Adama Science and Technology University

Chapter 4 part II
Thermodynamics

By

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Energy Relationships in Chemical Reactions

- **Thermodynamics is the science of the relationships between heat and other forms of energy.**
- **Thermochemistry is one area of thermodynamics. It concerns the study of the quantity of heat absorbed or evolved (given off) by chemical reactions.**

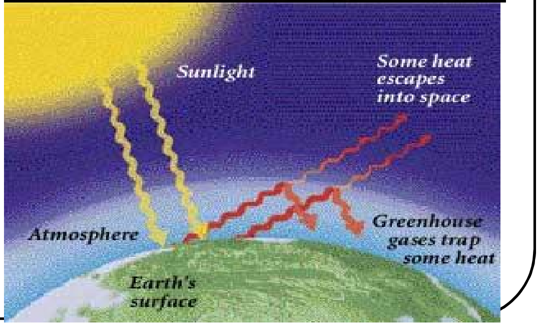
Thermochemistry is the study of heat change in chemical reactions.

Nature of Energy and Types of Energy

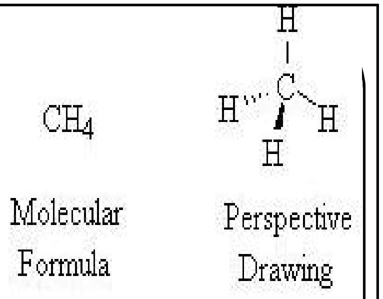
- *Energy* is usually defined as *the capacity to do work.*
- Causes changes
- Energy classify into two general types: **Kinetic and Potential energy**
- **Kinetic energy**—the energy produced by a moving object
- **Potential energy** is the energy available by virtue of an object's position

- **Thermal energy** is the energy associated with the random motion of atoms and molecules

Radiant energy comes from the sun and is earth's primary energy source. Electromagnetic energy that travels in transverse waves

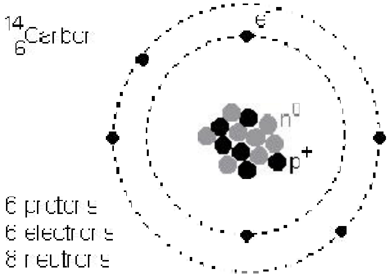


Chemical energy is the energy stored within the bonds of chemical substances.



Nuclear energy is the energy stored within the collection of **neutrons and protons** in the atom.

Energy stored in the nucleus of the atom



All forms of energy can be converted (at least in principle) from one form to another.

As the water falls over the dam, its potential energy is converted to kinetic energy.

Generate electricity

Solar-powered vehicles use panels of photovoltaic cells.

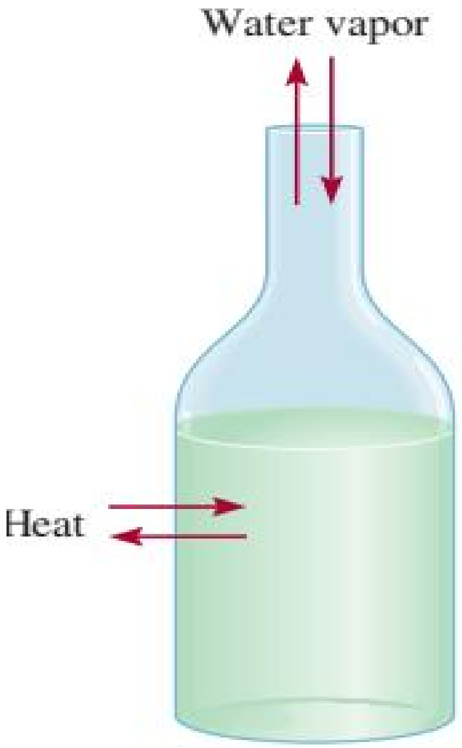
Conversion of light energy to kinetic energy

Energy Changes in Chemical Reactions

- **Energy change take place during chemical reactions.**
- **Almost all chemical reactions absorb or produce (release) energy in the form of heat.**
- ***Heat* is *the transfer of thermal energy between two bodies that are at different temperatures.***
- **To analyze energy changes associated with chemical reactions we must first define the *system*.**
- **System is the specific part of the universe that is interest to the study.**
- **The *surroundings* are *the rest of the universe outside the system***

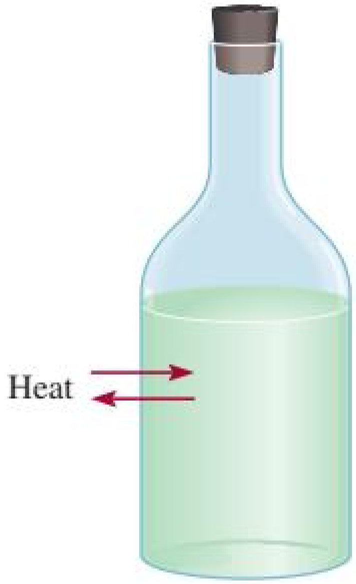
System and Surrounding

Three types of systems



open system

can exchange mass and energy



closed system

transfer of energy (heat) but not mass

Isolated system

does not allow the transfer of either mass or energy,

Chemical reactions or physical changes are classified as exothermic or endothermic.

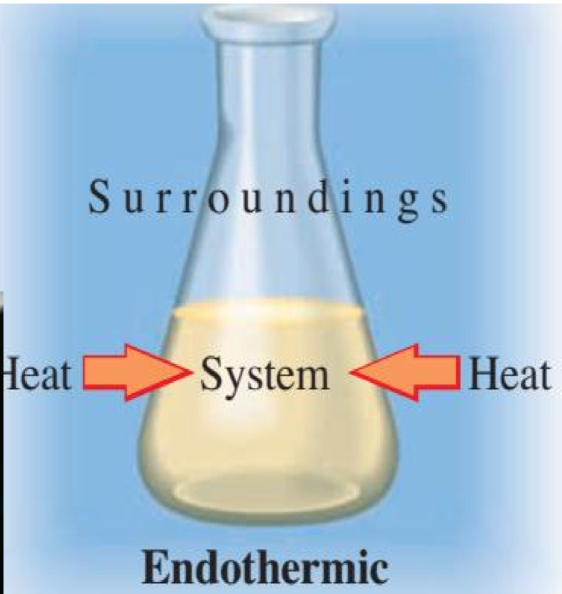
Exothermic process is any process that gives off heat – transfers thermal energy from the system to the surroundings.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

Reaction is exothermic.

the heat of reaction -890 kJ.

Endothermic process is any process in which heat has to be supplied to the system from the surroundings.



Example Decomposition of mercury(II) oxide (HgO) at high temperatures:

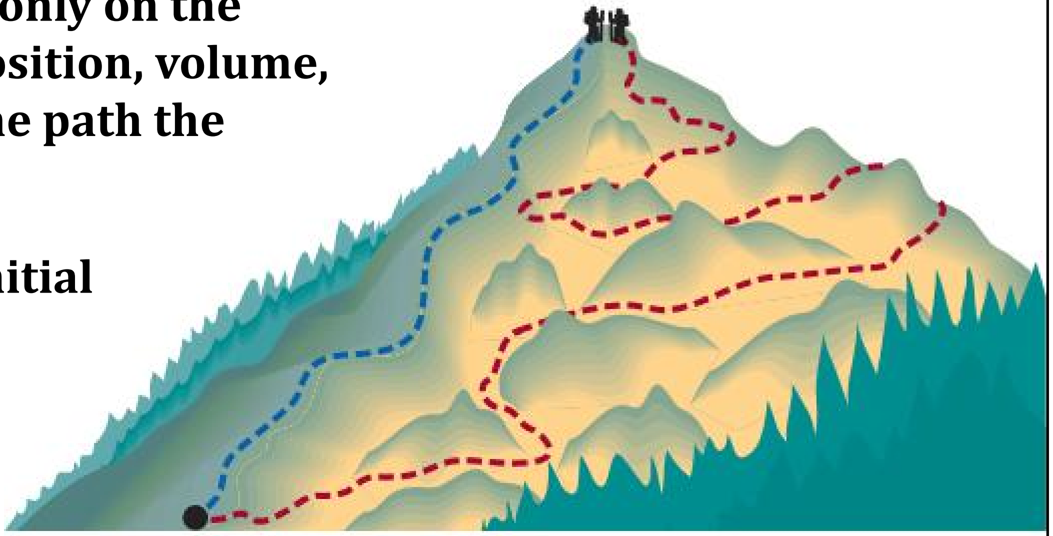
$$\text{energy} + 2HgO(s) \longrightarrow 2Hg(l) + O_2(g)$$

Thermodynamics

- ***Thermodynamics,*** **which is *the scientific study of the interconversion of heat and other kinds of energy.***
- **In thermodynamics, study changes in the *state of a system***

State function, a property dependent only on the current state of the system (its composition, volume, pressure, and temperature), not on the path the system took to reach that state;

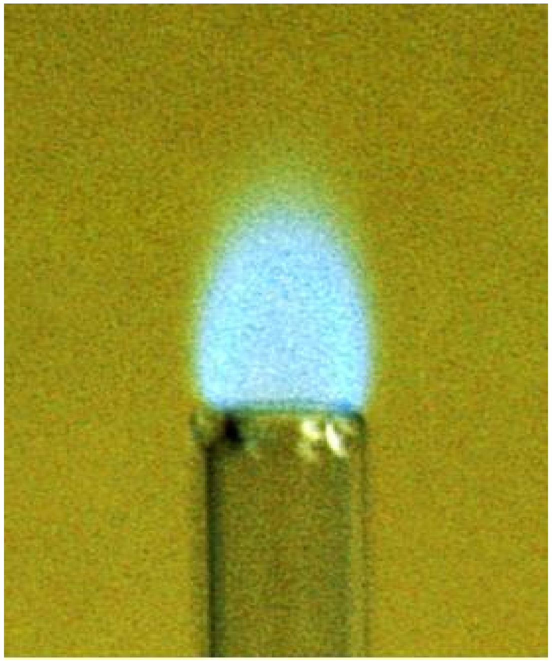
state function depends only on the initial and final states of the system



First Law of Thermodynamics

- **States that *energy can be converted from one form to another, but cannot be created or destroyed.***
- **law of conservation of energy**

$DU_{system} + DU_{surroundings} = 0$ or $DU_{system} = -DU_{surroundings}$



$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O + \text{energy}$

Exothermic chemical reaction!

