

# ***GENERAL CHEMISTRY***

## ***Chapter 4***

# **Chemical Thermodynamics**

1

## **Chemical Thermodynamics**

- ❖ **In thermodynamics** we study the energy changes that accompany physical and chemical processes.
- ❖ In this chapter we study the two main aspects:
  - ✓ **The first** is concerned with how we observe, measure, and predict energy changes for both physical changes and chemical reactions.
  - ✓ We will learn to use energy changes to tell whether or not a given process can occur under specified conditions to give predominantly products (or reactants) and how to make a process more (or less) favorable..
- ❖ We will **consider enthalpy** and **entropy**.

2

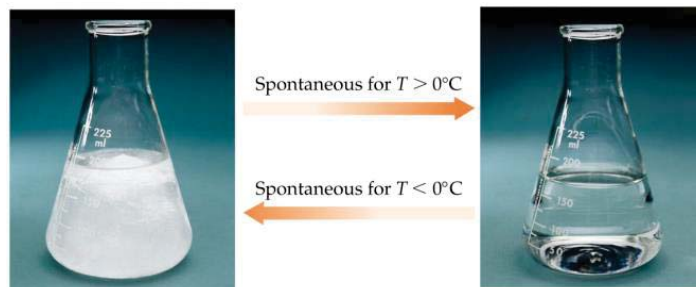
# Spontaneous Processes

- ❖ Any process that occurs without outside intervention is spontaneous.
- ❖ When two eggs are dropped they spontaneously break.
- ❖ The reverse reaction is not spontaneous.
- ❖ We can conclude that a spontaneous process has a direction.

3

## Spontaneous Processes Direction

- ❖ A process that is spontaneous in one direction is not spontaneous in the opposite direction.
- ❖ The direction of a spontaneous process can depend on temperature: Ice turning to water is spontaneous at  $T > 0^{\circ}\text{C}$ , Water turning to ice is spontaneous at  $T < 0^{\circ}\text{C}$ .



4

## Class Example Problem

- Predict whether the following processes are spontaneous as described, are spontaneous in the reverse direction, or are in equilibrium: (a) When a piece of metal heated to 150 °C is added to water at 40 °C, the water gets hotter. (b) Water at room temperature decomposes into  $\text{H}_2(\text{g})$  and  $\text{O}_2(\text{g})$ . (c) Benzene vapor at a pressure of 1 atm condenses to liquid benzene at the normal boiling point of benzene, 80.1 °C.

5

## Reversible Processes

A **reversible process** is one that can go back and forth between states along the same path.

❖ **Chemical systems in equilibrium are reversible.**

- ✓ They can interconvert between reactants and products
- ✓ For example, consider the interconversion of water and ice at 0 °C.
- ❖ There is only one reversible path between any two states of a system.

6

# Irreversible Processes

A **irreversible process** is one that cannot be reversed to restore the system to its original state.

- ✓ To get back to the original state a different pathway must be followed.
- ✓ In any **spontaneous process**, the path between reactants and products **is irreversible**.

7

## Systems and Surroundings

### Analyzing Energy Changes

- **System**: part of the universe we are interested in.
- **Surroundings**: the rest of the universe.

8

# Transferring Energy

## ❖ Work and Heat

- ❖ **Force** is a push or pull on an object.
- ❖ **Work** is the product of force applied to an object over a distance:  
$$w = F \times d$$
- ❖ **Energy** is the work done to move an object against a force.
- ❖ **Heat** is the transfer of energy between two objects.
- ❖ **Energy** is the capacity to do work or transfer heat.

9

# The First Law of Thermodynamics

## ❖ First Law of Thermodynamics:

- ✓ **The total amount of energy in the universe is constant.**
- ✓ **Or energy is neither created nor destroyed in ordinary chemical reactions and physical changes.**
- ✓  **$\Delta E = q + w$ ,**

where

- $\Delta E$  = internal energy change
- $q$  = heat absorbed
- $w$  = the work done

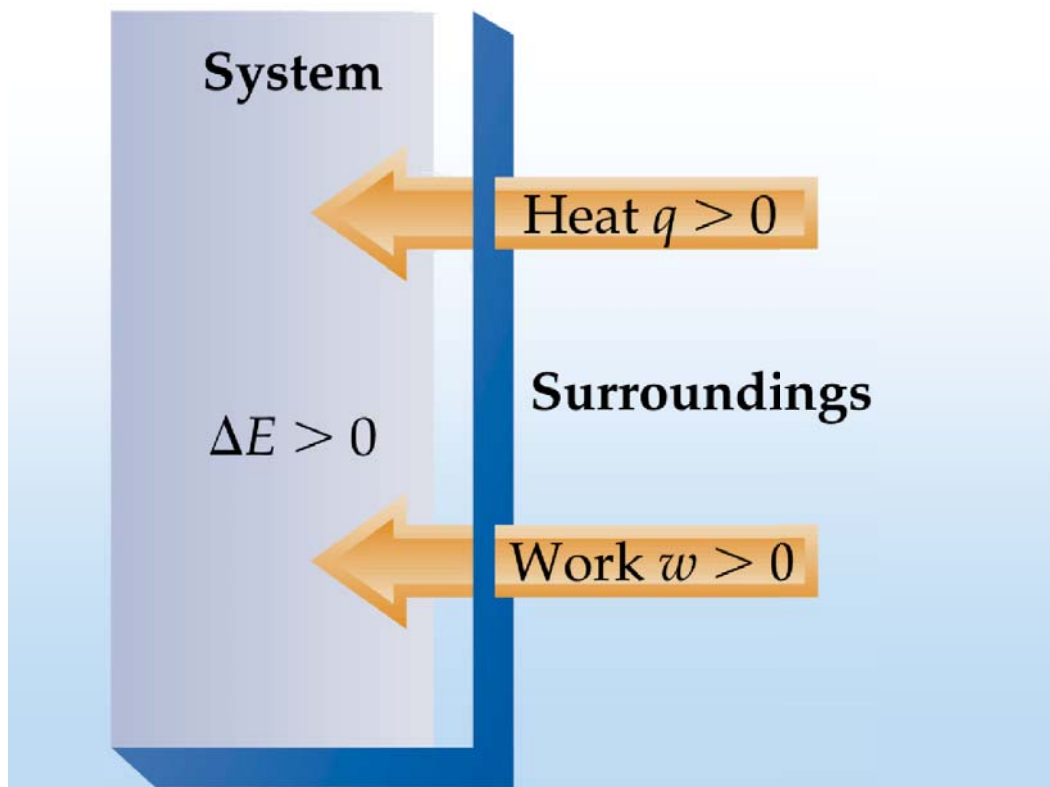
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# The First Law of Thermodynamics

