

## Chapter 9

### Energy, Enthalpy, and Thermochemistry

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### The Nature of Energy

- **Energy** is the capacity to do work or produce heat.
- The **law of conservation of energy** states that energy can be converted from one form to another but can neither be created nor destroyed.
- Energy can be classified as either potential energy or kinetic energy.
- **Potential Energy** is energy due to position or composition.
- Example: Water behind a dam has potential energy that can be converted to work when the water flows down through turbines, thereby creating electricity. Attractive and repulsive forces also lead to potential energy. The energy released when gasoline is burned results from differences in the attractive forces between nuclei and electrons in the reactants and products.

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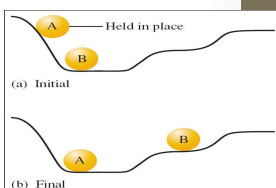
### The Nature of Energy

- **Kinetic Energy** of an object is due to the motion of the object and depends on the mass of the object (m) and its velocity (v):

$$KE = 1/2mv^2$$

- Energy can be converted from one form to another easily.

- Ball A, because of its higher position, initially has more potential energy than Ball B. When A is released, it moves down the hill and strikes B.




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### The Nature of Energy

- The potential energy of A has decreased: since energy is conserved, all the energy lost by A must be accounted for. How is this energy distributed?
- Initially, the potential energy of A is changed to kinetic energy as the ball rolls down the hill. Part of this kinetic energy has been transferred to B, causing it to be raised to a higher final position. Thus the potential energy of B has increased.
- However, since the final position of B is lower than the original position of A, some of the energy is still unaccounted for.

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### The Nature of Energy

- As A rolls down the hill, some of its kinetic energy is transferred to the surface of the hill as heat. This transfer of energy is called **frictional heating**. The temperature of the hill increases very slightly as the ball rolls down.
- Heat and temperature are decidedly different.
- **Temperature** is a property that reflects the random motions of the particles in a particular substance.
- **Heat** involves the transfer of energy between two objects due to a temperature difference.
- Ball B gains potential energy because ball A has done work on B.
- **Work** is defined as a force acting over a distance.

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### The Nature of Energy

- Thus energy can be transferred through **work** and through **heat**.
- Ball A always loses the same amount of potential energy. However, the way that this energy transfer is divided between work and heat depends on the specific conditions: **the pathway**.
- For example, the surface of the hill might be so rough that the energy of A is expended completely through frictional heating. A is moving so slowly when it hits B that it cannot move B to the next level.
- Regardless of the condition of the hill's surface, the total energy transferred will be constant.

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## The Nature of Energy

- A **state function** or state property refers to a property of the system that depends only on its present state.
- The value of a state function does not depend on how the system arrived at the present state, it depends only on the characteristics of the present state.
- **Energy is a state function, work and heat are not.**

7

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## Chemical Energy

- The combustion of methane:  

$$\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) + \text{energy (heat)}$$
- **System:** we define the system as the reactants and products of the reaction.
- **Surroundings:** consist of the reaction container, the room, and everything else.
- When a reaction results in the evolution of heat, it is said to be **exothermic, heat flows out of the system.**
- Reactions that absorb energy from the surroundings are said to be **endothermic, heat flows into a system.**
- Example: endothermic physical process  

$$\text{H}_2\text{O}(\text{l}) + \text{energy} \longrightarrow \text{H}_2\text{O}(\text{g})$$

8

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## Chemical Energy

- Where does the energy, released as heat, come from in an exothermic reaction? The answer lies in the difference in potential energy between the products and reactants.
- **The energy gained by the surroundings must be equal to the energy lost by the system.**
- In any exothermic reaction, the potential energy stored in the chemical bonds is being converted to thermal energy (random kinetic energy) *via* heat.
- $\Delta$  PE represents the *change* in potential energy stored in the bonds of the products as compared with the bonds of the reactants.

9

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## Chemical Energy

- The change in potential energy represents the difference between the energy required to break the bonds in the reactants and the energy released when the bonds in the products are formed.
- In an exothermic process the bonds in the products are stronger (on average) than those of the reactants.
- For an endothermic reaction, the situation is reversed.
- Energy that flows into the system as heat is used to increase the potential energy of the system. In this case, the products have higher potential energy (weaker bonds on average) than the reactants.

