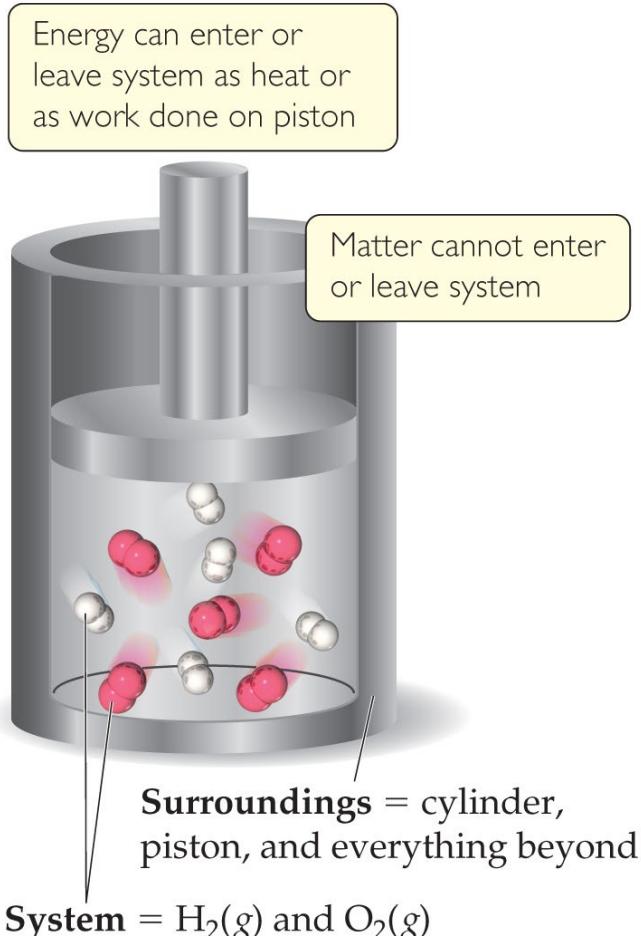


First Law of Thermodynamics

- Energy is neither created nor destroyed.
- In other words, the total energy of the universe is a constant; if the system loses energy, it must be gained by the surroundings, and vice versa.

Definitions: System and Surroundings

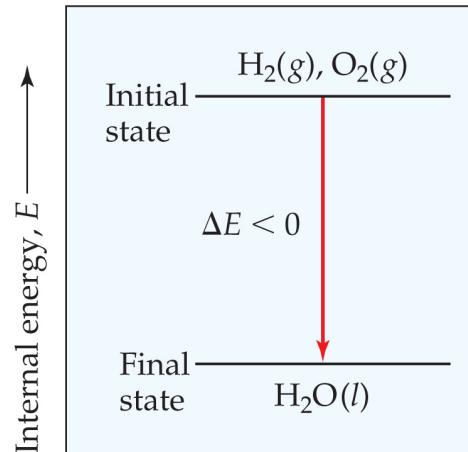


- The **system** includes the molecules we want to study (here, the hydrogen and oxygen molecules).
- The **surroundings** are everything else (here, the cylinder and piston).

Internal Energy

By definition, the change in internal energy, ΔE , is the final energy of the system minus the initial energy of the system:

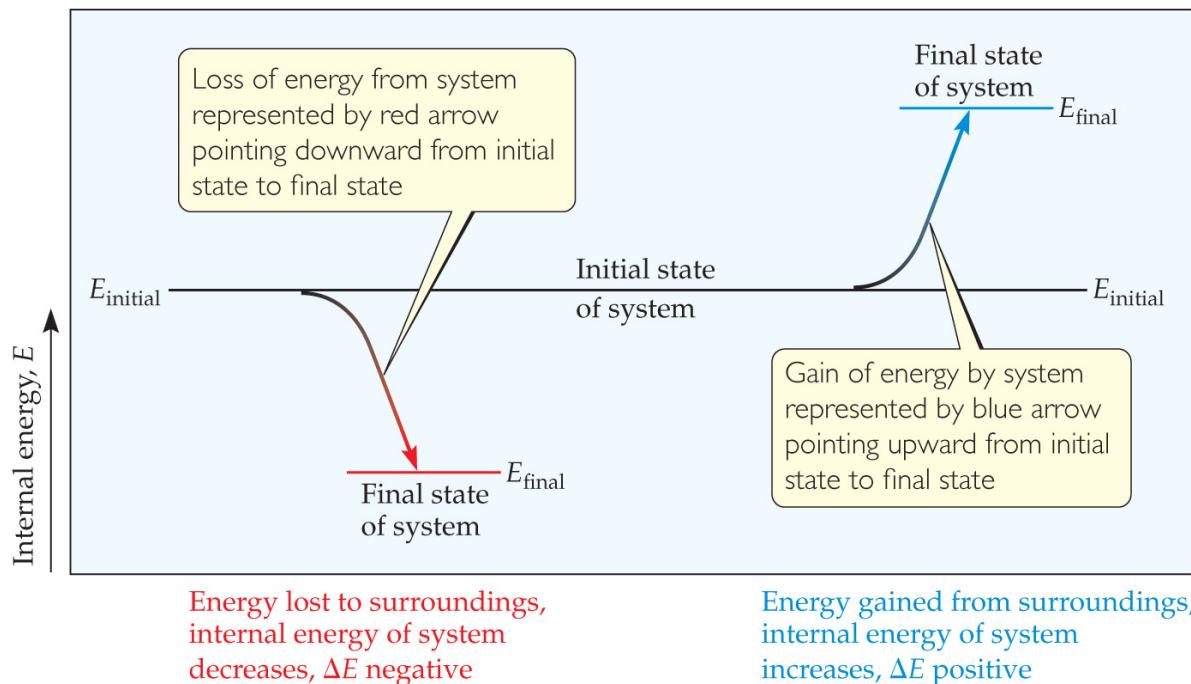
$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$



E_{initial} greater than E_{final} ; therefore, energy is released from system to surroundings during reaction and $\Delta E < 0$