- ❖ Total energy lost by a system equals the total energy gained by a system.
- ❖ **Internal Energy:** total energy of a system (kinetic + potential).
- ❖ Cannot measure absolute internal energy.
- ❖ Change in internal energy:

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

11



12

# Sign Conventions

Sign Convention for $q$ :	Sign of $\Delta E = q + w$
$q > 0$ : Heat is transferred from the surroundings to the system	$q > 0$ and $w > 0$ : $\Delta E > 0$
$q < 0$ : Heat is transferred from the system to the surroundings	$q > 0$ and $w < 0$ : The sign of $\Delta E$ depends on the magnitudes of $q$ and $w$
<b>Sign Convention for <math>w</math>:</b>	$q < 0$ and $w > 0$ : The sign of $\Delta E$ depends on the magnitudes of $q$ and $w$
$w > 0$ : Work is done by the surroundings on the system	
$w < 0$ : Work is done by the system on the surroundings	$q < 0$ and $w < 0$ : $\Delta E < 0$

13

## Exothermic and Endothermic Processes

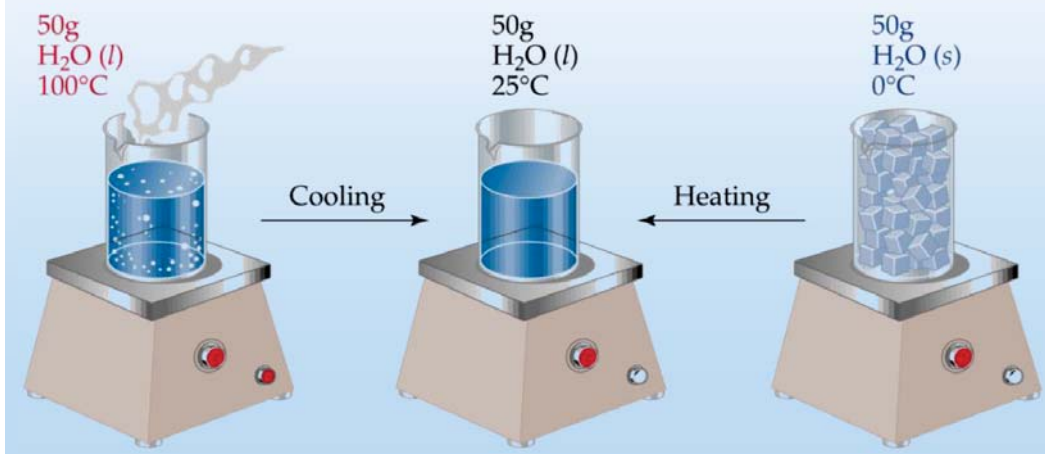
- ❖ **Endothermic**: absorbs heat from the surroundings.
- ❖ **Exothermic**: transfers heat to the surroundings.
- ✓ An endothermic reaction feels cold.
- ✓ An exothermic reaction feels hot.

Endothermic: *thu nhiệt*  
Exothermic: *tỏa nhiệt*

14

# State Functions

- **State function:** depends only on the initial and final states of system, not on how the internal energy is used.



15

# Work

- ❖ **Chemical reactions** can absorb or release heat.
- ❖ However, they also have the ability to do work.
- ❖ For example, when a gas is produced, then the produced gas can be used to push a piston, thus doing work.

