $\Delta H^\circ$  for the following reactions:
- $\text{H}_2\text{(g)} + \text{I}_2\text{(s)} \rightarrow 2\text{HI(g)}$
- $\text{CS}_2\text{(g)} + 3\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + 2\text{SO}_2\text{(g)}$

 $\Delta H^\circ_f$ :

HI	CS <sub>2</sub>	CO <sub>2</sub>	SO <sub>2</sub>
26.5	117.4	-393.51	-296.83