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## Chemical Energy

- **Thermodynamics** is the study of energy and its inter-conversions. The law of conservation of energy is often called the **first law of thermodynamics: The energy of the universe is constant.**
  - The **internal energy (E)** of a system can be defined most precisely as the sum of the kinetic and potential energies of all the particles in the system.
- $$E = q + w$$
- E represents the change in the system's internal energy, q represents heat, and w represents work.
    - When heat is absorbed,  $q = +x$
    - When heat is released,  $q = -x$

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11

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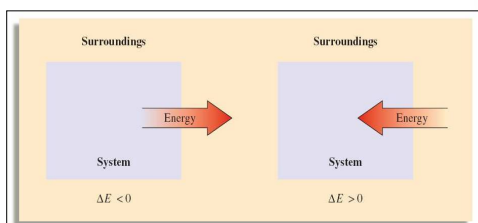
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$$E = q + w$$

- If the system does work on the surroundings (energy flows out of the system), **w is negative.** If the surroundings do work on the system (energy flows into the system), **w is positive.**



Energy Flowing into and out of a System

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12

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$$E = q + w$$

- $\Delta V$  = final volume – initial volume
- The gas (the system) is expanding. Thus the system is doing work on the surroundings.
- For an expanding gas  $\Delta V$  is positive, because volume is increasing. Thus  $\Delta V$  and  $w$  must have opposite signs, which leads to the equation:  $w = -P\Delta V$
- $w$  and  $P\Delta V$  have opposite signs since when the gas expands ( $\Delta V$  is positive), work flows into the surroundings ( $w$  is negative).
- External pressure  $P$ ,  $w$  is negative, since work flows out of the system. When a gas is compressed,  $\Delta V$  is negative (the volume decreases), which makes  $w$  a positive quantity (work flows into the system).

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13

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### Example

- A balloon is inflated, the volume changes from  $4.00 \times 10^6 \text{ L}$  to  $4.50 \times 10^6 \text{ L}$  by addition of  $1.3 \times 10^8 \text{ J}$  of energy as heat. Assume constant  $P$  of  $1.0 \text{ atm}$ . Calculate  $\Delta E$ .

$$E = q + w$$

$$1.3 \times 10^8 \text{ J of energy is added as heat, } q = 1.3 \times 10^8 \text{ J}$$

$$w = -P\Delta V \quad \text{and} \quad \Delta V = V_{\text{final}} - V_{\text{initial}}$$

$$w = -1.0 \text{ atm} \times 5.0 \times 10^5 \text{ L} = -5.0 \times 10^5 \text{ L atm}$$

*Negative sign for  $w$  makes sense, since the gas is expanding.*

To calculate  $E$ , we must add  $q$  and  $w$ .  $q$  is given in units of J and  $w$  is given in units of L atm.

$$w = -5.0 \times 10^5 \text{ L atm} \times 101.3 \text{ J} = -5.1 \times 10^7 \text{ J}$$

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14

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### Example

- $\Delta E = q + w = (+1.3 \times 10^8 \text{ J}) + (-5.1 \times 10^7 \text{ J}) = 8 \times 10^7 \text{ J}$
- Since more energy is added through heating than the gas expands doing work, hence  $\Delta E$  is positive.
- The conversion factor between L atm and J can be obtained from the values of  $R$ :
  - $0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$  and  $8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$
  - $1 \text{ L atm} = 101.3 \text{ J}$

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15

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## Enthalpy (H)

- **Enthalpy  $H = E + PV$**  where E is the internal energy of the system, P is the pressure of the system, and V is the volume of the system.
- A change in enthalpy does not depend on the pathway between two states - enthalpy is a state function.

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

- At constant pressure (where only PV work is allowed) the change in enthalpy ( $\Delta H$ ) of the system is equal to the energy flow of heat.
- Heat of reaction and change in enthalpy are used interchangeably.

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

- $\Delta H$  will be positive if the reaction is endothermic at constant P and negative if the reaction is exothermic.

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16

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## Thermodynamics of Ideal Gases

- The thermodynamic characteristics of the ideal gas - the hypothetical condition approached by real gases at high temperatures and low pressures such that they obey the relationship  $PV = nRT$ .

- For an ideal gas:  **$KE_{\text{avg}} = 3/2RT$**

- Where  $KE_{\text{avg}}$  represents the average, random, translational energy for 1 mole of gas at a given temperature T (in Kelvins).

- **The energy (heat) required to change the energy of 1 mole of an ideal gas by  $\Delta T$  is:  $3/2R\Delta T$ .**

- Note that for a temperature change of 1 K ( $\Delta T=1$ ), the energy required is  $3/2R$ .

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17

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## Thermodynamics of Ideal Gases

- The **molar heat capacity** of a substance is defined as the energy required to raise the temperature of 1 mole of that substance by 1K. We might conclude that the molar heat capacity of an ideal gas is  $3/2R$ .

### Heating an Ideal Gas at Constant Volume

- There can be no PV work  $\Delta V = 0$
- $C_v$  - molar heat capacity of an ideal gas at constant volume is  $3/2R$ .
- $C_v = 3/2R$  = heat required to change the temperature of 1 mol of gas by 1 K at constant volume.