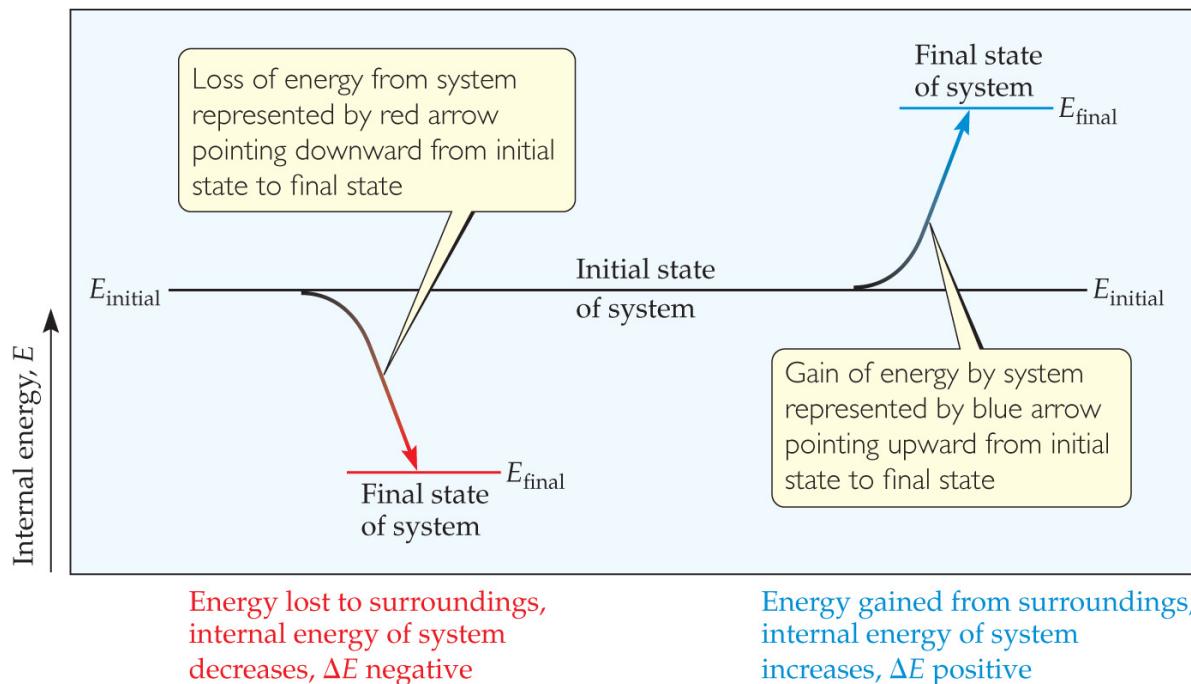
Changes in Internal Energy

- If $\Delta E > 0$, $E_{\text{final}} > E_{\text{initial}}$
 - Therefore, the system *absorbed* energy from the surroundings.
 - This energy change is called **endergonic**.

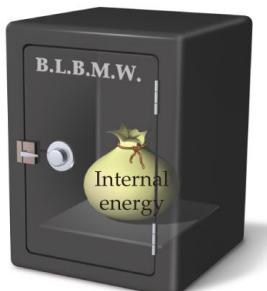


Changes in Internal Energy

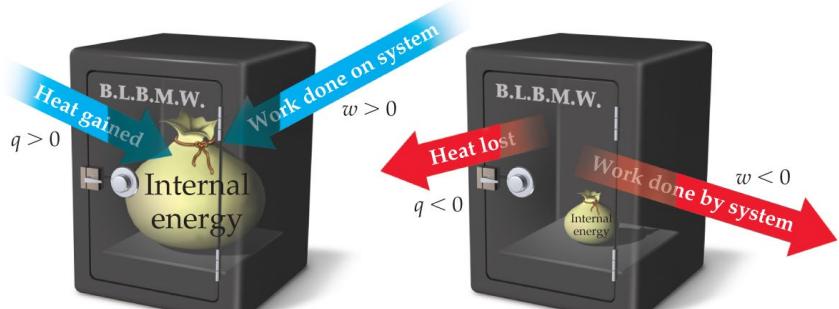
- If $\Delta E < 0$, $E_{\text{final}} < E_{\text{initial}}$
 - Therefore, the system *released* energy to the surroundings.
 - This energy change is called **exergonic**.



Changes in Internal Energy



System is interior of vault



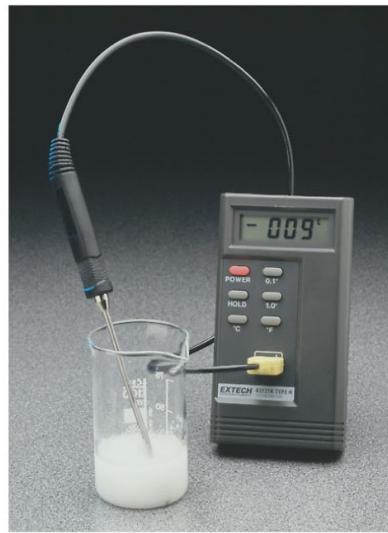
- When energy is exchanged between the system and the surroundings, it is exchanged as either heat (q) or work (w).
- That is, $\Delta E = q + w$.

Exchange of Heat between System and Surroundings

- When heat is absorbed by the system from the surroundings, the process is **endothermic**.

System: reactants + products

Surroundings: solvent,
initially at room temperature



(a) An endothermic reaction

Heat flows from surroundings into system, temperature of surroundings drops, thermometer reads temperature well below room temperature

Exchange of Heat between System and Surroundings

- When heat is released by the system into the surroundings, the process is **exothermic**.

System: reactants + products

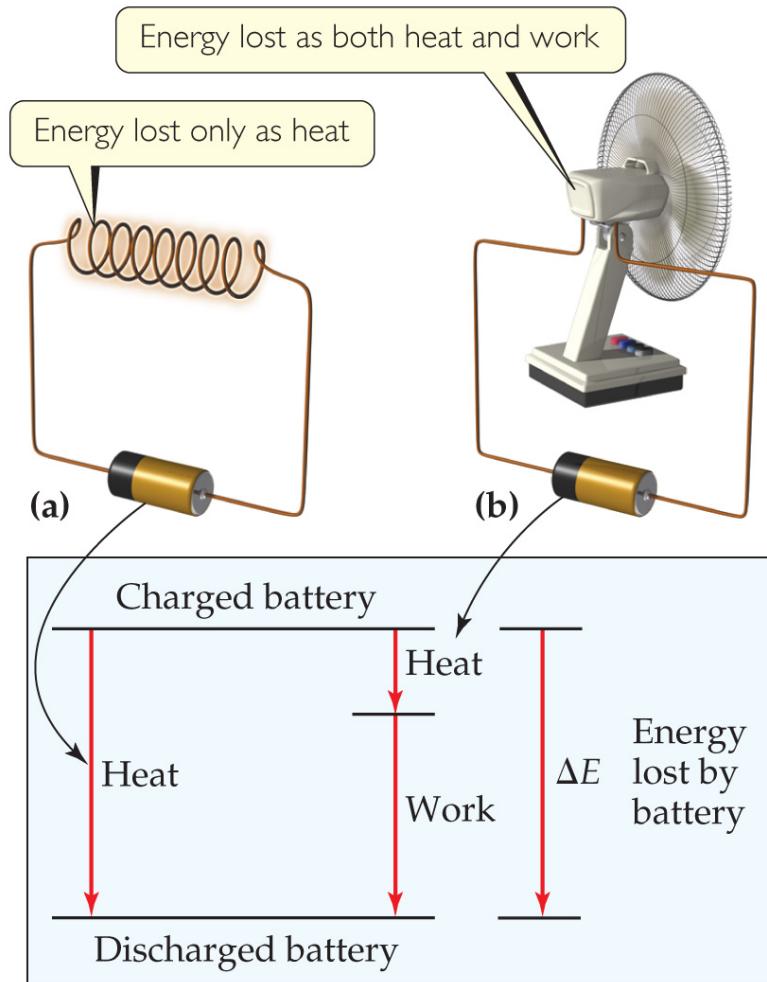
Surroundings:
air around reactants



(b) An exothermic reaction

Heat flows (violently) from system into surroundings, temperature of surroundings increases

State Functions



- However, q and w are *not* state functions.
- Whether the battery is shorted out or is discharged by running the fan, its ΔE is the same.
 - But q and w are different in the two cases.