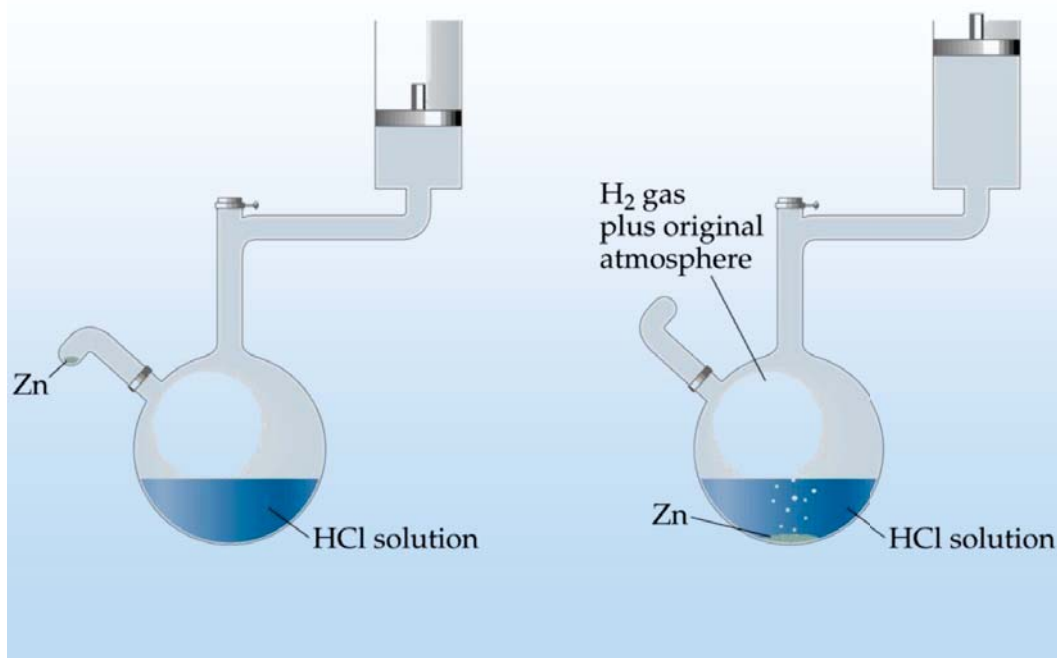


- ❖ The work performed by the above reaction is called *pressure-volume* work.
- ❖ When the **pressure is constant**,

$$w = -P\Delta V$$

16





17

## Enthalpy

- ❖ **Enthalpy,  $H$ :** Heat transferred between the system and surroundings carried out under constant pressure.

$$H = E + PV$$

- ❖ Units of  $H$ : kJ/mol or kcal/mol
- ❖ **Enthalpy is a state function.**
- ❖ If the process occurs at constant pressure,

$$\begin{aligned}\Delta H &= \Delta(E + PV) \\ &= \Delta E + P\Delta V\end{aligned}$$

18

# Enthalpy

- Since we know that

$$w = -P\Delta V$$

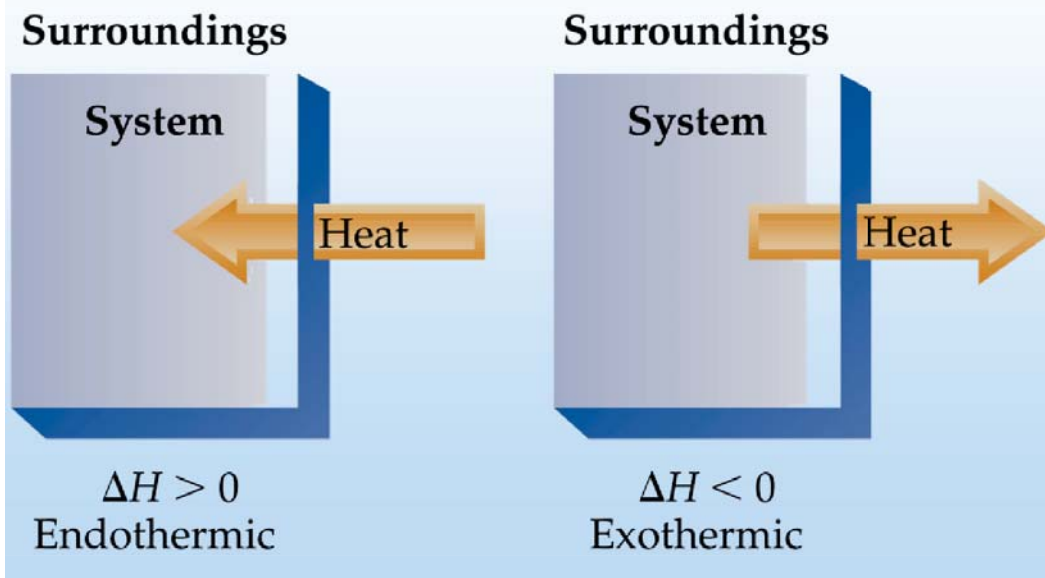
- We can write

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

- When  $\Delta H$ , is positive, the system gains heat from the surroundings.
- When  $\Delta H$ , is negative, the surroundings gain heat from the system.

19

# Enthalpy



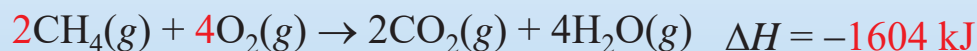
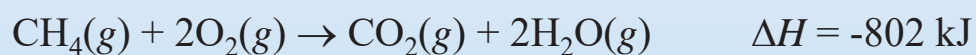
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## Enthalpies of Reaction

- For a reaction:

$$\begin{aligned}\Delta H &= H_{\text{final}} - H_{\text{initial}} \\ &= H_{\text{products}} - H_{\text{reactants}}\end{aligned}$$

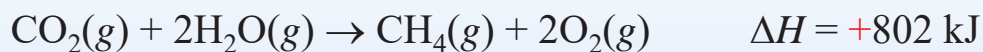
- Enthalpy is an *extensive* property (magnitude  $\Delta H$  is directly proportional to amount):



21

## Enthalpies of Reaction

- When we **reverse a reaction**, we **change the sign of  $\Delta H$** :