### Heating an Ideal Gas at Constant Pressure

- Heat required to increase the T of 1 mol of gas by 1 K at constant P =  $3/2R + R = 5/2R = C_v + R = C_p$
- $C_p$  the molar heat capacity of an ideal gas at constant P is  $5/2R$  or  $C_v + R$

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18

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## Heating a Polyatomic Gas

- Monoatomic real gases, such as helium, have measured values of  $C_v$  very close to  $3/2R$ .
- However, gases such as  $\text{SO}_2$  and  $\text{CHCl}_3$  that contain polyatomic molecules have observed values for  $C_v$  that are significantly greater than  $3/2R$ .
- For example, the value of  $C_v$  for  $\text{SO}_2$  is almost  $4R$  at  $25^\circ\text{C}$ .
- This larger value for  $C_v$  results because polyatomic molecules absorb energy to excite rotational and vibrational motions in addition to translational motions. That is, at  $25^\circ\text{C}$ , the molecules in such a gas are rotating, and the atoms in the molecule are vibrating, as if the bonds were springs.

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19

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## Heating a Polyatomic Gas

- As a polyatomic gas is heated, the gas molecules absorb energy to increase their rotational and vibrational motions as well as to move through space (translate) at higher speeds.
- $C_v$  is greater than  $3/2R$  for a gas in which the individual particles are molecules because some of the energy added *via* heat flow is stored in motions that do not directly raise the  $T$  of the gas. This effect is not related to whether or not the gas is behaving ideally.
- Monoatomic gases have  $C_v$  values equal to  $3/2R$  ( $12.47 \text{ J K}^{-1} \text{ mol}^{-1}$ ).
- Note that as the molecules become more complex (more atoms),  $C_v$  increases. This result is expected because the presence of more atoms means that more non-translational motions are available to absorb energy. Finally, notice that in all cases  $C_p - C_v = R$ .

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## Heating a Gas: Energy and Enthalpy

- Average translational energy of an ideal gas  $E$  is:

$$E = 3/2 RT \text{ (per mole)}$$

$$\Delta E = 3/2 R \Delta T$$

TABLE 9.1

Molar Heat Capacities of Various Gases at 298 K

Gas	$C_v \left( \frac{\text{J}}{\text{K mol}} \right)$	$C_p \left( \frac{\text{J}}{\text{K mol}} \right)$	$C_p - C_v$
He, Ne, Ar	12.47	20.80	8.33
$\text{H}_2$	20.54	28.86	8.32
$\text{N}_2$	20.71	29.03	8.32
$\text{N}_2\text{O}$	30.38	38.70	8.32
$\text{CO}_2$	28.95	37.27	8.32
$\text{C}_2\text{H}_6$	44.60	52.92	8.32

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21

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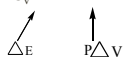
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## Energy and Enthalpy

- $\Delta E = C_v \Delta T$  (per mole)
- $\Delta E = nC_v \Delta T$  (n moles)
- Heat required =  $q_p = nC_p \Delta T = n(C_v + R) \Delta T = nC_v \Delta T + nR \Delta T$



- Consider the change in enthalpy:

$$H = E + PV \text{ so that } \Delta H = \Delta E + \Delta(PV)$$

$$\Delta H = \Delta E + \Delta(nRT) = \Delta E + nR\Delta T$$

$$\Delta H = nC_v \Delta T + nR\Delta T$$

$$= n(C_v + R) \Delta T = nC_p \Delta T$$

$$\Delta H = nC_p \Delta T$$

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22

## Energy and Enthalpy

- The only way to change H and E for an ideal gas is to change the temperature of the gas. Thus, for any process involving an ideal gas at constant temperature,  $\Delta H = 0$  and  $\Delta E = 0$ .
- Thus both the energy E and the enthalpy H of an ideal gas depend only on T, not on P or V.
- **E ∝ T    H ∝ T**
- In the calculation of heat flow for an ideal gas: **q = nCΔT**
- **ΔH = nC<sub>p</sub>ΔT** and **E = nC<sub>v</sub>ΔT** for a temperature change of an ideal gas regardless of whether pressure or volume (or neither) is constant.
- At constant V: Heat flow = **q<sub>v</sub> = ΔE**
- At constant P: Heat flow = **q<sub>p</sub> = ΔH**

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23

## Thermodynamics of Ideal Gases

TABLE 9.2

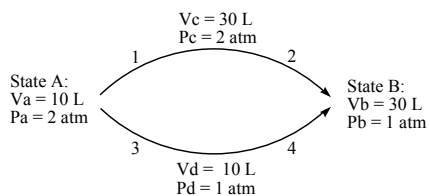
Thermodynamic Properties of an Ideal Gas