Chemical energy lost by combustion = Energy gained by the surroundings

system surroundings

- **Another form of the *first law* for u_{system}**

$$\Delta U = q + w$$

ΔU is the change in internal energy of a system

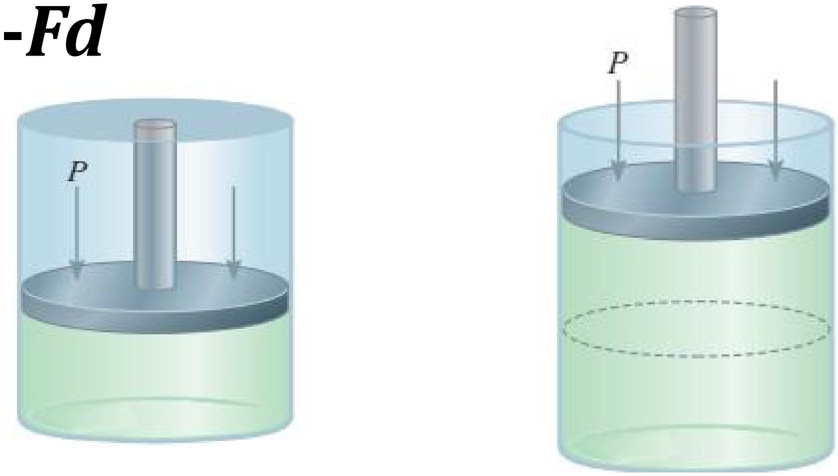
q is the heat exchange between the system and the surroundings

w is the work done on (or by) the system

$w = -P\Delta V$ when a gas expands against a constant external pressure

Work Done by the System

- ***w* = -*Fd***



Work is not a state function.

- D*V* = *A* x *h*, h= D*V* /*A*

$$w = -F \times h = -F \times \frac{\Delta V}{A} = -\frac{F}{A} \times \Delta V$$

W= - ***p***D*V*

Note that *F/A* is the pressure, *P*.

$D\cancel{w} = w_{final} - w_{initial}$

For gas expansion (work done by the system) D*V* **>0, so -*P*D*V* is a negative quantity**

For gas compression (work done on the system), D*V* **< 0, and -*P*D*V* is a positive quantity.**

Example-1

- A certain gas expands in volume from 2.0 L to 6.0 L at constant temperature. Calculate the work done by the gas if it expands at constant pressure of 1.2 atm.
- Solution
  - Work is done by the system on the surrounding
    - W= -pDv

$$1\ \mathrm{L \cdot atm} = 101.3\ \mathrm{J}$$

$$\begin{aligned} w &= -P\Delta V \\ &= -(1.2\ \mathrm{atm})(6.0 - 2.0)\ \mathrm{L} \\ &= -4.8\ \mathrm{L \cdot atm} \end{aligned}$$

$$\begin{aligned} w &= -4.8\ \mathrm{L \cdot atm} \times \frac{101.3\ \mathrm{J}}{1\ \mathrm{L \cdot atm}} \\ &= \boxed{-4.9 \times 10^{2}\ \mathrm{J}} \end{aligned}$$

Because this is gas expansion (work is done by the system on the surroundings), the work done has a negative sign.

- **Example 2: A sample of nitrogen gas expands in volume from 1.6 L to 5.4 L at constant temperature. What is the work done in joules if the gas expands.**

A. **against a vacuum**

B. **against a constant pressure of 3.7 atm?**

$$w = -P\,DV$$

(a) $DV = 5.4\text{ L} - 1.6\text{ L} = 3.8\text{ L}$ $\quad P = 0\text{ atm}$

$$W = -0\text{ atm x } 3.8\text{ L} = 0\text{ L•atm} = 0\text{ joules}$$

(b) $DV = 5.4\text{ L} - 1.6\text{ L} = 3.8\text{ L}$ $\quad P = 3.7\text{ atm}$

$$w = -3.7\text{ atm x } 3.8\text{ L} = -14.1\text{ L•atm}$$

$$w = -14.06\text{ L•atm x } \frac{101.3\text{ J}}{1\text{L•atm}} = -1424.3\text{ J}$$

- **The other component of internal energy is heat, *q*.**

1. **Heat flowing out from a system, q is negative,**
2. **Heat flowing into a system. $q > 0$**

Process	Sign
Work done by the system on the surroundings	−
Work done on the system by the surroundings	+
Heat absorbed by the system from the surroundings (endothermic process)	+
Heat absorbed by the surroundings from the system (exothermic process)	−

- **Example 3: The work done when a gas is compressed is 387 J. During this process, there is a heat transfer of 152 J from the gas to the surroundings. Calculate the energy change for this process.**
- **Solution**

  Work of compression is positive and because heat is released by the gas, *q* is negative.
- $U = q + w$

  $= - 152 \text{J} + 387 \text{ J}$

  $=235 \text{ J}$

Exercise

1. A gas expands from 264 mL to 971 mL at constant temperature. Calculate the work done (in joules) by the gas if it expands
   - A. Against a vacuum
   - B. Against a constant pressure of 4.00 atm.
2. A gas expands and does *P*-*V* work on the surroundings equal to 279 J. At the same time, it absorbs 216 J of heat from the surroundings. What is the change in energy of the system?
3. The work done to compress a gas is 74 J. As a result, 26 J of heat is given off to the surroundings. Calculate the change in energy of the gas.

Enthalpy of Chemical Reactions

- **Enthalpy is a property of substances that is related to the heat of reaction q_p.**
- **Enthalpy (denoted H) is *an extensive property of a substance that can be used to obtain the heat absorbed or evolved in a chemical reaction.***
- **Extensive property is a property that depends on the amount of substance. Other examples of extensive properties are mass and volume.**
- **Enthalpy change, ΔH, the quantity of heat transferred into or out of a system as it undergoes a chemical or physical change at constant pressure, q_p**
- $\Delta U = q + w$
- $= q_p - p\Delta v$

$$q_p = \Delta u + p\Delta v$$

$$\Delta H = q_p = \Delta u + p\Delta v$$

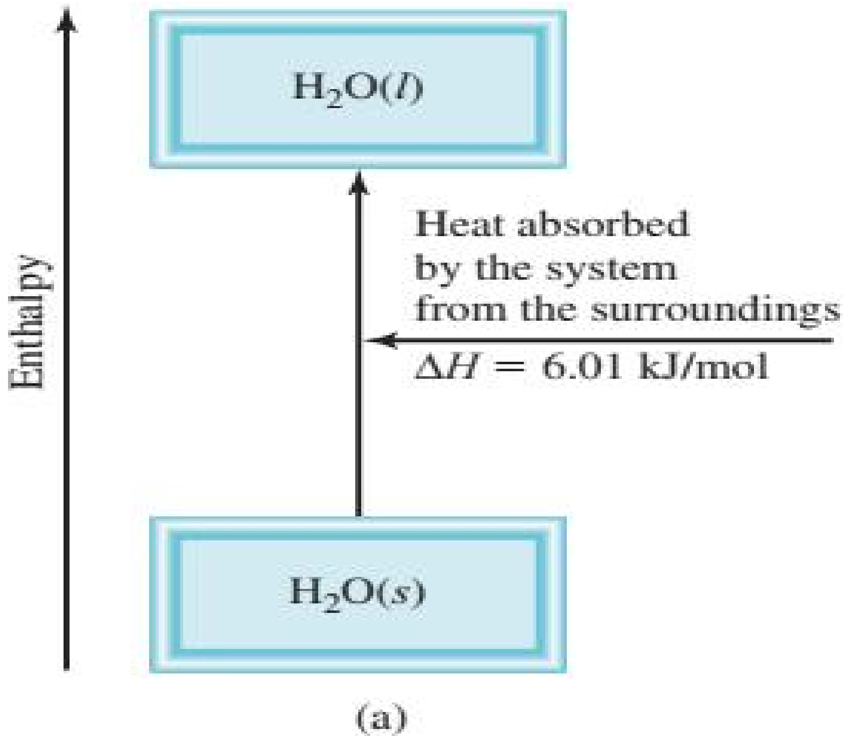
Enthalpy of Reactions

- ***Enthalpy of reaction,* D *H, as the difference between the enthalpies of the products and the enthalpies of the reactants:***
- **D *H* = *H*(products) - *H*(reactants)**

The enthalpy of reaction can be positive or negative, depending on the process.