Enthalpy

- Since $\Delta E = q + w$ and $w = -P\Delta V$, we can substitute these into the enthalpy expression:

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

$$\Delta H = (q + w) - w$$

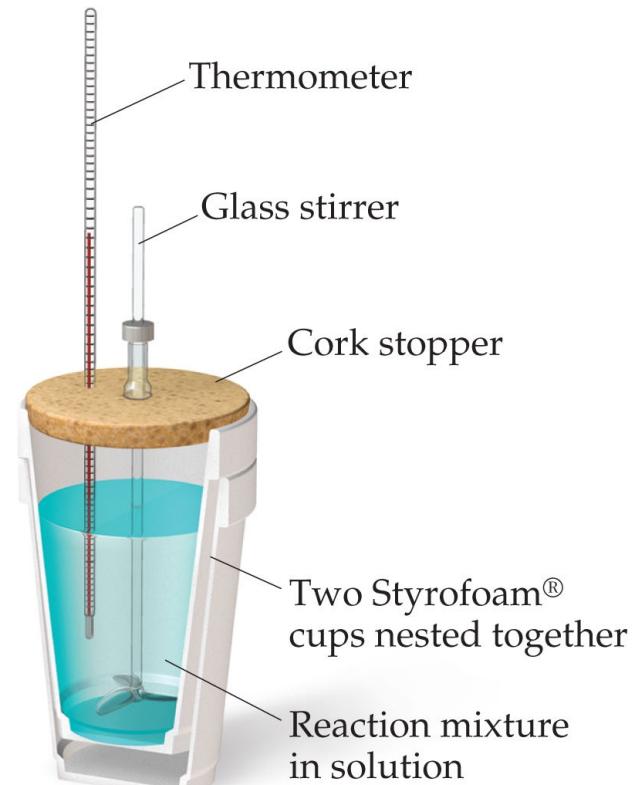
$$\Delta H = q$$

- So, at **constant pressure**, the change in enthalpy *is* the heat gained or lost.

Constant Pressure Calorimetry

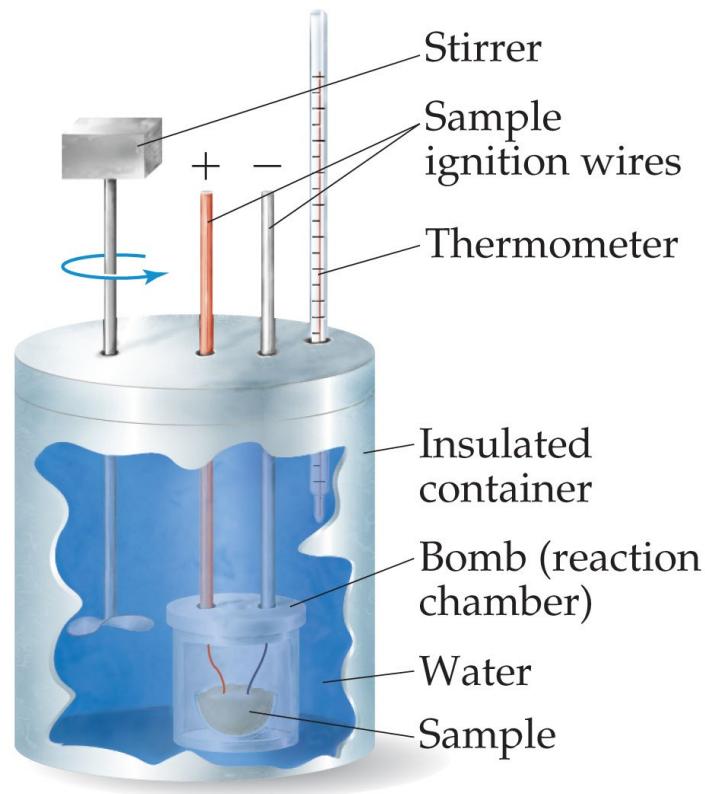
- By carrying out a reaction in aqueous solution in a simple calorimeter, the heat change for the system can be found by measuring the heat change for the water in the calorimeter.
- The specific heat for water is well known (4.184 J/g·K).
- We can calculate ΔH for the reaction with this equation:

$$q = m \times C_s \times \Delta T$$



Bomb Calorimetry

- Because the volume in the bomb calorimeter is constant, what is measured is really the change in internal energy, ΔE , not ΔH .
- For most reactions, the difference is very small.



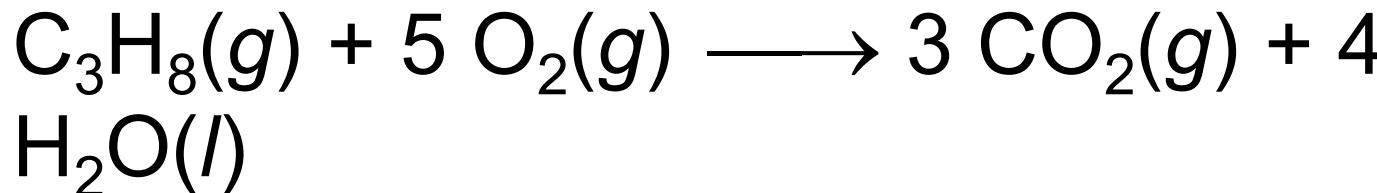
$$\Delta H = \Delta E + P\Delta V$$

Enthalpies of Formation

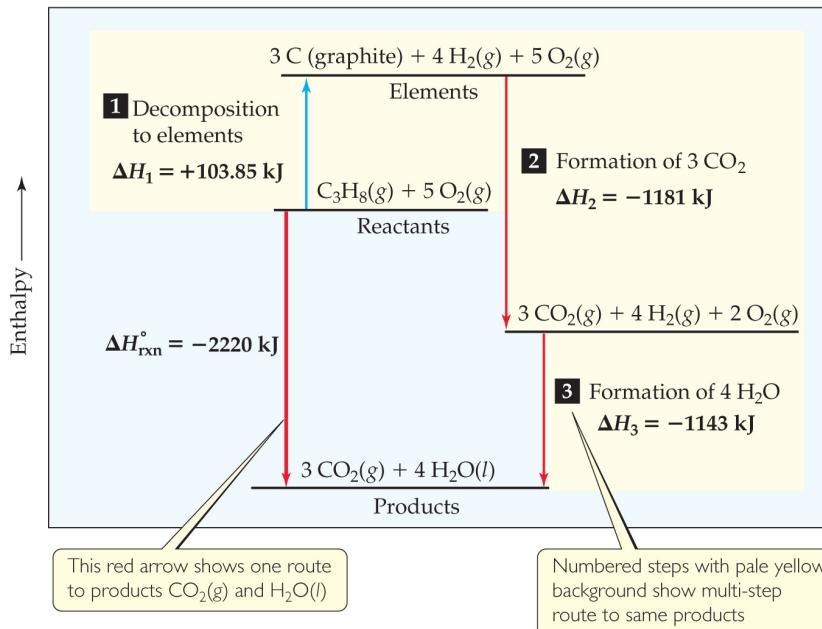
An **enthalpy of formation**, ΔH_f , is defined as the enthalpy change for the reaction in which **a compound is made from its constituent elements in their elemental forms.**