Expression	Application
$C_v = \frac{3}{2}R$	Monatomic ideal gas
$C_v > \frac{3}{2}R$	Polyatomic ideal gas (value must be measured experimentally)
$C_p = C_v + R$	All ideal gases
$C_p = \frac{5}{2}R = \frac{3}{2}R + R$	Monatomic ideal gas
$C_p > \frac{5}{2}R$	Polyatomic ideal gas (specific value depends on the value of $C_v$ )
$\Delta E = nC_v \Delta T$	All ideal gases
$\Delta H = nC_p \Delta T$	All ideal gases



### Example 9.2

Consider 2 mol of a monoatomic ideal gas



Pathway 1: steps 1 and 2  
Pathway 2: steps 3 and 4

Calculate  $q$ ,  $w$ ,  $\Delta E$ ,  $\Delta H$  for each pathway

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### Example 9.2

Pathway 1:

Step 1:  $P\Delta V = nR\Delta T$

$$P\Delta V = (2 \text{ atm})(20 \text{ L}) = 40 \text{ L}\cdot\text{atm}$$

$$P\Delta V = 40 \text{ L}\cdot\text{atm} \times 101.3 = 4.05 \times 10^3 \text{ J}$$

$$\Delta T = P\Delta V/nR = 4.05 \times 10^3 \text{ J}/nR$$

$$w_1 = -P\Delta V = -4.05 \times 10^3 \text{ J}$$

$$q_1 = q_p = \Delta H_1 = nC_p\Delta T = n(5R/2)(4.05 \times 10^3 \text{ J}/nR) = 1.01 \times 10^4 \text{ J}$$

$$\Delta E_1 = nC_v\Delta T = n(3R/2)(4.05 \times 10^3 \text{ J}/nR) = 6.08 \times 10^3 \text{ J}$$

26

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### Example 9.2

Pathway 1:

Step 2:  $\Delta P V = nR\Delta T$

$$\Delta T = \Delta P V/nR = -30 \text{ L}\cdot\text{atm}/nR = -3.04 \times 10^3 \text{ J}/nR$$

$$w_2 = 0$$

$$q_2 = q_v = \Delta E_2 = nC_v\Delta T = n(3R/2)(-3.04 \times 10^3 \text{ J}/nR) = -4.56 \times 10^3 \text{ J}$$

$$\Delta H_2 = nC_p\Delta T = n(5R/2)(-3.04 \times 10^3 \text{ J}/nR) = -7.6 \times 10^3 \text{ J}$$

Pathway 1:

$$q_{\text{one}} = q_1 + q_2 = 5.5 \times 10^3 \text{ J}$$

$$w_{\text{one}} = w_1 + w_2 = -4.05 \times 10^3 \text{ J}$$

$$\Delta E_{\text{one}} = q_{\text{one}} + w_{\text{one}} = 1.5 \times 10^3 \text{ J}$$

$$\Delta H_{\text{one}} = \Delta H_1 + \Delta H_2 = 2.5 \times 10^3 \text{ J}$$

27

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### Exercise 9.2: Result Summary

- Work and heat are different for the two pathways between states A and B.
- Heat and work are both pathway-dependent
- Note that the sum of  $q$  and  $w$  is the same for both pathways:  
 **$\Delta E = q + w$  and that  $E$  is a state function.**
- Note also that the overall  $\Delta H$  value for pathway one equals that for pathway two because enthalpy is also a state function.

28

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### Calorimetry

- We can determine the heat associated with a chemical reaction experimentally by using a device called a **calorimeter**.
- **Calorimetry** - the science of measuring heat - is based on observing the temperature change when a body absorbs or discharges energy as heat.
- The heat capacity ( $C$ ) of a substance is:
 
$$C = \frac{\text{heat absorbed}}{\text{increase in temperature}}$$
- **Specific heat capacity:** the energy required to raise the temperature of 1g of a substance by 1°C (Units:  $\text{J K}^{-1}\text{g}^{-1}$  or  $\text{J}^\circ\text{C}^{-1}\text{g}^{-1}$ ).
- **Molar heat capacity:** the energy required to raise the temperature of 1 mol of a substance by 1°C (Units:  $\text{J K}^{-1}\text{mol}^{-1}$  or  $\text{J}^\circ\text{C}^{-1}\text{mol}^{-1}$ ).