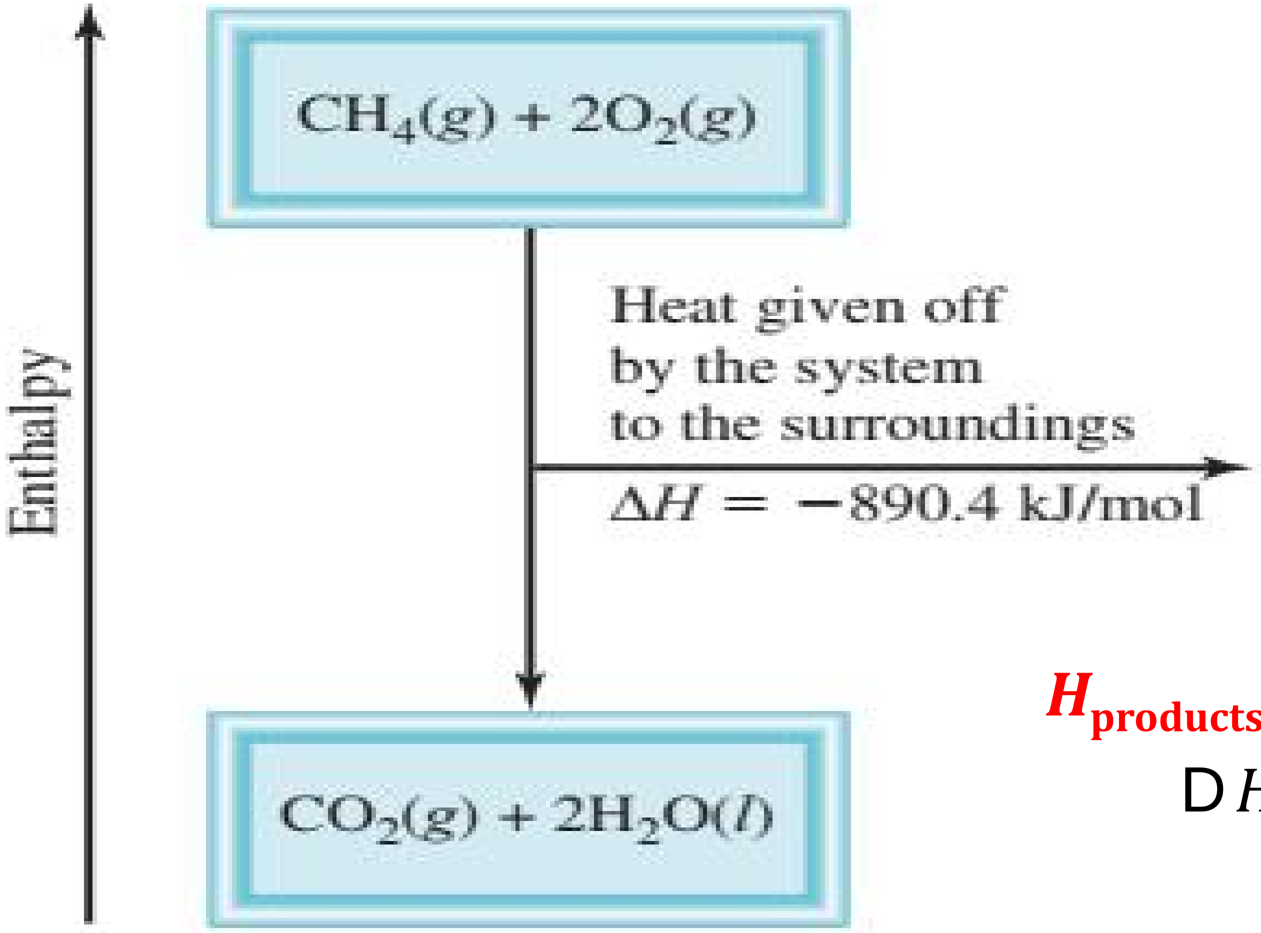
Endothermic process (heat absorbed by the system from the surroundings).

D *H* is positive



$H_{\text{products}} > H_{\text{reactants}}$

D $H > 0$



(b)

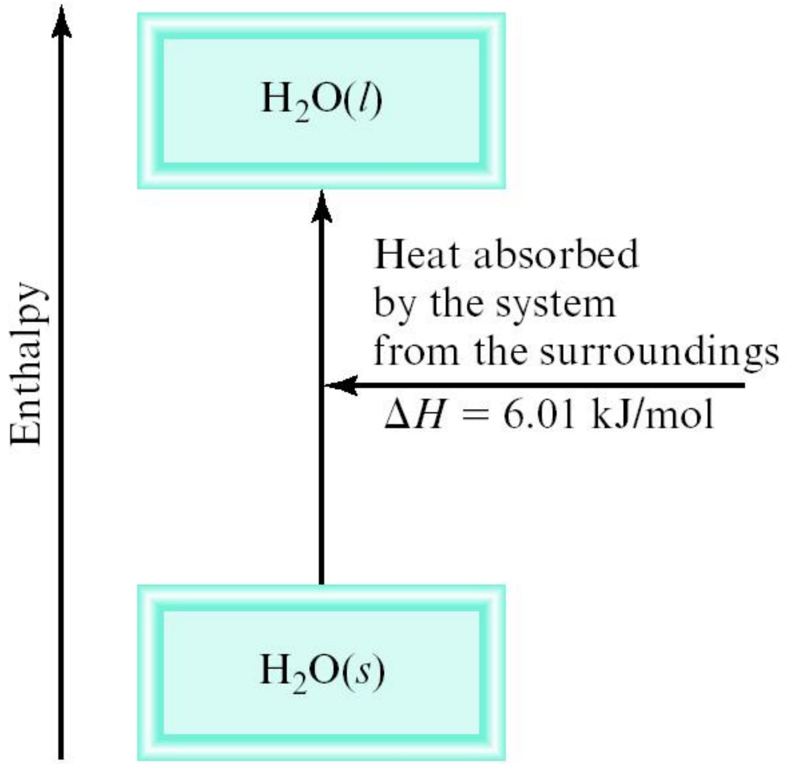
$H_{products} < H_{reactants}$

$\Delta H < 0$

Exothermic process (heat released by the system to the surroundings), ΔH is negative (that is, $\Delta H < 0$).

Thermochemical Equations

which *show the enthalpy changes as well as the mass relationships*



Is ΔH negative or positive?

System absorbs heat

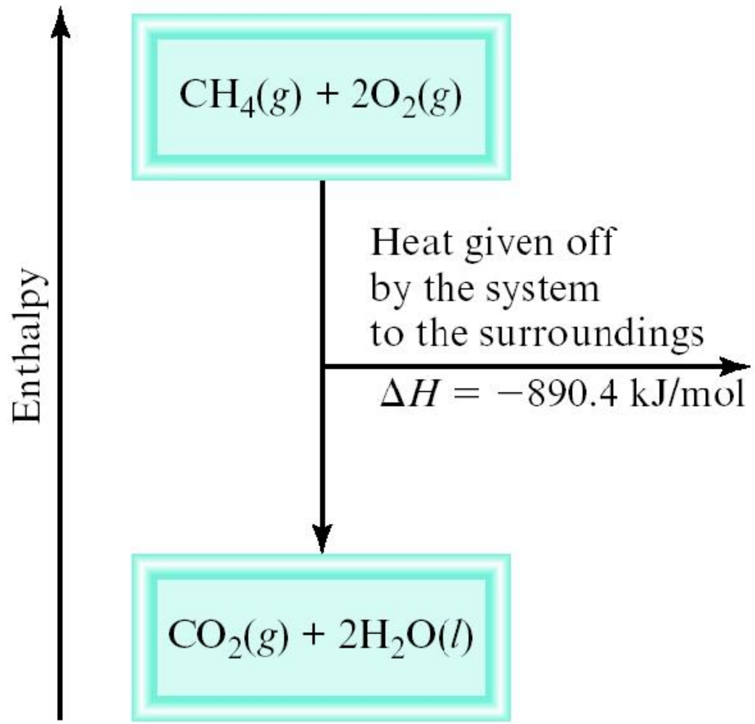
Endothermic

$\Delta H > 0$

6.01 kJ are absorbed for every 1 mole of ice that melts at 0^0C and 1 atm.

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

Thermochemical Equations



Is ΔH negative or positive?

System gives off heat

Exothermic

$\Delta H < 0$

890.4 kJ are released for every 1 mole of methane that is combusted at 25^0C and 1 atm.