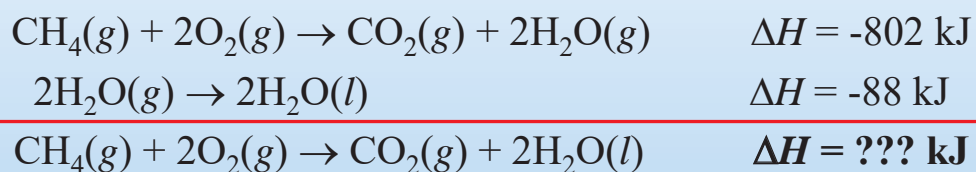
- Change in enthalpy depends on state:



22

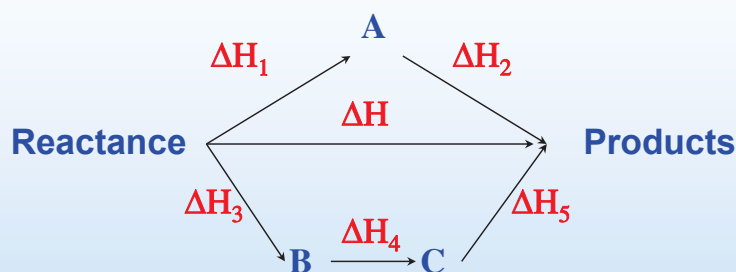
## Hess's Law

- **Hess's law:** if a reaction is carried out in a number of steps,  $\Delta H$  for the overall reaction is the sum of  $\Delta H$  for each individual step.
- For example:



23

## Hess's Law



$$\Delta H = \Delta H_1 + \Delta H_2 = \Delta H_3 + \Delta H_4 + \Delta H_5$$

24

## Hess's Law

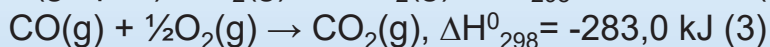
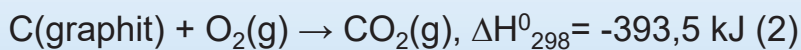
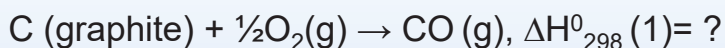


$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

25

## Hess's Law

**Use the thermochemical equations shown here to determine enthalpy,  $\Delta H^0_{298}$ , for the following reaction:**



Sol:

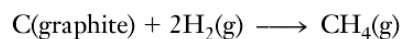
$$\rightarrow \Delta H^0_{298} \text{ CO(g)} = -393,5 - (-283,0) = -110,5 \text{ kJ/mol}$$

26

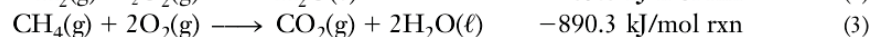


### EXAMPLE 15-7 Combining Thermochemical Equations: Hess's Law

Use the thermochemical equations shown here to determine  $\Delta H_{\text{rxn}}^0$  at 25°C for the following reaction.



$\Delta H^0$



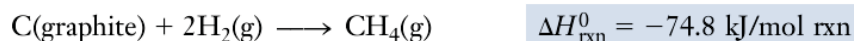
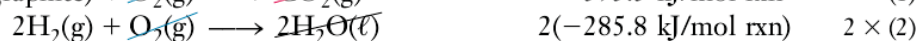
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27



### Solution

$\Delta H^0$



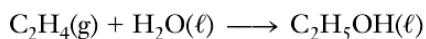
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28

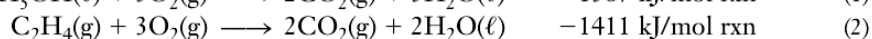
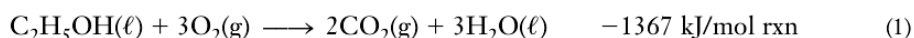


### EXAMPLE 15-8 Combining Thermochemical Equations: Hess's Law

Given the following thermochemical equations, calculate the heat of reaction at 298 K for the reaction of ethylene with water to form ethanol.

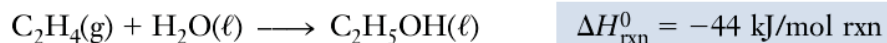
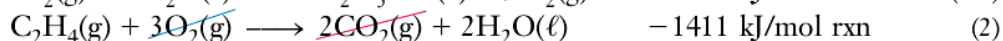
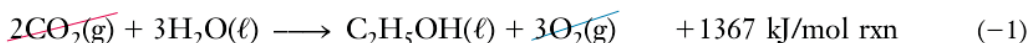


$\Delta H^\circ$



#### Solution

$\Delta H^\circ$



*Chapter 6 Thermochemistry*

29

## Enthalpies of Formation

- The standard molar **enthalpy of formation**,  $\Delta H_f^\circ$ , of a substance is the enthalpy change for the reaction in which **one mole of the substance** in a specified state is formed **from its elements** in their standard states.
- Standard conditions (standard state): 1 atm and 25 °C (298 K).
- Standard enthalpy,  $\Delta H^\circ$ , is the enthalpy measured when everything is in its standard state.

30

## Enthalpies of Formation

- If there is **more than one state** for a substance under **standard conditions**, the **more stable one is used**.
- The  $\Delta H_f^\circ$  value for any **element** in its standard state is **zero**.