29

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### Solution Calorimetry Constant-Pressure Calorimetry

- Since the pressure remains constant during the process, constant pressure calorimetry is used in determining the changes in enthalpy occurring in solution.
- Assume  $V$  is constant when two liquids are mixed.
- $w = 0$  ;  $q = \Delta H$  ;  $q = \Delta E$  so that  $\Delta E = \Delta H$
- 1.  $q = \Delta E = \Delta H = mc\Delta T$                        $m = dxV$
- 2.  $q = nc\Delta T$
- **Specific heat capacity:**  $\text{J/g} \cdot \text{K}$  or  $\text{J/g} \cdot ^\circ\text{C}$
- **Molar heat capacity:**  $\text{J/mol} \cdot \text{K}$  or  $\text{J/mol} \cdot ^\circ\text{C}$

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## Constant-Pressure Calorimetry

- Example: Find  $q$  or  $\Delta H$  /  $n$  moles of X  
Find  $q$  or  $\Delta H$  / 1 mole of X

- **Exothermic:**  $q = \Delta H = -ve$
- **Endothermic:**  $q = \Delta H = +ve$

- If temperature increases  $\Delta T = +ve$   $q = +ve$   
➤ If temperature decreases  $\Delta T = -ve$   $q = -ve$

➤ At constant Pressure:

- For exothermic reactions:  $|\Delta H| = q$  but  $\Delta H = -ve$   
➤ For endothermic reactions:  $|\Delta H| = q$  but  $\Delta H = +ve$

31

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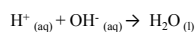
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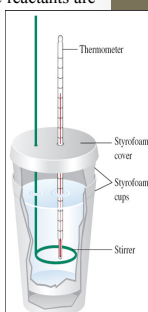
## Exercise

- Suppose we mix 50.0 mL of 1.0 M HCl at 25.0°C with 50.0 mL of 1.0 M NaOH also at 25.0°C in a calorimeter. After the reactants are mixed, the T is observed to increase to 31.9°C.



- The temperature of the mixed solution is observed to increase. Thus the chemical reaction must be releasing energy as heat. This increases the random motions of the solution components, which in turn increases the temperature.

- For an approximate result we will assume that the calorimeter does not absorb or leak any heat and that the solution can be treated as if it were pure water with a density of 1.0 g/mL.




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## Exercise

- Specific heat capacity of water is 4.18 J°C<sup>-1</sup>g<sup>-1</sup>. This means 4.18 J of energy is required to raise the temperature of 1g water by 1°C.

➤ Calculate the heat (change in enthalpy):

- **Energy released by reaction = energy absorbed by the solution = specific heat capacity x mass of solution x increase in temperature.**

- Increase in temperature =  $\Delta T = 31.9^\circ\text{C} - 25.0^\circ\text{C} = 6.9^\circ\text{C}$   
mass of solution = 100.0 mL x 1.0 g/mL = 1.0 x 10<sup>2</sup>g.

$$\text{Energy released} = (4.18 \text{ J}^\circ\text{C}^{-1} \text{ g}^{-1})(1.0 \times 10^2 \text{ g})(6.9^\circ\text{C}) = 2.9 \times 10^3 \text{ J}$$

- The number of moles of H<sup>+</sup> ions consumed in the preceding experiment is:  $\frac{50.0 \text{ mL}}{1000 \text{ mL/L}} \times \frac{1.0 \text{ mol H}^+}{\text{L}} = 5.0 \times 10^{-2} \text{ mol H}^+$

33

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### Exercise

➤ Thus  $2.9 \times 10^3 \text{ J}$  of heat was released when  $5.0 \times 10^{-2} \text{ mol}$  of  $\text{H}^+$  ions reacted.

$$\frac{2.9 \times 10^3 \text{ J}}{5.0 \times 10^{-2} \text{ mol H}^+} = 5.8 \times 10^4 \text{ J}$$

is the heat released per mol of  $\text{H}^+$  ions  
neutralized

➤ Since heat is evolved,  $\Delta H = -58 \text{ kJ/mol}$  (exothermic reaction).

➤ **EX 9.3 H.W.**

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### Calorimetry for Gas Reactions

➤ In the examples of constant-pressure calorimetry we have considered so far, the reactions have occurred in solution, where no appreciable volume changes occur.

➤ The total volume of the reactant solution is the sum of the volumes of the solutions that are mixed and remains constant as the reaction proceeds).

➤ No work occurs since  $\Delta V = 0$ ,  $P\Delta V = 0$ , and  $w = 0$ .