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

- **The stoichiometric coefficients always refer to the number of moles of a substance.**

$$H_2O\ (s) \longrightarrow H_2O\ (l) \qquad DH = 6.01\ \mathrm{kJ/mol}$$

- **If you reverse a reaction, the sign of DH changes**

$$H_2O\ (l) \longrightarrow H_2O\ (s) \quad \Delta H = -6.01\ \mathrm{kJ/mol}$$

- **If you multiply both sides of the equation by a factor *n*, then DH must change by the same factor *n*.**

$$2H_2O\ (s) \longrightarrow 2H_2O\ (l) \quad DH = 2 \times 6.01 = 12.0\ \mathrm{kJ}$$

- **The physical states of all reactants and products must be specified in thermochemical equations.**

$$H_2O\ (s) \longrightarrow H_2O\ (l) \qquad \Delta H = 6.01\ \mathrm{kJ/mol}$$

$$H_2O\ (l) \longrightarrow H_2O\ (g) \qquad \Delta H = 44.0\ \mathrm{kJ/mol}$$

Example:4

- **Given the thermochemical equation**

$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$ DH = -198.2KJ

- **Calculate the heat evolved when 93.4 g of SO_2 (molar mass = 64.07 g/mol) is converted to SO_3.**

solution

- Form the reaction equation

2 mole of SO_2 = -198.2 kj/mol

Mole of SO_2 = 93.4g/64 g/mol = 1.46 mol

$$\Delta H = 93.4\ \cancel{\text{g SO}_2} \times \frac{1\ \cancel{\text{mol SO}_2}}{64.07\ \cancel{\text{g SO}_2}} \times \frac{-198.2\ \text{kJ}}{2\ \cancel{\text{mol SO}_2}} = \boxed{-144\ \text{kJ}}$$

- **How much heat is evolved when 266 g of white phosphorus (P_4) burn in air?**

$P_4\,(s) + 5O_2\,(g) \longrightarrow P_4O_{10}\,(s)$ DH = -3013 kJ/mol

A Comparison of ΔH and ΔU

- **What is the relationship between ΔH and ΔU for a process?**
- $\Delta U = \Delta H - P\Delta V$
- **In ideal gas behavior and constant temperature.**

$$Pv = nRT$$

$$\Delta U = \Delta H - \Delta(nRT)$$
$$= \Delta H - RT\Delta n$$

- ***n* = number of moles of product - number of moles of reactant**
- **R –ideal gas constant= 8.314J/K.mol**

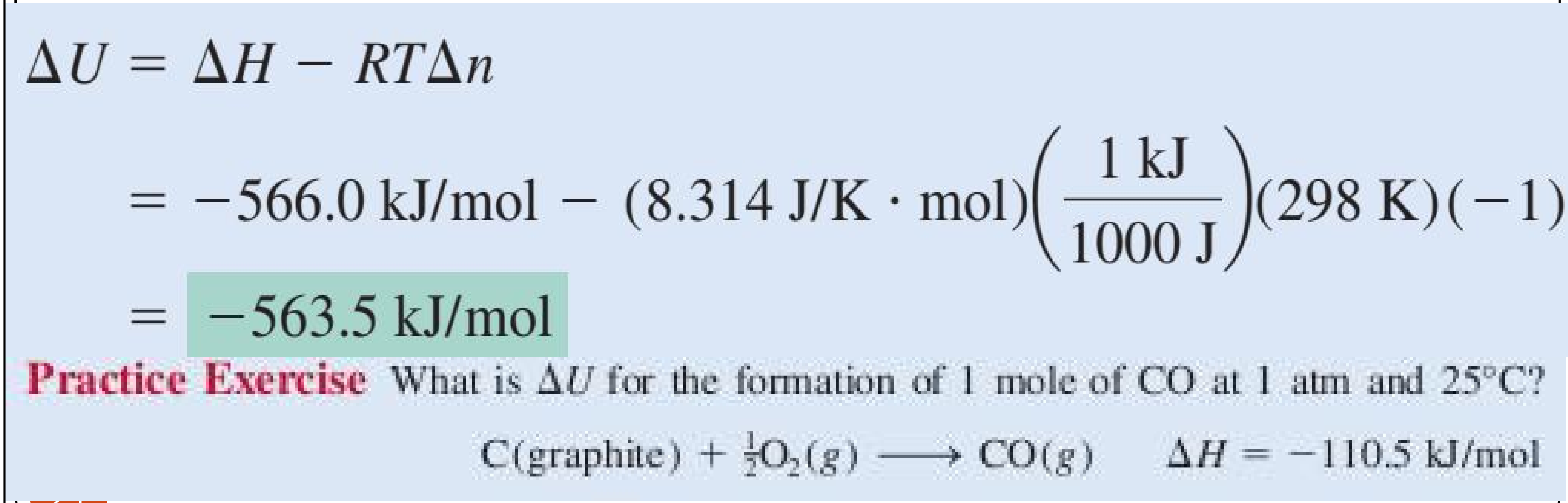
- **Example 5:** **Calculate the change in internal energy when 2 moles of CO are converted to 2 moles of CO_2 at 1 atm and 25°C:**

  $2CO(g) + O_2(g) \longrightarrow 2CO_2(g) \qquad \mathrm{D}\,H = -566.0\ \text{kJ/mol}$

- Solution
- $\mathrm{D}\,n$ = moles of product - moles of reactant

  $= 2\text{-}3$

  $= -1$



$$\Delta U = \Delta H - RT\Delta n$$

$$= -566.0\ \text{kJ/mol} - (8.314\ \text{J/K}\cdot\text{mol})\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)(298\ \text{K})(-1)$$

$$= \boxed{-563.5\ \text{kJ/mol}}$$

Practice Exercise What is ΔU for the formation of 1 mole of CO at 1 atm and 25°C?

$$\text{C(graphite)} + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H = -110.5\ \text{kJ/mol}$$

Calorimetry

- **Heat changes in physical and chemical processes are measured with a *calorimeter***
- ***Calorimetry, the measurement of heat changes,* will depend on an understanding of specific heat and heat capacity.**

Specific Heat and Heat Capacity

- **Heat is required to raise the temperature of a given amount of substance and the quantity of heat (q) absorbed by an object is proportional to its temperature change:**

$$q \propto \Delta T \qquad \text{or} \qquad q = \text{constant} \times \Delta T \qquad \text{or} \qquad \frac{q}{\Delta T} = \text{constant}$$

- **Heat capacity (C) of a substance is the amount of heat required to raise the temperature of a given quantity of the substance by one degree Celsius**
- ***Heat capacity(s)=*** $\frac{q}{\mathrm{D\ \ T}}$ ***in unit J/K***

- The ***specific heat (s)* of a substance** is ***the amount of heat required to raise the temperature of one gram of the substance by one degree Celsius*.**
- ***specific heat capacity(s)=*** $\frac{q}{mass\ \Delta T}$ ***in unit J/g.K***

- **The relationship between the heat capacity and specific heat of a substance is**

  $C = ms$

  - ***m* is the mass of the substance in grams**
  - **s is *specific heat* of the substance**

- **Example 6: The specific heat capacity of water is 4.184 J/g . °C, find the heat capacity of 60.0 g of water.**
  - **60 g x 4.184J/g.^{0}C = 251 J/^{0}C**

Example: 7

- **A 394-g sample of water is heated from 10.75°C to 83.20°C. Calculate the amount of heat absorbed (in kilojoules) by the water.**

- **Solution**

$$
\begin{aligned}
q &= ms\Delta t \\
&= (394\ \text{g})(4.184\ \text{J/g}\cdot{}^\circ\text{C})(83.20^\circ\text{C} - 10.75^\circ\text{C}) \\
&= 1.19 \times 10^5\ \text{J} \times \frac{1\ \text{kJ}}{1000\ \text{J}} \\
&= 119\ \text{kJ}
\end{aligned}
$$

Because heat is absorbed by the water from the surroundings, it has a positive sign.

Exercise

1. **An iron bar of mass 869 g cools from 94°C to 5°C. The Specific heat of Fe is 0.444 (J/g .°C) .Calculate the heat released (in kilojoules) by the metal**

$$s \text{ of Fe} = 0.444 \text{ J/g} \bullet {}^{o}\text{C}$$

$$\Delta t = t_{\text{final}} - t_{\text{initial}} = 5^{o}\text{C} - 94^{o}\text{C} = -89^{o}\text{C}$$

$$q = ms\Delta t \quad = 869\ \cancel{\text{g}} \text{ x } 0.444 \text{ J}/\cancel{\text{g}} \bullet \cancel{{}^{o}\text{C}} \text{ x } -89\cancel{{}^{o}\text{C}} \qquad = -34{,}000 \text{ J}$$

2. **A piece of silver of mass 362 g has a heat capacity of 85.7 J/°C. What is the specific heat of silver?**
3. **A 6.22-kg piece of copper metal is heated from 20.5°C to 324.3°C. Calculate the heat absorbed (in kJ) by the metal.**

Standard Enthalpy of Formation and Reaction

- **Standard enthalpy of formation (ΔH^0) is the heat change that results when one mole of a compound is formed from its elements at a pressure of 1 atm.**