31

## Standard Enthalpies of Formation at 298 K

Substance	Formula	$\Delta H_f^\circ$ (kJ/mol)
Acetylene	$\text{C}_2\text{H}_2(\text{g})$	226.7
Ammonia	$\text{NH}_3(\text{g})$	-46.19
Benzene	$\text{C}_6\text{H}_6(\text{l})$	49.0
Calcium carbonate	$\text{CaCO}_3(\text{s})$	-1207.1
Calcium oxide	$\text{CaO}(\text{s})$	-635.5
Carbon dioxide	$\text{CO}_2(\text{g})$	-393.5
Carbon monoxide	$\text{CO}(\text{g})$	-110.5
Diamond	$\text{C}(\text{s})$	1.88
Ethane	$\text{C}_2\text{H}_6(\text{g})$	-84.68
Ethanol	$\text{C}_2\text{H}_5\text{OH}(\text{l})$	-277.7
Ethylene	$\text{C}_2\text{H}_4(\text{g})$	52.30
Glucose	$\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	-1273
Hydrogen bromide	$\text{HBr}(\text{g})$	-36.23

32



## Using Enthalpies of Formation to Calculate Enthalpies of Reaction

- We use Hess' Law to calculate enthalpies of a reaction from enthalpies of formation.
- For a reaction

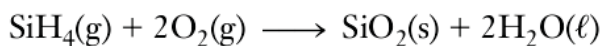
$$\Delta H^{\circ}_{\text{rxn}} = \sum n \Delta H^{\circ}_f(\text{products}) - \sum m \Delta H^{\circ}_f(\text{reactants})$$

33



### EXAMPLE 15-9 Using $\Delta H^{\circ}_f$ Values: Hess's Law

Calculate  $\Delta H^{\circ}_{\text{rxn}}$  for the following reaction at 298 K.



	$\text{SiH}_4(\text{g})$	$\text{O}_2(\text{g})$	$\text{SiO}_2(\text{s})$	$\text{H}_2\text{O}(\ell)$
$\Delta H^{\circ}_f$ kJ/mol:	34.3	0	-910.9	-285.8

#### Solution

$$\Delta H^{\circ}_{\text{rxn}} = \sum n \Delta H^{\circ}_f \text{ products} - \sum n \Delta H^{\circ}_f \text{ reactants}$$

$$\Delta H^{\circ}_{\text{rxn}} = [\Delta H^{\circ}_f \text{ SiO}_2(\text{s}) + 2 \Delta H^{\circ}_f \text{ H}_2\text{O}(\ell)] - [\Delta H^{\circ}_f \text{ SiH}_4(\text{g}) + 2 \Delta H^{\circ}_f \text{ O}_2(\text{g})]$$

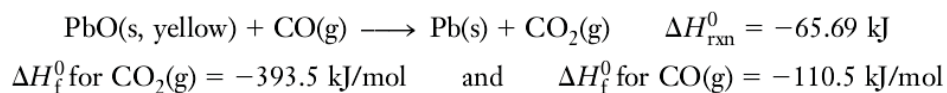
$$\Delta H^{\circ}_{\text{rxn}} = -1515.7 \text{ kJ/mol rxn}$$

Chapter 6 Thermodynamics

34

### EXAMPLE 15-10 Using $\Delta H_f^0$ Values: Hess's Law

Use the following information to determine  $\Delta H_f^0$  for PbO(s, yellow).



#### Solution

$$\Delta H_f^0 \text{ PbO(s, yellow)} = 65.69 - 393.5 + 110.5 = -217.3 \text{ kJ/mol of PbO}$$

*Chapter 6 Thermochemistry*

35

## Heat of Combustion

- ❖ The **heat of combustion** ( $\Delta H_c^0$ ) is the energy released as heat when one mole of a compound undergoes complete combustion with oxygen. The chemical reaction is typically a hydrocarbon reacting with oxygen to **form carbon dioxide, water and heat**.
- ❖ Standard Enthalpy of Combustion:  $\Delta H_{c,298}^0$ .
- ❖ Standard enthalpy of combustion is defined as the enthalpy change when 1 mole of a compound is completely burnt in oxygen gas at 298K and 1 bar pressure.
- ❖ **Examples:**  
 $\text{C}_8\text{H}_{18}\text{(l)} + 12\frac{1}{2}\text{O}_2\text{(g)} \rightarrow 8\text{CO}_2\text{(g)} + 9\text{H}_2\text{O(l)}, \Delta H_{c,298}^0 = -5512\text{kJ}\cdot\text{mol}^{-1}$   
 $\text{C}_6\text{H}_{12}\text{O}_6\text{(s)} + 6\text{O}_2\text{(g)} \rightarrow 6\text{CO}_2\text{(g)} + 6\text{H}_2\text{O(l)}, \Delta H_{c,298}^0 = -2816\text{kJ}\cdot\text{mol}^{-1}$

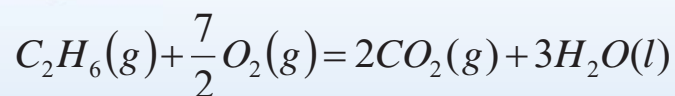
36

Heat of Combustion for some common fuels			
Fuel	kJ/g	kcal/g	BTU/lb
Hydrogen	141.9	33.9	61,000
Gasoline	47.0	11.3	20,000
Diesel	45.0	10.7	19,300
Ethanol	29.8	7.1	12,000
Propane	49.9	11.9	21,000
Butane	49.2	11.8	21,200
Wood	15.0	3.6	6,000
Coal (Lignite)	15.0	4.4	8,000
Coal (Anthracite)	27.0	7.8	14,000
Natural Gas	54.0	13.0	23,000