➤  $\Delta E = q_p + w = \Delta H + 0$

➤ So  $\Delta E = \Delta H$

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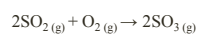
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### Calorimetry for Gas Reactions



➤  $P = \text{ct}$ ;  $T = \text{ct}$ ;  $V \neq \text{ct}$  (since gases)

➤  $w \neq 0$  and  $\Delta E \neq \Delta H$

➤  $\Delta E = \Delta H + w$  and  $\Delta H = q_p$

➤  $PV = nRT$   $V$  and  $n$  not constant

$$P\Delta V = \Delta nRT$$

➤  $E = q + w$

➤  $q_p = H$

➤  $w = -P\Delta V = -\Delta nRT$

➤  $\Delta n = \text{moles of product} - \text{moles of reactant}$

$R = 8.3145 \text{ J/mol}\cdot\text{K}$   $T = \text{Temperature in K}$

36

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### Example 9.4

- When 2.00 mol of  $\text{SO}_2(\text{g})$  reacts completely with 1.00 mol of  $\text{O}_2(\text{g})$  to form 2.00 mol of  $\text{SO}_3(\text{g})$  at  $25^\circ\text{C}$  and a constant pressure of 1.00 atm, 198 kJ of energy is released as heat. Calculate  $\Delta H$  and  $\Delta E$  for this process.

**Solution:**

P is constant,  $\Delta H = q_p = -198\text{kJ}$ , energy flows out of the system.

$$\Delta E = q + w$$

$$q = -198 \text{ kJ, and } w = -P \Delta V$$

$$\Delta V = \frac{\Delta n (RT)}{P}$$

T and P are constant

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37

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### Example 9.4

- $\Delta n = n_{\text{final}} - n_{\text{initial}} = 2\text{mol} - 3\text{mol} = -1 \text{ mol}$
- $w = -P \Delta V = -P (\Delta n \times RT/P) = -\Delta n(RT)$
- $\Delta n = -1 \text{ mol}$ ;  $R = 8.3145 \text{ J/K} \cdot \text{mol}^{-1}$ ;  $T = 25^\circ\text{C} + 273 = 298 \text{ K}$
- $w = -(-1\text{mol})(8.3145\text{J})(298\text{K}) = 2.48 \text{ kJ}$   
K mol
- $\Delta E = q + w = \Delta H + w = -198 \text{ kJ} + 2.48 \text{ kJ} = -196 \text{ kJ}$
- Note that  $\Delta E$  and  $\Delta H$  are different because the volume changes.

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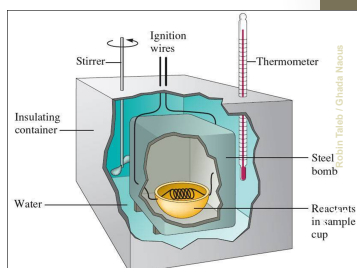
### Bomb Calorimeter

- Measures  $\Delta E$  not  $\Delta H$ ;  $V = \text{ct}$ ;  $w = 0$
- $\Delta E = q$
- $q = \Delta E = C\Delta T / \text{mg substance}$

- Find  $q / n$  moles of substance

- Find  $q / 1$  mole of substance

- Exothermic:  $q = -\text{ve}$
- Endothermic:  $q = +\text{ve}$



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## Bomb Calorimeter

- Calorimetry experiments can also be performed at constant volume.
- A **bomb calorimeter** is used to study energy changes in reactions under conditions of constant volume
- For a constant volume process  $\Delta V = 0$ , so  $w = 0$ .

$$\Delta E = q + w = q = q_v$$

- A 0.5269 g sample of octane is placed in a bomb calorimeter with a heat capacity of 11.3 kJ/°C. The octane is ignited in the presence of excess oxygen, causing the temperature of the calorimeter to increase by 2.25°C.

- Energy released by the reaction = temperature increase x energy required to change the temperature by 1°C

$$\text{Energy released} = \Delta T \times \text{heat capacity of calorimeter.}$$

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- This means that 25.4 kJ of energy was released by the combustion of 0.5269 g of octane.

- $0.5269 \text{ g octane} \times \frac{1 \text{ mol octane}}{114.2 \text{ g octane}} = 4.614 \times 10^{-3} \text{ mol octane.}$

$$\frac{25.4 \text{ kJ}}{4.614 \times 10^{-3} \text{ mol}} = 5.50 \times 10^3 \text{ kJ/mol}$$

- Reaction is exothermic,  $\Delta E$  is negative

$$\Delta E_{\text{combustion}} = -5.50 \times 10^3 \text{ kJ/mol}$$

- Note since  $w = 0$  here,  $\Delta E$  is equal to the heat:

$$\Delta E = q + w = q = -5.50 \times 10^3 \text{ kJ/mol}$$

- **Ex 9.5 H.W.**

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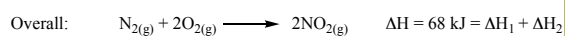
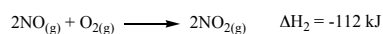
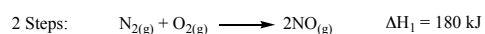
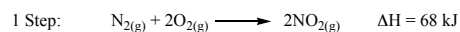
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## Hess's Law



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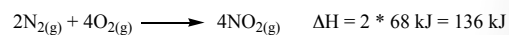
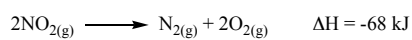
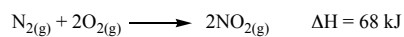
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### Hess's Law



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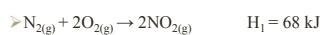
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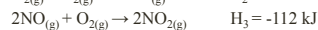
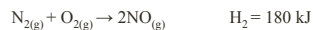
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### Hess's Law

➤ **Hess's Law:** Since enthalpy is a state function, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.