Calculation of ΔH using Values from the Standard Enthalpy Table



$$\begin{aligned}\Delta H &= [3(-393.5 \text{ kJ}) + 4(-285.8 \text{ kJ})] - [1(-103.85 \text{ kJ}) + 5(0 \text{ kJ})] \\ &= [(-1180.5 \text{ kJ}) + (-1143.2 \text{ kJ})] - [(-103.85 \text{ kJ}) + (0 \text{ kJ})] \\ &= (-2323.7 \text{ kJ}) - (-103.85 \text{ kJ}) = -2219.9 \text{ kJ}\end{aligned}$$



22) The reaction



is _____, and therefore heat is _____ by the reaction.

- A) endothermic, released
- B) endothermic, absorbed
- C) exothermic, released
- D) exothermic, absorbed
- E) thermoneutral, neither released nor absorbed

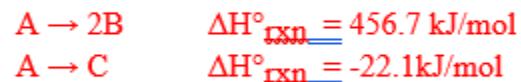
34) For which one of the following reactions is $\Delta H^\circ_{\text{rxn}}$ equal to the heat of formation of the product?

- A) $\text{N}_2 \text{ (g)} + 3\text{H}_2 \text{ (g)} \rightarrow 2\text{NH}_3 \text{ (g)}$
- B) $(1/2)\text{N}_2 \text{ (g)} + \text{O}_2 \text{ (g)} \rightarrow \text{NO}_2 \text{ (g)}$
- C) $6\text{C (s)} + 6\text{H (g)} \rightarrow \text{C}_6\text{H}_6 \text{ (l)}$
- D) $\text{P (g)} + 4\text{H (g)} + \text{Br (g)} \rightarrow \text{PH}_4\text{Br (l)}$
- E) $12\text{C (g)} + 11\text{H}_2 \text{ (g)} + 11\text{O (g)} \rightarrow \text{C}_6\text{H}_{22}\text{O}_{11} \text{ (g)}$

35) Of the following, ΔH_f° is not zero for _____.

- A) $\text{O}_2 \text{ (g)}$
- B) C (graphite)
- C) $\text{N}_2 \text{ (g)}$
- D) $\text{F}_2 \text{ (s)}$
- E) $\text{Cl}_2 \text{ (g)}$

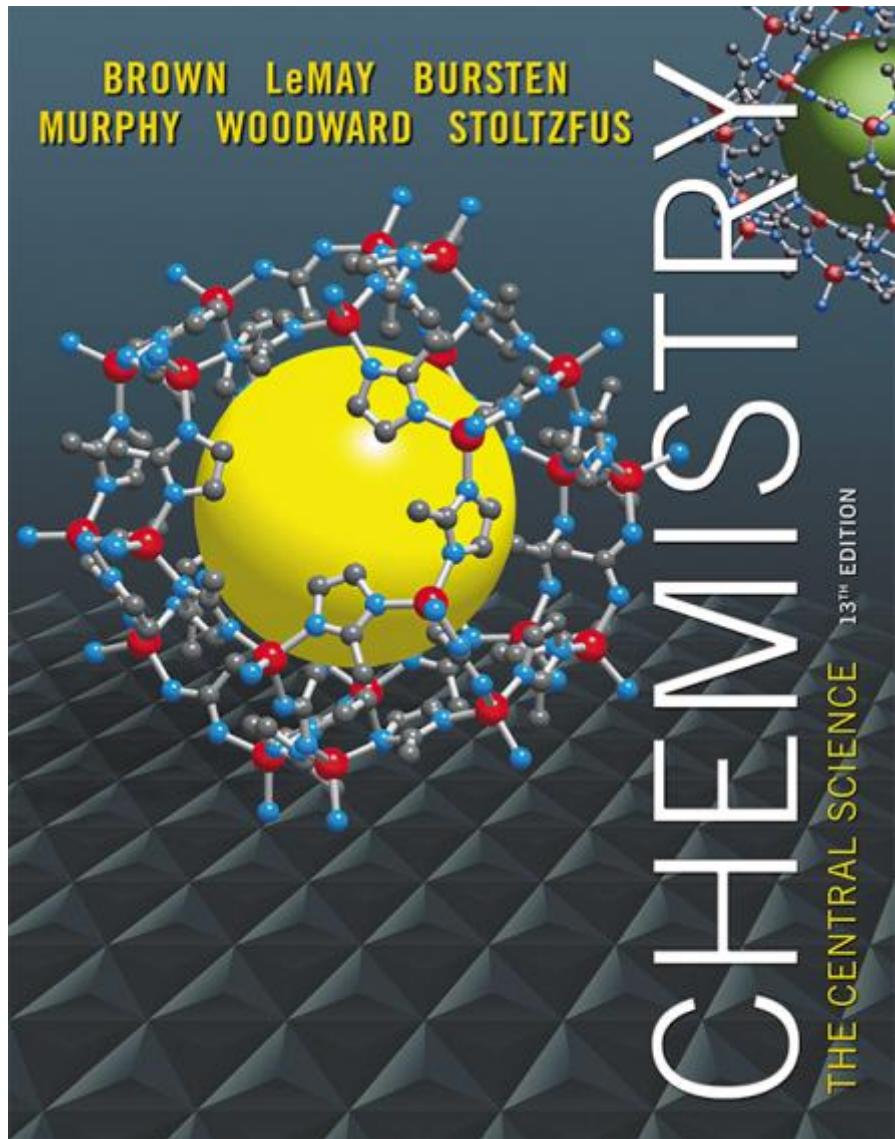
37) Consider the following two reactions:



Determine the enthalpy change for the process:



- A) -478.8 kJ/mol
- B) -434.6 kJ/mol
- C) 434.6 kJ/mol
- D) 478.8 kJ/mol
- E) More information is needed to solve the problem.



Lecture Presentation

Chapter 19

Chemical Thermodynamics

Questions: what's the similarity of the following phenomenon?

Why does **hot water get cold**?

Why does **an orderly desk become disorganized**?

Why is **laziness easier than self-discipline**?

Why is **sleep more acceptable than work**?

Why do dynasties always change, no matter how strong they are, they eventually will fall or are replaced ?