37

## Heat of Combustion

### Example:



$$\Delta H^0_{\text{rxn}} = -372.82 \text{ kcal}$$

$$\Delta H^0_{\text{c},298} (C_2H_6) = -372.82 \text{ kcal}$$

38

## Using heat combustion to Calculate Enthalpies of Reaction

- We use Hess' Law to calculate enthalpies of a reaction from heat combustion.
- For a reaction

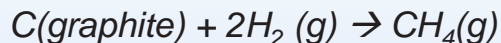
$$\Delta H^{\circ}_{\text{rxn}} = \sum m\Delta H^{\circ}_c(\text{reactants}) - \sum n\Delta H^{\circ}_c(\text{products})$$

39

## Heat of Combustion

### **Example:**

Calculate  $\Delta H^{\circ}_{\text{rxn}}$  at 298K of following reaction:



Given heat of combustion of C(graphite) ,  $\text{H}_2(\text{g})$ ,  $\text{CH}_4(\text{g})$  is: -393.5 kJ/mol, -285.8 kJ/mol, -890.3 kJ/mol, respectively.

40

# Entropy

- ❖ **Entropy,  $S$** , is a thermodynamic quantity that is measure the randomness or **disorder** in a system.
- ❖  $S$  is state function.
- ❖ Spontaneous reactions proceed to lower energy or higher entropy (i.e., the **more disorder** the **higher the entropy** of the system).
- ❖ For example, ice molecules are very well ordered because of the H-bonds. Thus, ice has a low entropy.
- ❖ **As ice melts**, the intermolecular forces are broken (requires energy), but the order is interrupted (so **entropy increases**).
- ❖ Water is more random than ice, so ice spontaneously melts at room temperature.

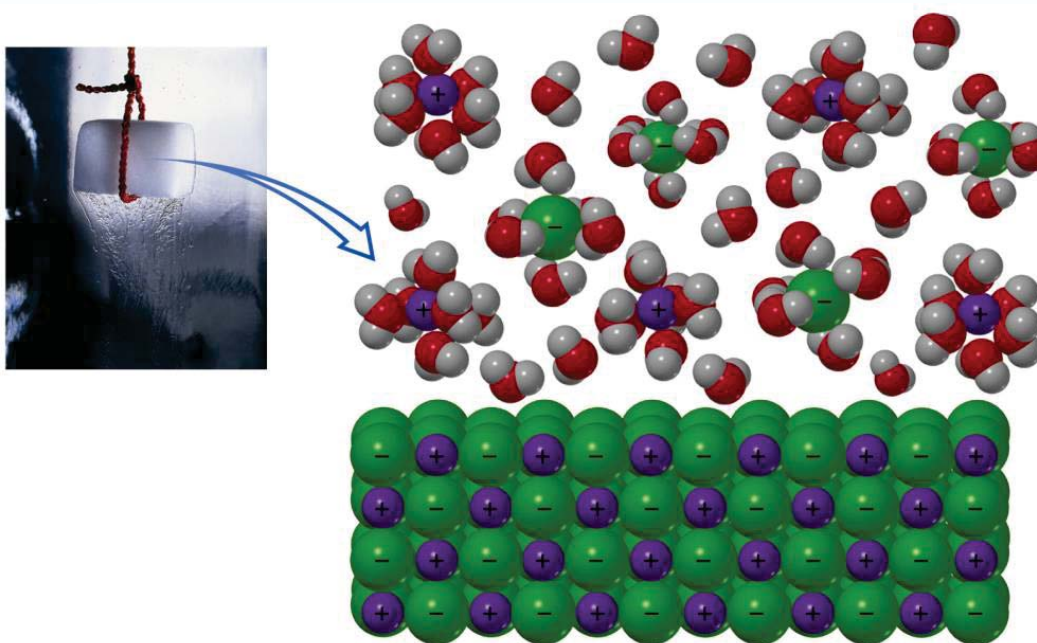
41

# Energy and Entropy

- ❖ There is a balance between energy and entropy considerations.
- ❖ When an ionic solid (KCl) is placed in water two things happen:
  - ✓ The ions in the crystal dissociate (the hydrated ions are less ordered than the crystal), so the entropy increases.
  - ✓ The water organizes into hydrates about the ions (so the entropy decreases)
- ❖ Thus, both disordering and ordering occurs **when dissolving a salt in water**, and the **disordered processes are usually dominant**.

42

## Energy and Entropy Schematic



43

## Expressing Entropy

- Generally, when an increase in entropy in one process is associated with a decrease in entropy in another, the increase in entropy dominates.
- Entropy is a state function.
- For a system,  $\Delta S = S_{\text{final}} - S_{\text{initial}}$ .
- If  $\Delta S > 0$  the randomness increases, if  $\Delta S < 0$  the order increases.

44

## Entropy Change for a Reaction

The following processes produces a **increase in the entropy** of the system:

1. A reaction in which a molecule is broken into two or more smaller molecules.
2. A reaction in which there is an increase in moles of gas. (This may result from a molecule breaking up, in which case Rules 1 and 2 are related.)
3. A process in which a solid changes to liquid or gas or a liquid changes to a gas.

### Exercise 18.4

Predict the sign of  $\Delta S^\circ$  for each of the following reactions.