➤ This reaction can also be carried out in two distinct steps



$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

44

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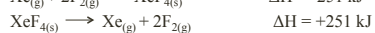
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### Characteristics of Enthalpy Changes

- 1. If a reaction is reversed, the sign of  $\Delta H$  is also reversed.
- 2. The magnitude of  $\Delta H$  is directly proportional to the quantities of reactants and products in a reaction.
  - If the coefficients in a balanced reaction are multiplied by an integer, the value of  $\Delta H$  is multiplied by the same integer.



➤ 251 kJ of energy is evolved for the reaction:  $\text{Xe}_{(\text{g})} + 2\text{F}_{2(\text{g})} \longrightarrow \text{XeF}_{4(\text{s})}$

➤ So for  $2\text{Xe}_{(\text{g})} + 4\text{F}_{2(\text{g})} \longrightarrow 2\text{XeF}_{4(\text{s})}$

➤  $\Delta H = 2(-251 \text{ kJ}) = -502 \text{ kJ}$

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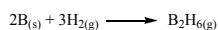
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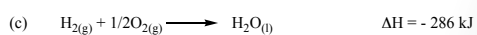
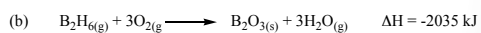
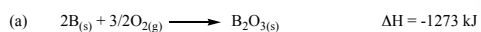
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### Hess's Law: Example 9.6

Calculate  $\Delta H$  for the synthesis of diborane:



using the following data:



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46

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#### ➤ Solution:

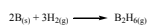
➤ To obtain  $\Delta H$  for the required reaction, we must somehow combine equations (a), (b), (c), and (d) to produce that reaction and add the corresponding  $\Delta H$  values.

➤ The reactants are  $\text{B}_{(s)}$  and  $\text{H}_{2(g)}$ , and the product is  $\text{B}_2\text{H}_{6(g)}$ .

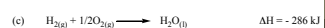
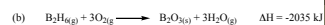
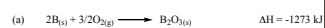
➤ Reaction (a) has  $\text{B}_{(s)}$  as a reactant, reaction (a) will be used as it is.

➤ Reaction (b) must be reversed, and the sign of  $\Delta H$  changed accordingly.

Calculate  $\Delta H$  for the synthesis of diborane:



using the following data:



**Answer:** (a) + (-b) + (3c) + (3d)

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### Standard Enthalpies of Formation

➤ The **standard enthalpy of formation**  $\Delta H_f^\circ$  of a compound is defined as the change in enthalpy that accompanies the formation of 1 mole of a compound from its elements with all substances in their standard states.

➤ The superscript zero on a thermodynamic function for example  $\Delta H^\circ$  indicates that the corresponding process has been carried out under standard conditions.

➤ The **standard state** for a substance is a precisely defined reference state.

➤ Standard state is not the same as standard temperature and pressure (STP) for a gas.

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48

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## Definitions of Standard States

1. For a gas the standard state is a pressure of exactly 1 atm.
2. For a substance present in a solution, the standard state is a concentration of exactly 1 M at an applied pressure of 1 atm.
3. For a pure substance in a condensed (liquid or solid), the standard state is the pure liquid or solid.
4. For an element the standard state is the form in which the element exists (is most stable) under conditions of 1 atm and the temperature of interest (usually 25°C)

• **Examples:**

- The standard state for oxygen is  $O_{2(g)}$  at a pressure of 1 atm.
- The standard state for sodium is  $Na_{(s)}$
- The standard state for mercury is  $Hg_{(l)}$

• Note: 1 bar = 100,000 Pa

49

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## Standard Enthalpies of Formation

**TABLE 9.4**

Standard Enthalpies of Formation for Several Compounds at 25°C

Compound	$\Delta H_f^\circ$ (kJ/mol)
$NH_3(g)$	-46
$NO_2(g)$	34
$H_2O(l)$	-286
$Al_2O_3(s)$	-1676
$Fe_2O_3(s)$	-826
$CO_2(g)$	-394
$CH_3OH(l)$	-239
$C_8H_{18}(l)$	-269

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## Example



- The standard state of carbon is graphite, the standard states for oxygen and hydrogen are the diatomic gases, and the standard state for methanol is the liquid.