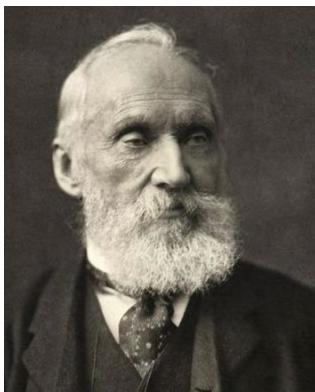
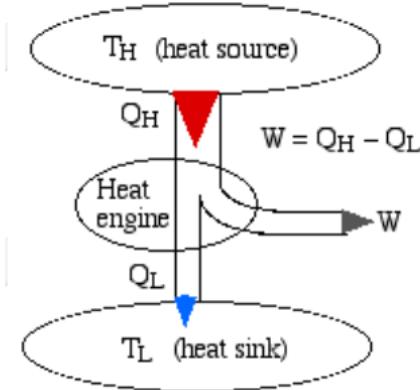
Spontaneous process

Involving energy change



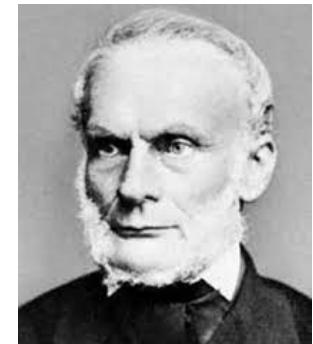
Carnot
1796–1832

Carnot's rule: All heat engines between two heat reservoirs are less efficient than a Carnot heat engine operating between the same reservoirs. The efficiency of the heat engine just depends on the temperature difference (ΔT)



Kelvins
1824-1907

It is impossible to convert the heat from a single source into work without any other effect.

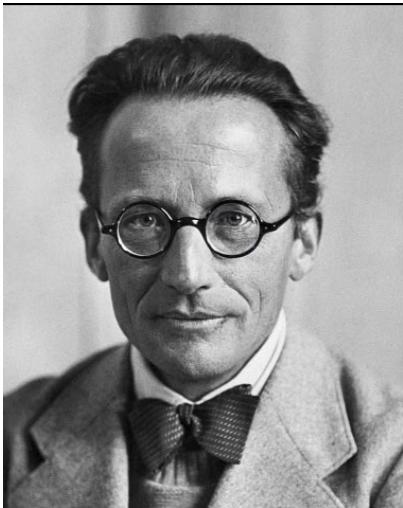


It is impossible to transfer heat from the low-temperature heat sources to a media with a higher temperature without providing the additional energy from an external source.

Clausius
1822–1888

Second law of thermodynamics

The entropy of the universe increases in any spontaneous process.



1943, Schrödinger introduced the entropy increase theory to biology



What is life?

The only reason life exists is to get negative entropy from the environment

First Law of Thermodynamics

- You will recall from Chapter 5 that energy cannot be created or destroyed.
- Therefore, the total energy of the universe is a constant.
- Energy can, however, be converted from one form to another or transferred from a system to the surroundings or vice versa.



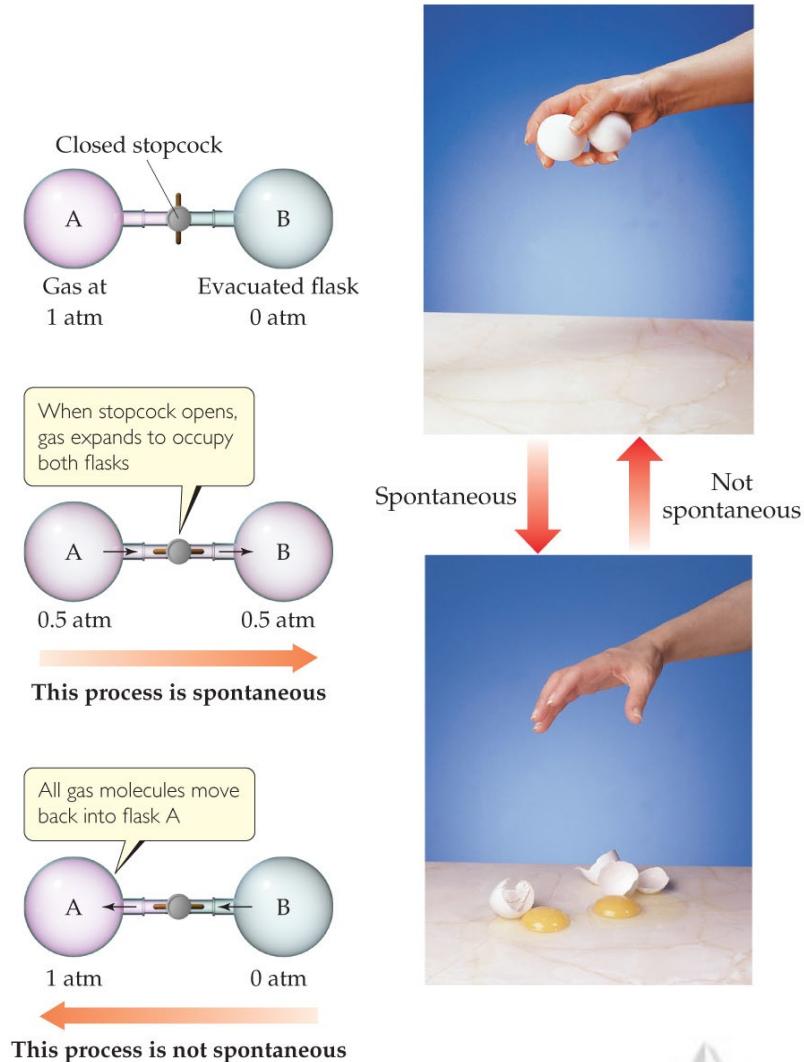
Enthalpy/Entropy

- Enthalpy is the heat absorbed by a system during a constant-pressure process.
- Entropy is a measure of the randomness in a system.
- Both play a role in determining whether a process is **spontaneous**.