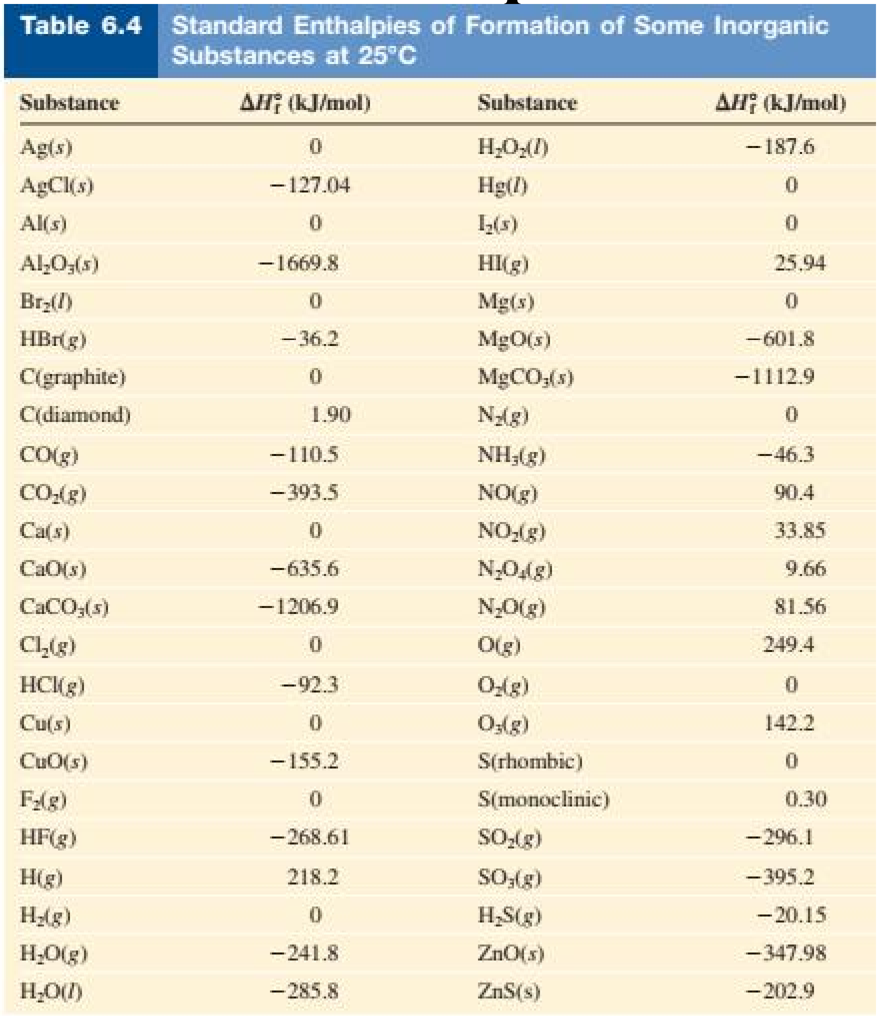


Table 6.4 Standard Enthalpies of Formation of Some Inorganic Substances at 25°C

Substance	ΔH_f° (kJ/mol)	Substance	ΔH_f° (kJ/mol)
Ag(*s*)	0	H_2O_2(*l*)	−187.6
AgCl(*s*)	−127.04	Hg(*l*)	0
Al(*s*)	0	I_2(*s*)	0
Al_2O_3(*s*)	−1669.8	HI(*g*)	25.94
Br_2(*l*)	0	Mg(*s*)	0
HBr(*g*)	−36.2	MgO(*s*)	−601.8
C(graphite)	0	$MgCO_3$(*s*)	−1112.9
C(diamond)	1.90	N_2(*g*)	0
CO(*g*)	−110.5	NH_3(*g*)	−46.3
CO_2(*g*)	−393.5	NO(*g*)	90.4
Ca(*s*)	0	NO_2(*g*)	33.85
CaO(*s*)	−635.6	N_2O_4(*g*)	9.66
$CaCO_3$(*s*)	−1206.9	N_2O(*g*)	81.56
Cl_2(*g*)	0	O(*g*)	249.4
HCl(*g*)	−92.3	O_2(*g*)	0
Cu(*s*)	0	O_3(*g*)	142.2
CuO(*s*)	−155.2	S(rhombic)	0
F_2(*g*)	0	S(monoclinic)	0.30
HF(*g*)	−268.61	SO_2(*g*)	−296.1
H(*g*)	218.2	SO_3(*g*)	−395.2
H_2(*g*)	0	H_2S(*g*)	−20.15
H_2O(*g*)	−241.8	ZnO(*s*)	−347.98
H_2O(*l*)	−285.8	ZnS(*s*)	−202.9

- ***Standard enthalpy of reaction,* D*H°rxn*, defined as *the enthalpy of a reaction carried out at 1 atm*.**

$$aA + bB \longrightarrow cC + dD$$

$$\Delta H^0_{rxn} = \Sigma n\Delta H^0_f(\text{products}) - \Sigma m\Delta H^0_f(\text{reactants})$$

$$\Delta H^0_{rxn} = [c\Delta H^0_f(C) + d\Delta H^0_f(D)] - [a\Delta H^0_f(A) + b\Delta H^0_f(B)]$$

Example 8: **Benzene (C_6H_6) burns in air to produce carbon dioxide and liquid water. How much heat is released per mole of benzene combusted? The standard enthalpy of formation of benzene is 49.04 kJ/mol.**

$$2C_6H_6\,(l) + 15O_2\,(g) \longrightarrow 12CO_2\,(g) + 6H_2O\,(l)$$

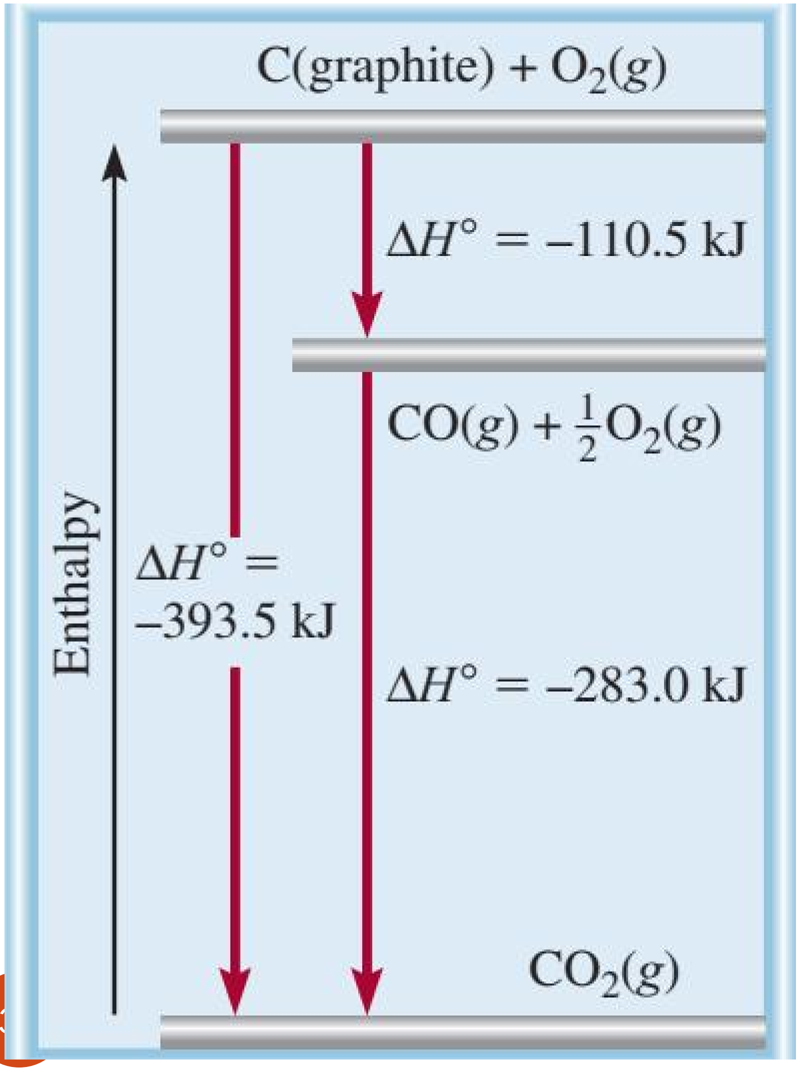
$$\Delta H^0_{rxn} = \Sigma n\Delta H^0_f(\text{products}) - \Sigma m\Delta H^0_f(\text{reactants})$$

$$\Delta H^0_{rxn} = [\,12\Delta H^0_f(CO_2) + 6\Delta H^0_f(H_2O)] - [\,2\Delta H^0_f(C_6H_6)]$$

$$\Delta H^0_{rxn} = [\,12\text{x}{-393.5} + 6\text{x}{-285.8}] - [\,2\text{x}49.04\,] = -6534.8\text{ kJ}$$

$$\frac{-6534.8\text{ kJ}}{2\text{ mol}} = -\,3267.4\text{ kJ/mol } C_6H_6$$

- ***Hess's law stated*** **:** ***When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.***



$$C\ (graphite) + 1/2O_2\ (g) \longrightarrow CO\ (g)$$

$$CO\ (g) + 1/2O_2\ (g) \longrightarrow CO_2\ (g)$$

$$C\ (graphite) + O_2\ (g) \longrightarrow CO_2\ (g)$$

- **Example 9: Calculate the standard enthalpy of formation of acetylene (C_2H_2) from its elements:**

$$2C(\text{graphite}) + H_2(g) \longrightarrow C_2H_2(g)$$

The equations for each step and the corresponding enthalpy changes are

A. $C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H^\circ_{rxn} = -393.5\ \text{kJ/mol}$

B. $H_2(g) + 1/2O_2(g) \longrightarrow H_2O(l) \quad \Delta H^\circ_{rxn} = -285.8\ \text{kJ/mol}$

C. $2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(l) \quad \Delta H^\circ_{rxn} = -2598.8\ \text{kJ/mol}$

Solution

- **Synthesis of C_2H_2, need 2 moles of graphite as reactant. So multiply equation (a) by 2 .**

d. $2C(\text{graphite}) + 2O_2(g) \longrightarrow 2CO_2(g) \quad \Delta H^\circ_{rxn} = -787.0\ \text{kJ/mol}$