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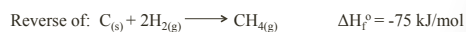
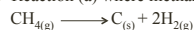
### Example

- Calculate the standard enthalpy change for the combustion of methane:



- Apply Hess's law and choose any convenient pathway from reactants to products

- Reaction (a) where methane is taken apart into its elements:



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52

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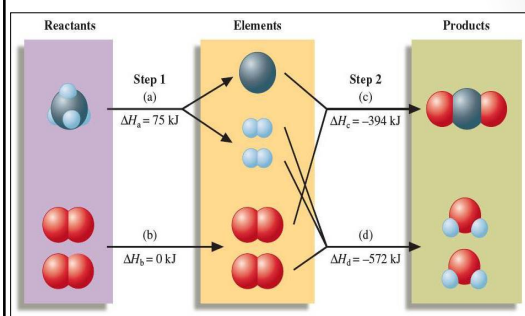
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FIGURE 9.11: Schematic of the energy changes for the separation of methane into its components



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- Reaction (b): oxygen is an element in its standard state, so no change is necessary. Thus  $\Delta H_{(b)}^\circ = 0$

- Reaction (c):  $\text{C}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) \quad \Delta H_f^\circ = -394 \text{ kJ/mol}$

- $\Delta H_{(c)}^\circ = \Delta H_f^\circ[\text{for } \text{CO}_2(\text{g})] = -394 \text{ kJ/mol}$

- Reaction (d) is the formation reaction of water:

- $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l}) \quad \Delta H_f^\circ = -286 \text{ kJ/mol}$

- Since 2 moles of water are required:  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{H}_2\text{O}(\text{l})$

- $\Delta H_{(d)}^\circ = 2 \times \Delta H_f^\circ[\text{for } \text{H}_2\text{O}(\text{l})] = 2(-286 \text{ kJ}) = -572 \text{ kJ}$

- $\Delta H_{\text{reaction}}^\circ = \Delta H_{(a)}^\circ + \Delta H_{(b)}^\circ + \Delta H_{(c)}^\circ + \Delta H_{(d)}^\circ$   
 $= -\Delta H_f^\circ[\text{for } \text{CH}_4(\text{g})] + 0 + \Delta H_f^\circ[\text{for } \text{CO}_2(\text{g})] + 2\Delta H_f^\circ[\text{for } \text{H}_2\text{O}(\text{l})]$   
 $= -(-75 \text{ kJ}) + 0 + (-394 \text{ kJ}) + (-572 \text{ kJ})$   
 $= -891 \text{ kJ}$

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## Enthalpy Change

➤ The enthalpy change for a given reaction can be calculated by subtracting the enthalpies of formation of the reactants from the enthalpies of formation of the products.

➤ Elements are not included in the calculation since elements require no change in form. We have in effect defined the enthalpy of formation of an element in its standard state as zero.

$$\Delta H^{\circ}_{\text{reaction}} = \sum \Delta H^{\circ}_{\text{f products}} - \sum \Delta H^{\circ}_{\text{f reactants}}$$

55

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## Key Concepts for Doing Enthalpy Calculations

1. When a reaction is reversed, the magnitude of  $\Delta H$  remains the same, but the sign changes.
2. When the balanced equation for a reaction is multiplied by an integer, the value of  $\Delta H$  for that reaction must be multiplied by the same integer.
3. The change in enthalpy for a given reaction can be calculated from the enthalpies of formation of the reactants and products:

$$\Delta H^{\circ}_{\text{reaction}} = \sum \Delta H^{\circ}_{\text{f products}} - \sum \Delta H^{\circ}_{\text{f reactants}}$$

4. Elements in their standard states are not included in the  $\Delta H_{\text{reaction}}$  calculations. That is,  $\Delta H^{\circ}_{\text{f}}$  for an element in its standard state is zero.

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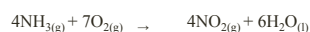
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## Example 9.7

➤ Using the standard enthalpies of formation listed in Table 9.4, calculate the standard enthalpy change for the overall reaction.



$$\begin{aligned} \Delta H^{\circ}_{\text{rxn}} &= \sum \Delta H^{\circ}_{\text{f products}} - \sum \Delta H^{\circ}_{\text{f reactants}} \\ &= [(4 \times 34) + 6(-286)] - [4 \times (-46) + 7(0)] \\ &= -1396 \text{ KJ} \end{aligned}$$

For  $\text{O}_2(\text{s})$  in its natural form,  $\Delta H^{\circ}_{\text{f}} = 0$

57

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