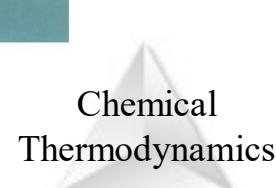
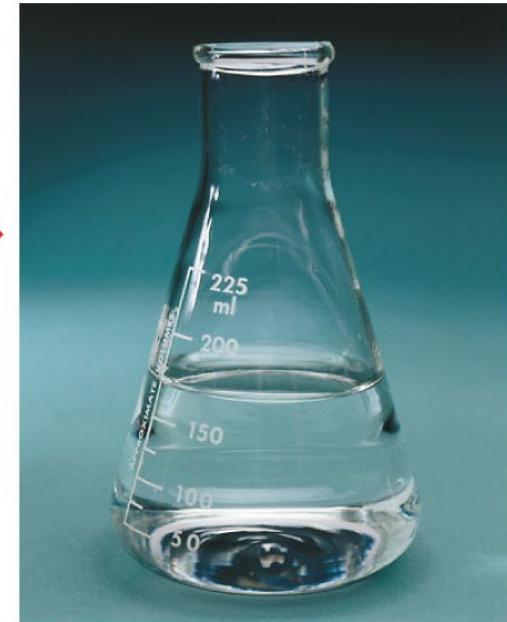
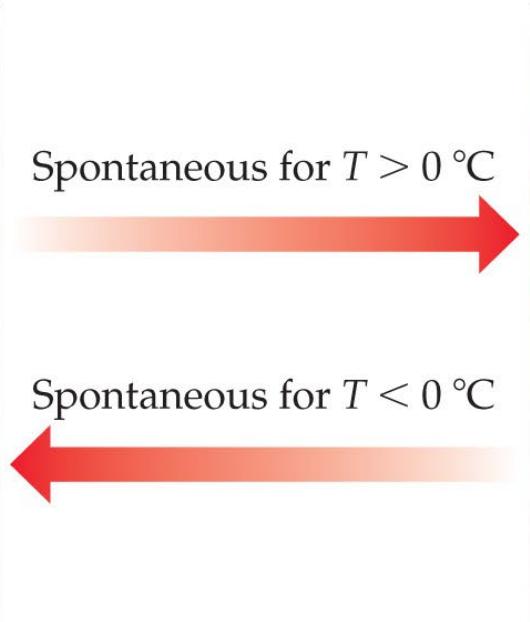
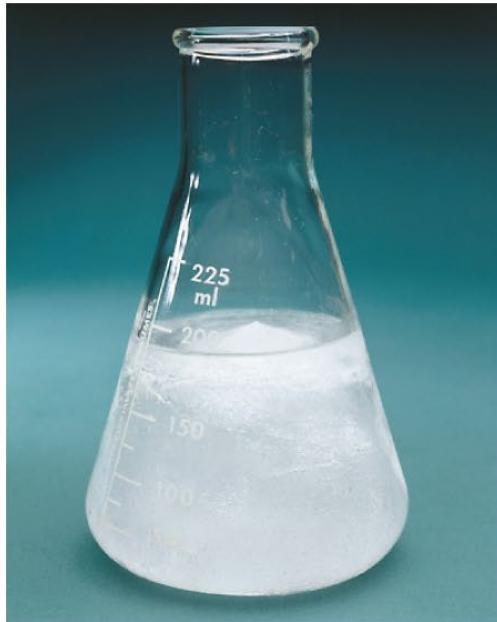
Spontaneous Processes

- **Spontaneous processes** proceed without any outside assistance.
- The gas in vessel A will spontaneously effuse into vessel B, but it will *not* spontaneously return to vessel A.
- Processes that are spontaneous in one direction are nonspontaneous in the reverse direction.

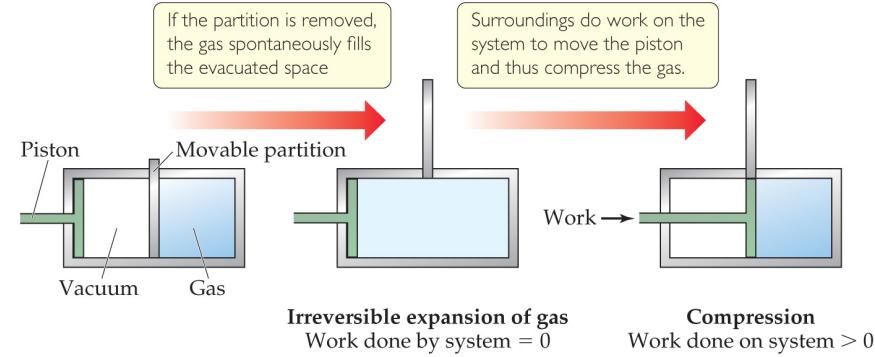
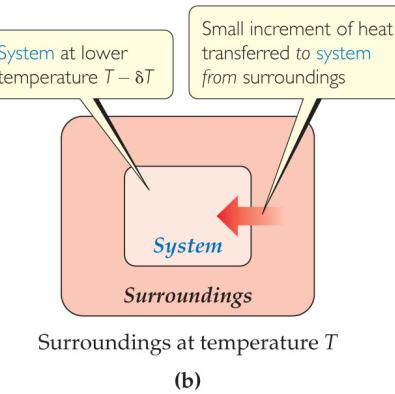
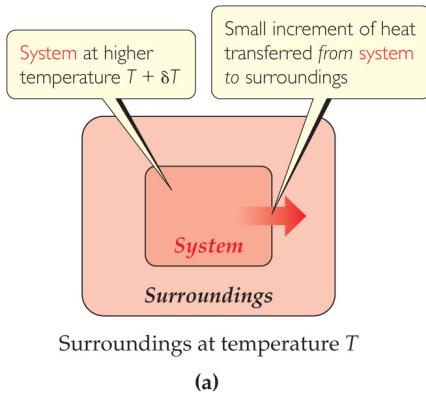


Experimental Factors Affect Spontaneous Processes

- Temperature and pressure can affect spontaneity.
- An example of how temperature affects spontaneity is ice melting or freezing.



Reversible and Irreversible Processes



Reversible process: A reversible process is one for which we can restore the system to its original condition with no change to the surroundings.

Irreversible processes: An irreversible process is one that leaves the surroundings somehow changed when the system is restored to its original state

Entropy

- **Entropy** can be thought of as a measure of the randomness of a system.
- It is a state function:

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

- It can be found by heat transfer from surroundings at a given temperature:

$$\Delta S = \frac{q_{\text{rev}}}{T} \quad (\text{constant } T)$$



Second Law of Thermodynamics

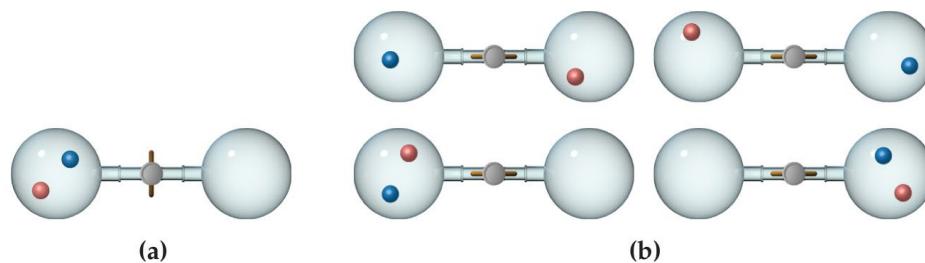
- The entropy of the universe increases in any spontaneous processes.
- This results in the following relationships:

$$\text{Reversible Process: } \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

$$\text{Irreversible Process: } \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

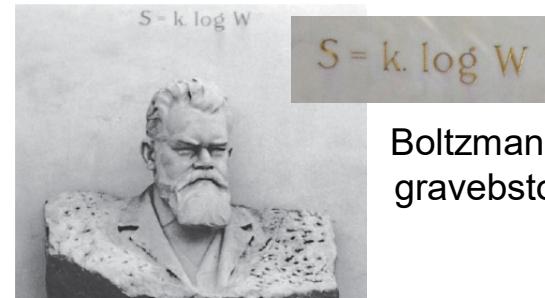


Entropy on the Molecular Scale



The two molecules are colored red and blue to keep track of them.