- **1 mole of C_2H_2 as a product formed but Equation (c) has 2 moles of C_2H_2 as a reactant so we need to reverse the equation and divide it by 2:**

e. $2CO_2(g) + H_2O(l) \longrightarrow C_2H_2(g) + 5/2O_2(g) \quad \Delta H^\circ rxn = 1/2(2598.8\ \text{kJ/mol})$

$= 1299.4\ \text{kJ/mol}$

- **Finally Adding Equations (d), (b), and (e) together**

- $2C(\text{graphite}) + \cancel{2O_2(g)} \longrightarrow \cancel{2CO_2(g)}$ $\Delta H^\circ_{rxn} = -787.0$ kJ/mol
- $H_2(g) + \cancel{1/2O_2(g)} \longrightarrow \cancel{H_2O(l)}$ $\Delta H^\circ_{rxn} = -285.8$ kJ/mol
- $\cancel{2CO_2(g)} + \cancel{H_2O(l)} \longrightarrow C_2H_2(g) + \cancel{5/2O_2(g)}$ $\Delta H^\circ_{rxn} = 1299.4$ kJ/mol

- $2C(\text{graphite}) + H_2(g) \longrightarrow C_2H_2(g)$ $\Delta H^\circ_{rxn} = 226.6$ kJ/mol

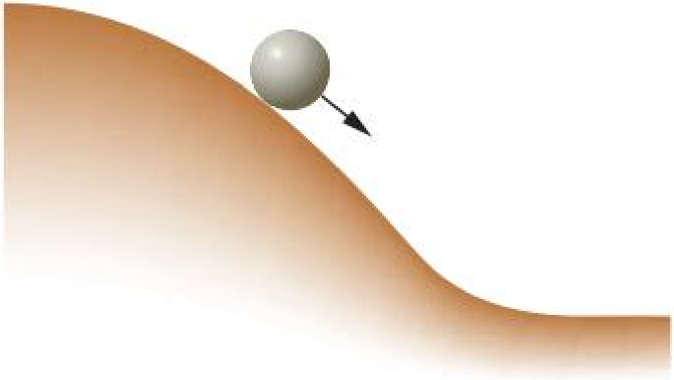
- This means that when 1 mole of C_2H_2 is synthesized from 2 moles of C (graphite) and 1 mole of H_2, 226.6 kJ of heat absorbed by the reacting system from the surroundings.

Endothermic process

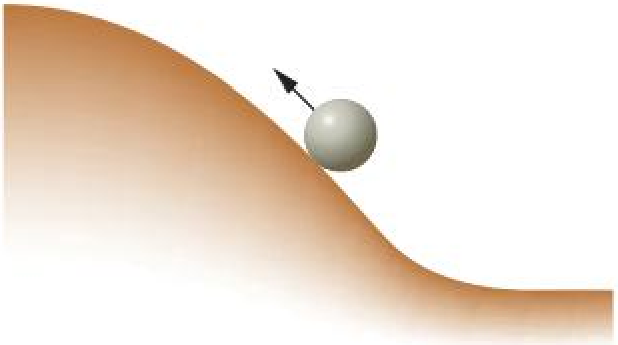
- **Exercise:** Calculate the standard enthalpy of formation of carbon disulfide (CS_2) from its elements, given that
  - $C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H^\circ rxn = -393.5$ kJ/mol
  - $S(\text{rhombic}) + O_2(g) \longrightarrow SO_2(g)$ $\Delta H^\circ rxn = -296.4$ kJ/mol
  - $CS_2(l) + 3O_2(g) \longrightarrow CO2(g) + 2SO_2(g)$ $\Delta H^\circ rxn = -1073.6$ kJ/mol

Spontaneous process

- A spontaneous process is *a physical or chemical change that occurs by itself.*
- **Processes occur spontaneously or naturally, without requiring an outside force or agency.**
  - **Examples**
  - **A rock at the top of a hill rolls down.**
  - **Heat flows from a hot object to a cold one.**
  - **Rusting of iron in moisture air.**



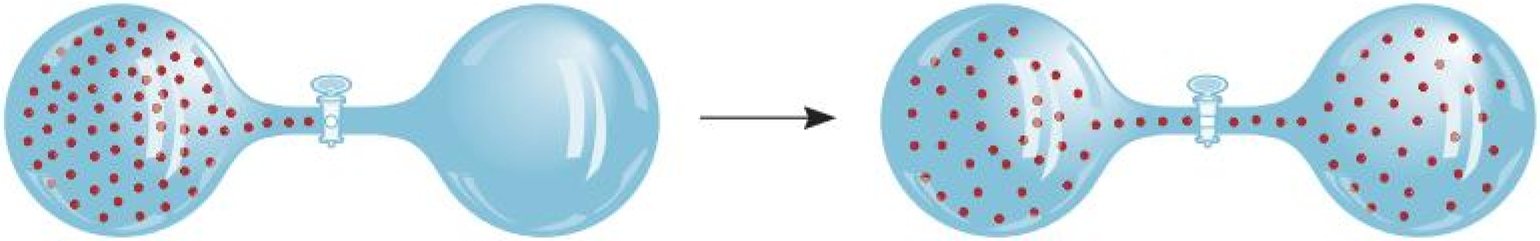
Spontaneous process



Nonspontaneous process

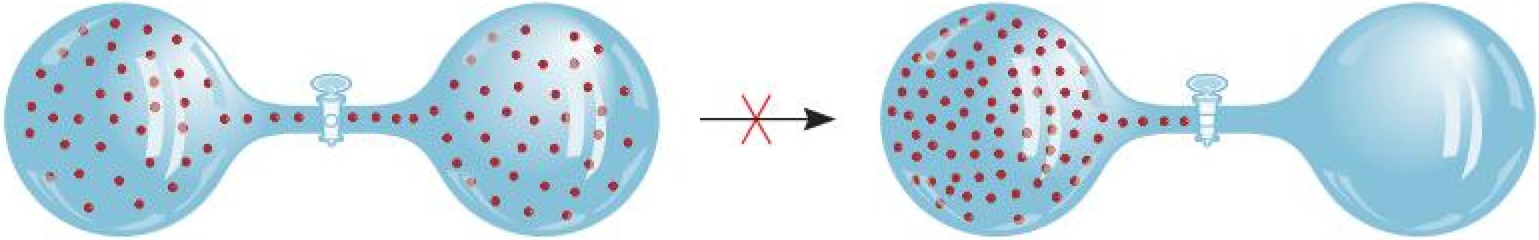
The rolling of a rock uphill is a nonspontaneous process.

- **The expansion of a gas into an evacuated bulb is a spontaneous process.**
- **Continue until equilibrium is reached.**



(a)

Spontaneous process.



(b)

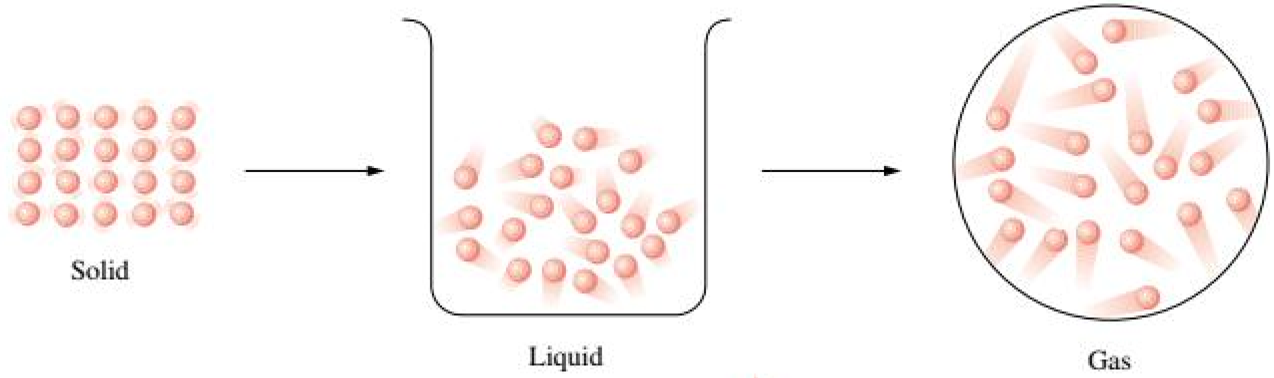
The reverse process, that is, the gathering of all the molecules into one bulb, is not spontaneous

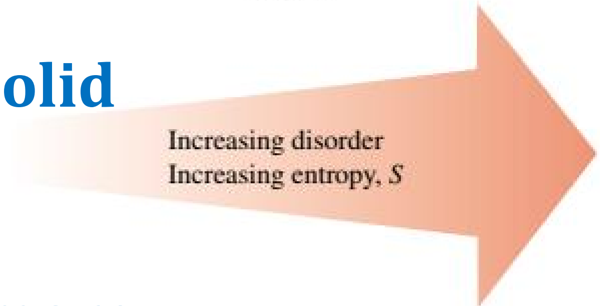
Nonspontaneous Process.