- a.  $\text{CaCO}_3(s) \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$
- b.  $\text{CS}_2(l) \longrightarrow \text{CS}_2(g)$
- c.  $2\text{Hg}(l) + \text{O}_2(g) \longrightarrow 2\text{HgO}(s)$
- d.  $2\text{Na}_2\text{O}_2(s) + 2\text{H}_2\text{O}(l) \longrightarrow 4\text{NaOH}(aq) + \text{O}_2(g)$

45

## The Change in Entropy

- Suppose a system changes reversibly between state 1 and state 2. Then, the change in entropy is given by

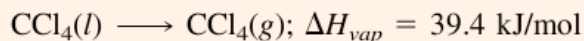
$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T}, \text{ (constant } T\text{)}$$

- at constant  $T$  where  $q_{\text{rev}}$  is the amount of heat added reversibly to the system. (Example: a phase change occurs at constant  $T$  with the reversible addition of heat.)

46

## The Change in Entropy

The heat of vaporization,  $\Delta H_{vap}$ , of carbon tetrachloride,  $\text{CCl}_4$ , at  $25^\circ\text{C}$  is  $39.4 \text{ kJ/mol}$ .



If 1 mol of liquid carbon tetrachloride at  $25^\circ\text{C}$  has an entropy of  $216 \text{ J/K}$ , what is the entropy of 1 mol of the vapor in equilibrium with the liquid at this temperature?

$$\Delta S = \frac{\Delta H_{vap}}{T} = \frac{39.4 \times 10^3 \text{ J/mol}}{298 \text{ K}} = 132 \text{ J/(mol}\cdot\text{K)}$$

47

## Absolute Entropy Changes in Chemical Reactions

- Absolute entropy can be determined from complicated measurements.
- Standard molar entropy,  $S^\circ$ : entropy of a substance in its standard state. Similar in concept to  $\Delta H^\circ$ .
- Units of  $S$ :  $\text{J/(mol}\cdot\text{K)}$ . Note units of  $\Delta H$ :  $\text{kJ/mol}$ .
- **Standard molar entropies of elements are not zero.**
- For a chemical reaction which produces  $n$  moles of products from  $m$  moles of reactants:

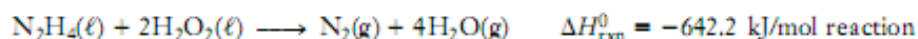
$$\Delta S^\circ = \sum nS^\circ(\text{products}) - \sum mS^\circ(\text{reactants})$$

48



### EXAMPLE 15-15 Calculation of $\Delta S_{rxn}^0$

Use the values of standard molar entropies in Appendix K to calculate the entropy change at 25°C and one atmosphere pressure for the reaction of hydrazine with hydrogen peroxide. This explosive reaction has been used for rocket propulsion. Do you think the reaction is spontaneous? The balanced equation for the reaction is



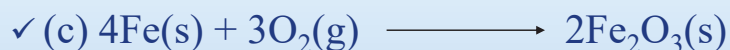
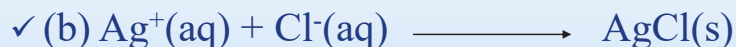
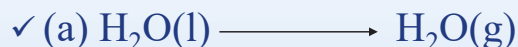
the  $S_{298}^0$  values that we obtain from Appendix K for each substance:

	$\text{N}_2\text{H}_4(\ell)$	$\text{H}_2\text{O}_2(\ell)$	$\text{N}_2(\text{g})$	$\text{H}_2\text{O}(\text{g})$
$S^0, \text{J/mol} \cdot \text{K}$	121.2	109.6	191.5	188.7

49

## Class Example Problem

❖ By considering the disorder in the reactants and products, predict whether entropy,  $\Delta S$ , is positive or negative for each of the following processes:



50

## Gibbs Free Energy

- For a spontaneous reaction the entropy of the universe must increase.
- Reactions with large negative  $\Delta H$  values are spontaneous.
- How do we balance  $\Delta S$  and  $\Delta H$  to predict whether a reaction is spontaneous?
- Gibbs free energy,  $G$ , of a state is

$$G = H - TS$$

- For a process occurring at constant temperature

$$\Delta G = \Delta H - T\Delta S$$

51

## Conditions of Gibbs Free Energy

- There are three important conditions:
  - If  $\Delta G < 0$  then the forward reaction is spontaneous.
  - If  $\Delta G = 0$  then reaction is at equilibrium and no net reaction will occur.
  - If  $\Delta G > 0$  then the forward reaction is not spontaneous. If  $\Delta G > 0$ , work must be supplied from the surroundings to drive the reaction.
- For a reaction the free energy of the reactants decreases to a minimum (equilibrium) and then increases to the free energy of the products.

52

## Standard Gibbs Free-Energy Changes

- We can tabulate standard free-energies of formation,  $\Delta G^\circ_f$  (c.f. standard enthalpies of formation).
- Standard states are: pure solid, pure liquid, 1 atm (gas), 1 *M* concentration (solution), and  $\Delta G^\circ = 0$  for elements.
- $\Delta G^\circ$  for a process is given by
 
$$\Delta G^\circ = \sum n \Delta G^\circ_f (\text{products}) - \sum m \Delta G^\circ_f (\text{reactants})$$
- The quantity  $\Delta G^\circ$  for a reaction tells us whether a mixture of substances will spontaneously react to produce more reactants ( $\Delta G^\circ > 0$ ) or products ( $\Delta G^\circ < 0$ ).

53

### EXAMPLE 15-16 Spontaneity of Standard Reaction

Diatomic nitrogen and oxygen molecules make up about 99% of all the molecules in reasonably “unpolluted” dry air. Evaluate  $\Delta G^\circ$  for the following reaction at 298 K, using  $\Delta G^\circ_f$  values from Appendix K. Is the standard reaction spontaneous?