Four possible arrangements (microstates) once the stopcock is opened.



Boltzmann's graveestone

- Boltzmann described entropy on the molecular level.
- Gas molecule expansion: Two molecules are in the apparatus above; both start in one side. What is the likelihood they both will end up there? $(1/2)^2$
- If one mole is used? $(1/2)^{6.02 \times 10^{23}}$! (No chance!)
- Gases spontaneously expand to fill the volume given.
- Most probable arrangement of molecules: approximately equal molecules in each side

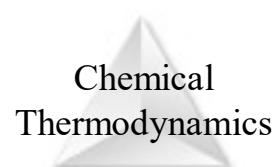
Statistical Thermodynamics

- Thermodynamics looks at bulk properties of substances (the *big* picture).
- We have seen what happens on the molecular scale.
- How do they relate?
- We use statistics (probability) to relate them.
The field is called statistical thermodynamics.
- Microstate: A single possible arrangement of position and kinetic energy of molecules

Boltzmann's Use of Microstates

- Because there are so many possible microstates, we can't look at every picture.
- W represents the number of microstates.
- Entropy is a measure of how many microstates are associated with a particular macroscopic state.
- The connection between the number of microstates and the entropy of the system is:

$$S = k \ln W$$



Entropy Change

- Since entropy is a state function, the final value minus the initial value will give the overall change.
- In this case, an increase in the number of microstates results in a positive entropy change (more disorder).

$$\Delta S = k \ln W_{\text{final}} - k \ln W_{\text{initial}} = k \ln \frac{W_{\text{final}}}{W_{\text{initial}}}$$



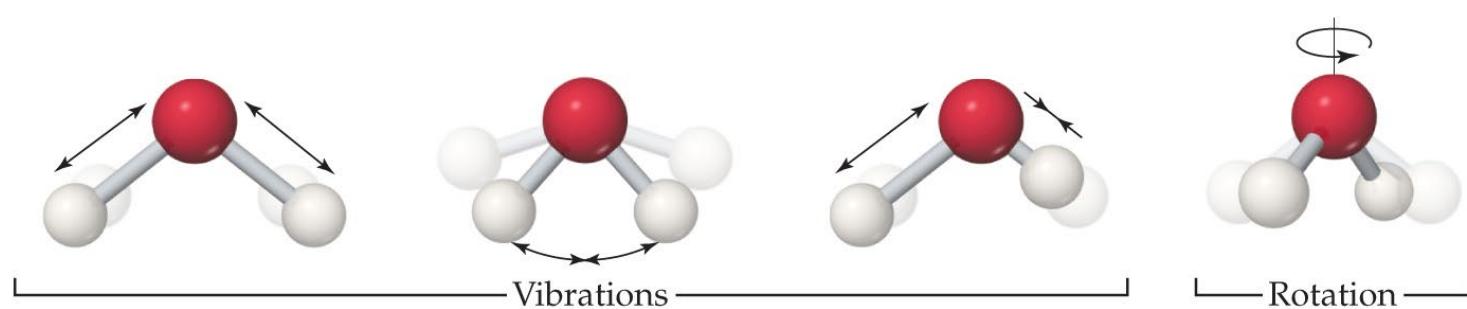
Effect of Volume and Temperature Change on the System

- If we increase volume, there are more positions possible for the molecules. This results in more microstates, so increased entropy.
- If we increase temperature, the average kinetic energy increases. This results in a greater distribution of molecular speeds. Therefore, there are more possible kinetic energy values, resulting in more microstates, increasing entropy.



Molecular Motions

- Molecules exhibit several types of motion.
 - Translational: Movement of the entire molecule from one place to another
 - Vibrational: Periodic motion of atoms within a molecule
 - Rotational: Rotation of the molecule about an axis
- Note: More *atoms* means more microstates (more possible molecular motions).



Chemical
Thermodynamics

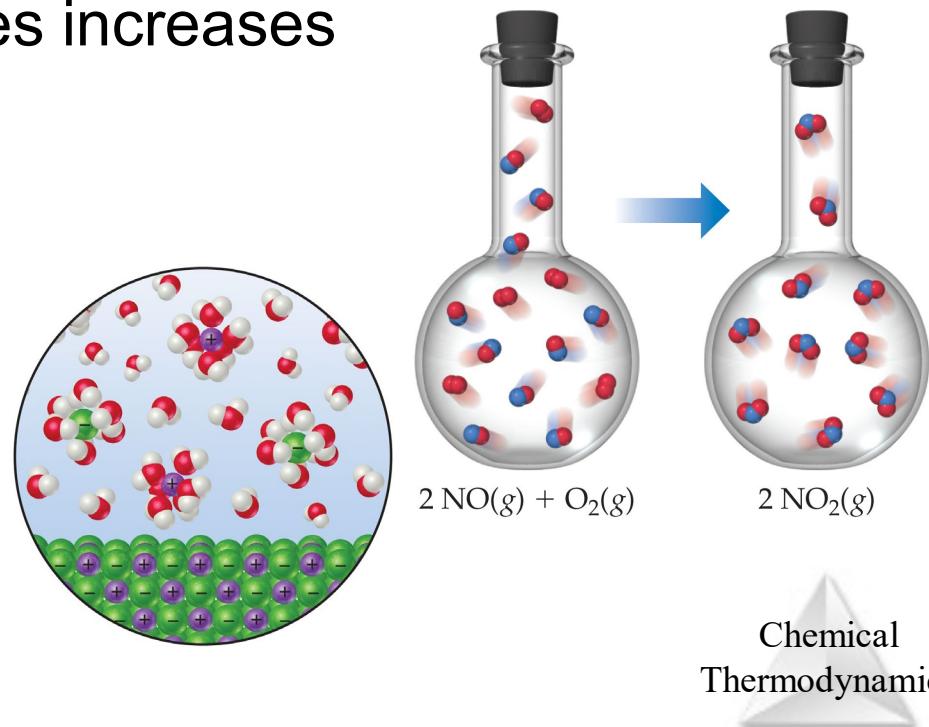
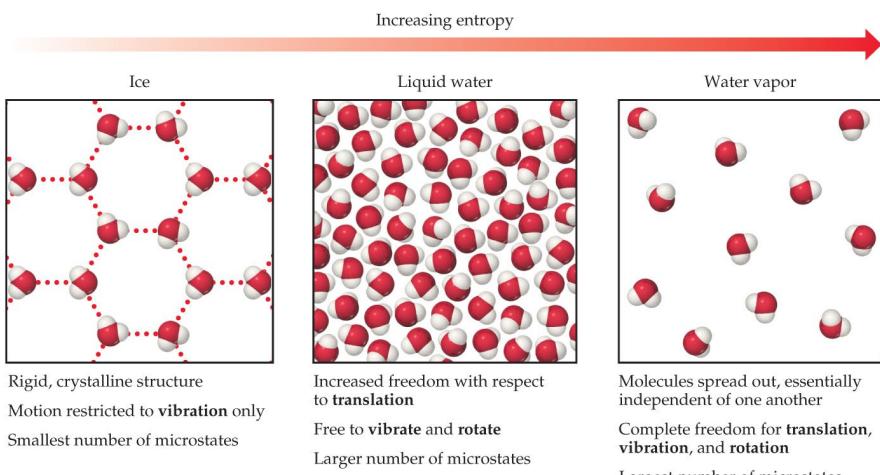
Entropy on the Molecular Scale

- The number of microstates and, therefore, the entropy tend to increase with increases in
 - temperature.
 - volume.
 - the number of independently moving molecules.