Under a given set of conditions, if a change is spontaneous in one direction, it is nonspontaneous in the other!

Entropy

- To predict the spontaneity of a process, introduce a new thermodynamic quantity called entropy.
- **Entropy(*S*) is a measure of the disorder of the system.**
- The greater the disorder of a system, the higher is its entropy.





As a sample changes from solid to liquid to gas

- its particles become increasingly less ordered (more disordered), so its entropy increases.

Second Law of Thermodynamics

- **The connection between entropy and the spontaneity of a reaction is expressed by the *second law of thermodynamics:***
- ***Second law of thermodynamics* which is states that *the entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process.***

- **For a spontaneous process:** $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$
- **For an equilibrium process:** $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$

Entropy Changes in the System(ΔS_{sys})

- **Suppose that the system is represented by the following reaction:**

$$aA + bB \longrightarrow cC + dD$$

- **The *standard entropy of reaction* ΔS^{0}_{rxn} is given by *the difference in standard entropies between products and reactants:***

$$\Delta S^\circ_{\mathrm{rxn}} = \Sigma n S^\circ(\mathrm{products}) - \Sigma m S^\circ(\mathrm{reactants})$$

$$\Delta S^\circ_{\mathrm{rxn}} = [cS^\circ(\mathrm{C}) + dS^\circ(\mathrm{D})] - [aS^\circ(\mathrm{A}) + bS^\circ(\mathrm{B})]$$

Example 9:

- **Calculate the standard entropy changes for the following reactions at 25°C using the following given data.**

Some Standard Entropy Values (S^O) for Some Substances at 25^0C

substances	S^O of the Substance (J/K.mol)
$CaCO_3(s)$	92.9
$CaO(s)$	39.8
$CO_2(g)$	213.6
$N_2(g)$	192
$NH_3(g)$	193
$H_2(g)$	131
$Cl_2(g)$	223
$HCl(g)$	187

A. $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

B. $N_2(g)\ \ 3H_2(g) \longrightarrow 2NH_3(g)$

$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

Solution

(a) $\Delta S^\circ_{\text{rxn}} = [S^\circ(\text{CaO}) + S^\circ(\text{CO}_2)] - [S^\circ(\text{CaCO}_3)]$

$= [(39.8\ \text{J/K}\cdot\text{mol}) + (213.6\ \text{J/K}\cdot\text{mol})] - (92.9\ \text{J/K}\cdot\text{mol})$

$= \boxed{160.5\ \text{J/K}\cdot\text{mol}}$

Thus, when 1 mole of $CaCO_3$ decomposes to form 1 mole of CaO and 1 mole of gaseous CO_2, there is an increase in entropy equal to 160.5 J/K · mol.

(b) $\Delta S^\circ_{\text{rxn}} = [2S^\circ(\text{NH}_3)] - [S^\circ(\text{N}_2) + 3S^\circ(\text{H}_2)]$

$= (2)(193\ \text{J/K}\cdot\text{mol}) - [(192\ \text{J/K}\cdot\text{mol}) + (3)(131\ \text{J/K}\cdot\text{mol})]$

$= \boxed{-199\ \text{J/K}\cdot\text{mol}}$

This result shows that when 1 mole of gaseous nitrogen reacts with 3 moles of gaseous hydrogen to form 2 moles of gaseous ammonia, there is a decrease in entropy equal to −199 J/K · mol.

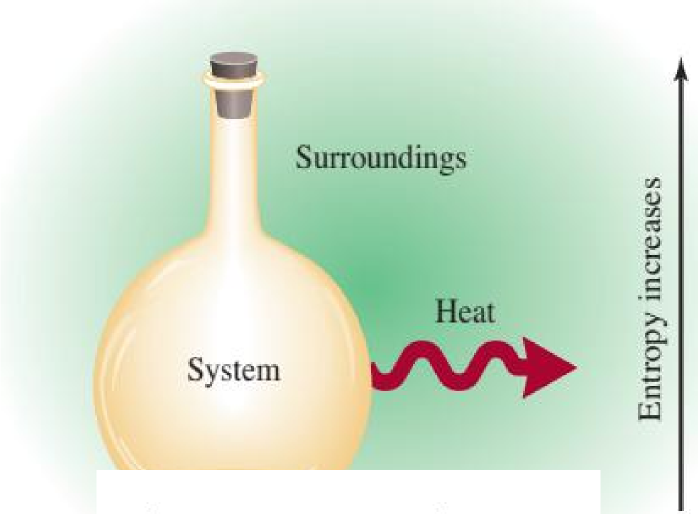
(c) $\Delta S^\circ_{\text{rxn}} = [2S^\circ(\text{HCl})] - [S^\circ(\text{H}_2) + S^\circ(\text{Cl}_2)]$

$= (2)(187\ \text{J/K}\cdot\text{mol}) - [(131\ \text{J/K}\cdot\text{mol}) + (223\ \text{J/K}\cdot\text{mol})]$

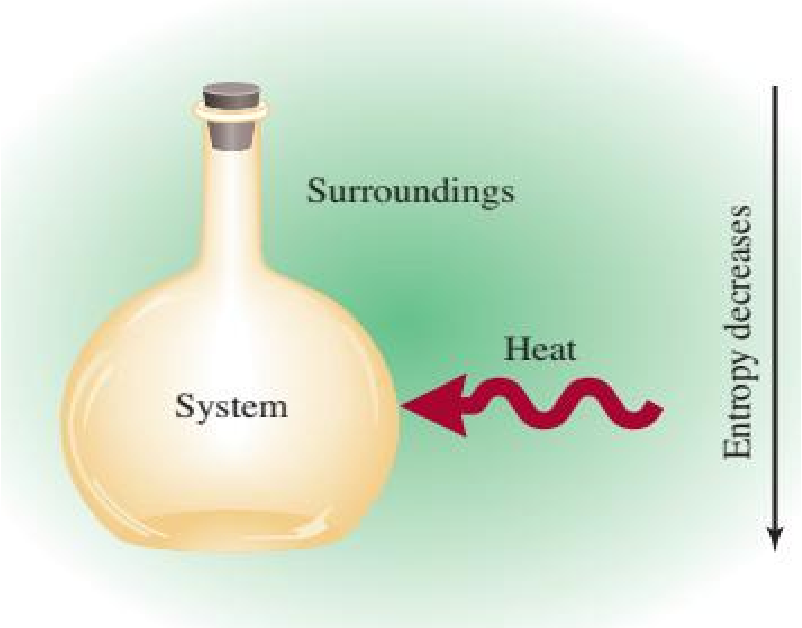
$= \boxed{20\ \text{J/K}\cdot\text{mol}}$

Entropy Changes in the Surroundings(ΔS_{surr})

- **Exothermic process**
- **The system released heat to the surroundings and enhances motion of the molecules in the surroundings.**
- **An endothermic process**
- **The system absorbs heat from the surroundings and so decreases the entropy of the surroundings because molecular motion decreases.**



$$\Delta S_{surr} \propto -\Delta H_{sys}$$



(b)

- The change in entropy for a given amount of heat absorbed also depends on the temperature.
- If the temperature of the surroundings is high, the molecules are already quite energetic.
- Absorption of heat from an exothermic process in the system will have relatively little impact on molecular motion
- The resulting increase in entropy of the surroundings will be small.

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T}$$

- Example 10
- Calculating ΔS_{univ} to the synthesis of ammonia ΔS_{sys} is -199 J/K.mol, and whether the reaction is spontaneous at 25°C:

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \quad \Delta H^\circ_{\text{rxn}} = -92.6\ \text{kJ/mol}$$

Solution

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T}$$

$$\Delta S_{\text{surr}} = \frac{-(-92.6 \times 1000)\ \text{J/mol}}{298\ \text{K}} = 311\ \text{J/K} \cdot \text{mol}$$

- **The change in entropy of the universe is**

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}}\\ &= -199\ \text{J/K}\cdot\text{mol} + 311\ \text{J/K}\cdot\text{mol}\\ &= 112\ \text{J/K}\cdot\text{mol}\end{aligned}$$

- **Because ΔS_{univ} is positive, reaction is spontaneous at 25°C.**

Third Law of Thermodynamics

- Third law of thermodynamics states that the entropy of a perfect crystalline substance is zero at the absolute zero of temperature.
- Molecular motions are kept at a minimum and the number of microstates (W) is one (there is only one way to arrange the atoms or molecules to form a perfect crystal)