	$\text{N}_2(\text{g})$	$\text{O}_2(\text{g})$	$\text{NO}(\text{g})$
$\Delta G^\circ_f$ kJ/mol:	0	0	86.57

#### Solution

$$\Delta G^\circ_{\text{rxn}} = \sum n \Delta G^\circ_{f \text{ products}} - \sum n \Delta G^\circ_{f \text{ reactants}}$$

$$\Delta G^\circ_{\text{rxn}} = +173.1 \text{ kJ/mol rxn}$$

54

### EXAMPLE 15-16 Spontaneity of Standard Reaction

Diatomic nitrogen and oxygen molecules make up about 99% of all the molecules in reasonably “unpolluted” dry air. Evaluate  $\Delta G^0$  for the following reaction at 298 K, using  $\Delta G_f^0$  values from Appendix K. Is the standard reaction spontaneous?



#### Solution

The values we obtain from Appendix K are:

	$\text{N}_2(\text{g})$	$\text{O}_2(\text{g})$	$\text{NO}(\text{g})$
$\Delta H_f^0$ , kJ/mol:	0	0	90.25
$S^0$ , J/mol · K:	191.5	205.0	210.7

55

$$\begin{aligned}\Delta H_{\text{rxn}}^0 &= \sum n \Delta H_f^0 \text{ products} - \sum n \Delta H_f^0 \text{ reactants} \\ &= 2 \Delta H_f^0 \text{NO}(\text{g}) - [\Delta H_f^0 \text{N}_2(\text{g}) + \Delta H_f^0 \text{O}_2(\text{g})] \\ &= [2(90.25)] - (0 + 0) = 180.5 \text{ kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta S_{\text{rxn}}^0 &= \sum n S_{\text{products}}^0 - \sum n S_{\text{reactants}}^0 \\ &= 2 S_{\text{NO}(\text{g})}^0 - [S_{\text{N}_2(\text{g})}^0 + S_{\text{O}_2(\text{g})}^0] \\ &= [2 (210.7)] - (191.5 + 205.0) = 24.9 \text{ J/mol} \cdot \text{K} = 0.0249 \text{ kJ/mol} \cdot \text{K}\end{aligned}$$

Now we use the relationship  $\Delta G^0 = \Delta H^0 - T \Delta S^0$ , with  $T = 298 \text{ K}$ , to evaluate the free energy change under standard state conditions at 298 K.

$$\begin{aligned}\Delta G_{\text{rxn}}^0 &= \Delta H_{\text{rxn}}^0 - T \Delta S_{\text{rxn}}^0 \\ &= 180.5 \text{ kJ/mol} - (298 \text{ K})(0.0249 \text{ kJ/mol} \cdot \text{K}) \\ &= 180.5 \text{ kJ/mol} - 7.42 \text{ kJ/mol}\end{aligned}$$

$$\Delta G_{\text{rxn}}^0 = +173.1 \text{ kJ/mol rxn, the same value obtained in Example 15-16.}$$

56

## Gibb Free Energy and Temperature

- Focus on  $\Delta G = \Delta H - T\Delta S$ :
  - If  $\Delta H < 0$  and  $\Delta S > 0$ , then  $\Delta G$  is always negative.
  - If  $\Delta H > 0$  and  $\Delta S < 0$ , then  $\Delta G$  is always positive. (That is, the reverse of 1.)
  - If  $\Delta H < 0$  and  $\Delta S < 0$ , then  $\Delta G$  is negative at low temperatures.
  - If  $\Delta H > 0$  and  $\Delta S > 0$ , then  $\Delta G$  is negative at high temperatures.
- Even though a reaction has a negative  $\Delta G$  it may occur too slowly to be observed.

57

## Gibb Free Energy and Temperature Chart

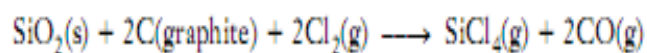
TABLE 19.4 Effect of Temperature on the Spontaneity of Reactions

$\Delta H$	$\Delta S$	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Characteristics	Example
-	+	-	Always negative	Spontaneous at all temperatures	$2\text{O}_3(\text{g}) \longrightarrow 3\text{O}_2(\text{g})$
+	-	+	Always positive	Nonspontaneous at all temperatures; reverse reaction always spontaneous	$3\text{O}_2(\text{g}) \longrightarrow 2\text{O}_3(\text{g})$
-	-	+	Negative at low $T$ ; positive at high $T$	Spontaneous at low $T$ ; becomes nonspontaneous at high $T$	$\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{O}(\text{s})$
+	+	-	Positive at low $T$ ; negative at high $T$	Nonspontaneous at low $T$ ; becomes spontaneous at high $T$	$\text{H}_2\text{O}(\text{s}) \longrightarrow \text{H}_2\text{O}(\text{l})$

58

### EXAMPLE 15-20 *Temperature Range of Spontaneity*

Estimate the temperature range for which the following standard reaction is product-favored.



From Appendix K:

	$\text{SiO}_2(\text{s})$	$\text{C}(\text{graphite})$	$\text{Cl}_2(\text{g})$	$\text{SiCl}_4(\text{g})$	$\text{CO}(\text{g})$
$\Delta H_f^\circ$ , kJ/mol:	-910.9	0	0	-657.0	-110.5
$S^\circ$ , J/mol·K:	41.84	5.740	223.0	330.6	197.6