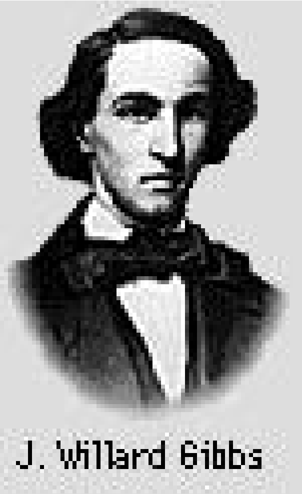
$$S = k \ln W$$

$$= k \ln 1 = 0$$

Gibbs Free Energy

- The second law of thermodynamics tells us that a spontaneous reaction increases the entropy of the universe;

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$$



J. Willard Gibbs

- Substituting $-\Delta H_{sys}/T$ for ΔS_{surr}, we write

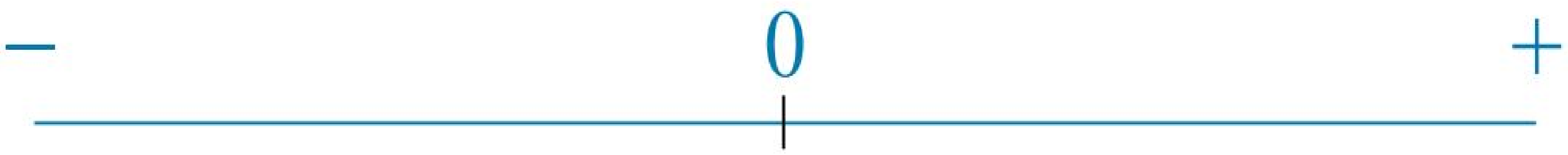
$$\Delta S_{univ} = \Delta S_{sys} - \frac{\Delta H_{sys}}{T} > 0$$

- Multiplying both sides of the equation by $-T$ gives

$$-T\Delta S_{univ} = \Delta H_{sys} - T\Delta S_{sys} < 0$$

$$\Delta G^o_{sys} = \Delta H^o_{sys} - T\Delta S^o_{sys}$$

ΔG	**Spontaneity of Reaction (constant T and P)**
ΔG is positive	Reaction is nonspontaneous (reactant-favored)
ΔG is zero	System is at equilibrium
ΔG is negative	Reaction is spontaneous (product-favored)



$\Delta G < 0$	$\Delta G > 0$
Reaction is spontaneous	Reaction is not spontaneous
Product-favored reaction	Reactant-favored reaction
Forward reaction is favored	Reverse reaction is favored

- $\Delta G^o_{sys} = \Delta H^o_{sys} - T\Delta S^o_{sys}$

ΔH	ΔS	ΔG
+	+	Reaction spontaneously at high temperatures and non-spontaneous at low temperatures
+	-	ΔG is always positive. Reaction is non-spontaneous in the forward direction and spontaneous in reverse direction at all temperatures.
-	+	ΔG always negative. Reaction proceeds spontaneously at all temperatures.
-	-	Reaction proceeds spontaneously at low temperatures. At high temperatures, the reverse reaction becomes spontaneous.

Temperature and Chemical Reactions

- **Calcium oxide (CaO), is an extremely valuable inorganic substance used in steelmaking, production of calcium metal, the paper industry, water treatment.**
- **It is prepared by decomposing limestone ($CaCO_3$) in a kiln at a high temperature**

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

- **The reaction is reversible and CaO readily combines with CO_2 to form $CaCO_3$.**
- **The value $\Delta H°$ and $\Delta S°$ 177.8 kJ/mol and 160.5 J/K.mol respectively**
- **Calculate free energy for the reaction at 25°C**

- **$\Delta G^o_{sys} = \Delta H^o_{sys} - T\Delta S^o_{sys}$**

$$\Delta G^\circ = 177.8\ \text{kJ/mol} - (298\ \text{K})(160.5\ \text{J/K}\cdot\text{mol})\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)$$
$$= 130.0\ \text{kJ/mol}$$

- **Because ΔG° is a large positive quantity, the reaction is not favored for product formation at 25°C (or 298 K).**
- **In order to make ΔG° negative, first have to find the temperature at which ΔG° is zero; that is,**

$$0 = \Delta H^\circ - T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$= \frac{(177.8\ \text{kJ/mol})(1000\ \text{J/1 kJ})}{160.5\ \text{J/K}\cdot\text{mol}}$$
$$= 1108\ \text{K or } 835^\circ\text{C}$$

- **At a temperature higher than 835°C, Δ*G*° becomes negative, indicating that the reaction now favors the formation of CaO and CO_2.**
- **For example, Calculate free energy at 840°C or 1113 K,**

$$
\begin{aligned}
\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\
&= 177.8\ \text{kJ/mol} - (1113\ \text{K})\ (160.5\ \text{J/K}\cdot\text{mol})\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right) \\
&= -0.8\ \text{kJ/mol}
\end{aligned}
$$

Phase Transitions

- **At the temperature at which a phase transition occurs (that is, at the melting point or boiling point) the system is at equilibrium ($\Delta G = 0$).**

$$\Delta G = \Delta H - T\Delta S$$
$$0 = \Delta H - T\Delta S$$

$$\Delta S = \frac{\Delta H}{T}$$

- **Let us first consider the ice-water equilibrium. For the ice - water transition, ΔH is the molar heat of fusion and T is the melting point. The entropy change is therefore**

$$\Delta S_{\text{ice} \longrightarrow \text{water}} = \frac{6010 \text{ J/mol}}{273 \text{ K}} = 22.0 \text{ J/K} \cdot \text{mol}$$

$$\Delta S_{\text{water} \longrightarrow \text{ice}} = \frac{-6010 \text{ J/mol}}{273 \text{ K}} = -22.0 \text{ J/K} \cdot \text{mol}$$

Example

- **The molar heats of fusion and vaporization of benzene are 10.9 kJ/mol and 31.0 kJ/mol, respectively. Calculate the entropy changes for the solid-liquid and liquid- vapor transitions for benzene. At 1 atm pressure, benzene melts at 5.5°C and boils at 80.1°C.**

The entropy change for melting 1 mole of benzene at 5.5°C is

$$\begin{aligned}\Delta S_{\text{fus}} &= \frac{\Delta H_{\text{fus}}}{\Delta T_{\text{f}}} \\ &= \frac{(10.9\ \text{kJ/mol})(1000\ \text{J/1 kJ})}{(5.5 + 273)\ \text{K}} \\ &= \boxed{39.1\ \text{J/K}\cdot\text{mol}}\end{aligned}$$

Similarly, the entropy change for boiling 1 mole of benzene at 80.1°C is

$$\begin{aligned}\Delta S_{\text{vap}} &= \frac{\Delta H_{\text{vap}}}{T_{\text{bp}}} \\ &= \frac{(31.0\ \text{kJ/mol})(1000\ \text{J/1 kJ})}{(80.1 + 273)\ \text{K}} \\ &= \boxed{87.8\ \text{J/K}\cdot\text{mol}}\end{aligned}$$

Free Energy and Chemical Equilibrium

$$DG = DG^0 + RT \ln Q$$

R is the gas constant (8.314 J/K•mol)

T is the absolute temperature (K)

Q is the reaction quotient

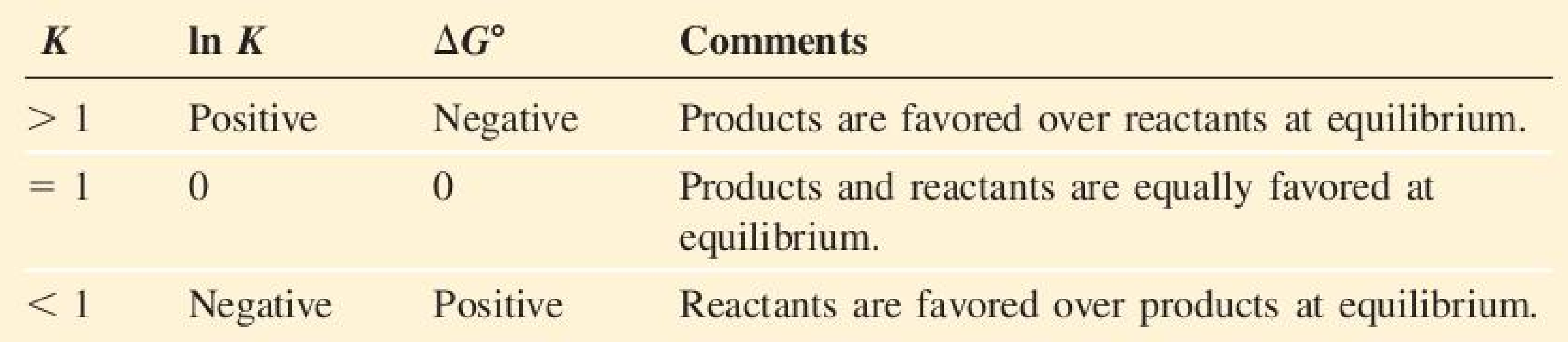
At Equilibrium

$$DG = 0 \qquad\qquad Q = K$$

$$0 = DG^0 + RT \ln K$$

$$DG^0 = - \ RT \ln K$$

Relation Between DG^{0} and K as Predicted by the Equation DG^{0} = -RT InK



K	ln K	$\Delta G°$	Comments
> 1	Positive	Negative	Products are favored over reactants at equilibrium.
= 1	0	0	Products and reactants are equally favored at equilibrium.
< 1	Negative	Positive	Reactants are favored over products at equilibrium.