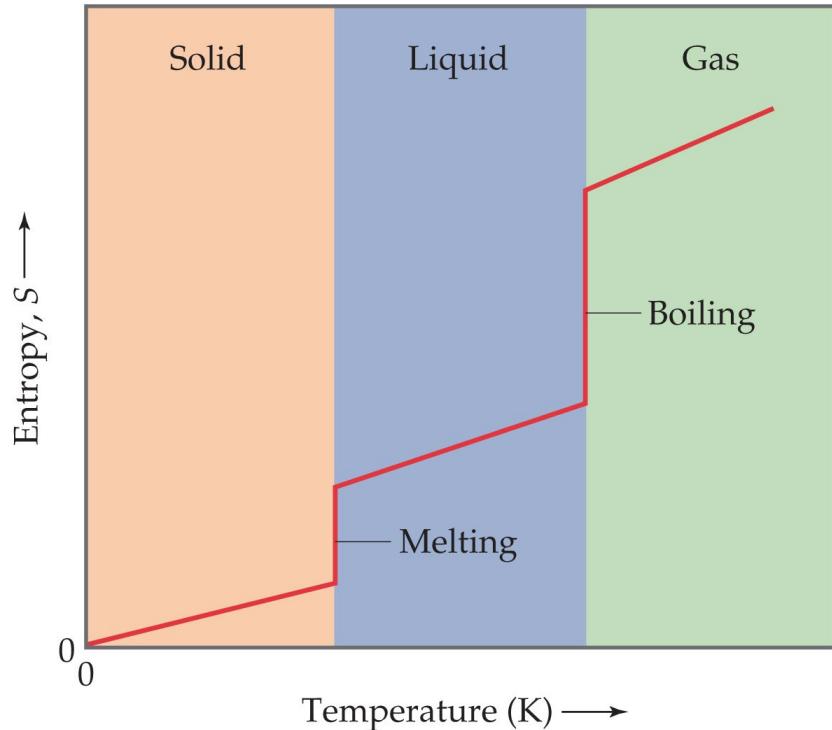


Entropy and Physical States

- Entropy increases with the freedom of motion of molecules.
- $S(g) > S(l) > S(s)$
- Entropy of a system increases for processes where
 - gases form from either solids or liquids.
 - liquids or solutions form from solids.
 - the number of gas molecules increases during a chemical reaction.



Third Law of Thermodynamics



- The entropy of a pure crystalline substance at absolute zero is 0.
- Consider all atoms or molecules in the perfect lattice at 0 K; there will only be *one* microstate.
- $S = k \ln W = k \ln 1 = 0$

Standard Entropies

- The reference for entropy is 0 K, so the values for elements are *not* 0 J/mol K at 298 K.
- Standard molar enthalpy for gases are generally greater than liquids and solids. (Be careful of size!)
- Standard entropies increase with molar mass.
- Standard entropies increase with number of atoms in a formula.

Table 19.1 Standard Molar Entropies of Selected Substances at 298 K

Substance	S° (J/mol-K)
H ₂ (g)	130.6
N ₂ (g)	191.5
O ₂ (g)	205.0
H ₂ O(g)	188.8
NH ₃ (g)	192.5
CH ₃ OH(g)	237.6
C ₆ H ₆ (g)	269.2
H ₂ O(l)	69.9
CH ₃ OH(l)	126.8
C ₆ H ₆ (l)	172.8
Li(s)	29.1
Na(s)	51.4
K(s)	64.7
Fe(s)	27.23
FeCl ₃ (s)	142.3
NaCl(s)	72.3

Entropy Changes

Entropy changes for a reaction can be calculated in a manner analogous to that by which ΔH is calculated:

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

where n and m are the coefficients in the balanced chemical equation.

Entropy Changes in Surroundings

- Heat that flows into or out of the system changes the entropy of the surroundings.
- For an isothermal process

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

- At constant pressure, q_{sys} is simply ΔH for the system.

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} \quad [\text{at constant P}]$$

Entropy Change in the Universe

- The universe is composed of the system and the surroundings.
- Therefore,

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

- For spontaneous processes

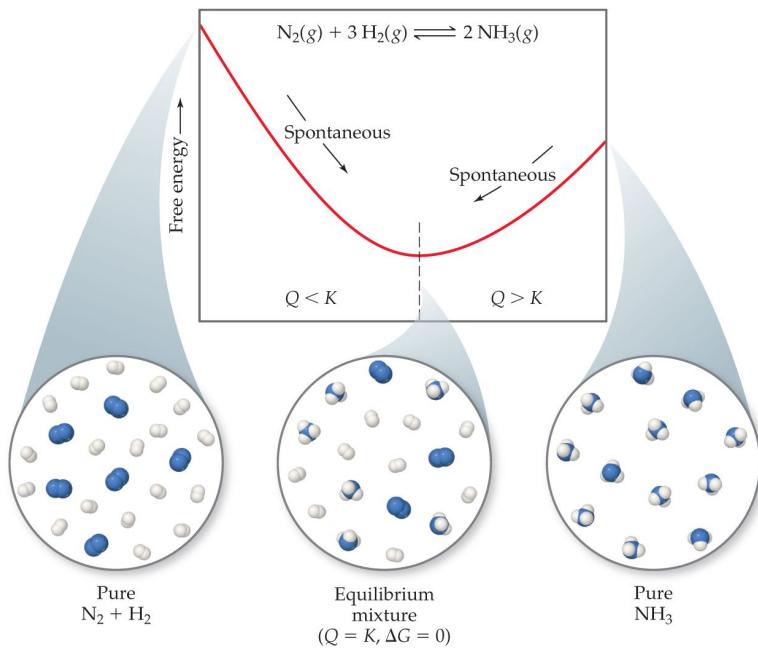
$$\Delta S_{\text{universe}} > 0$$



Total Entropy and Spontaneity

- $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$
- Substitute for the entropy of the surroundings:
 - $\Delta S_{\text{universe}} = \Delta S_{\text{system}} - \Delta H_{\text{system}}/T$
- Multiply by $-T$:
 - $-T\Delta S_{\text{universe}} = -T\Delta S_{\text{system}} + \Delta H_{\text{system}}$
- Rearrange:
 - $-T\Delta S_{\text{universe}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$
- Call $-T\Delta S_{\text{universe}}$ the **Gibbs Free Energy (ΔG)**:
 - $\Delta G = \Delta H - T\Delta S$

Gibbs Free Energy



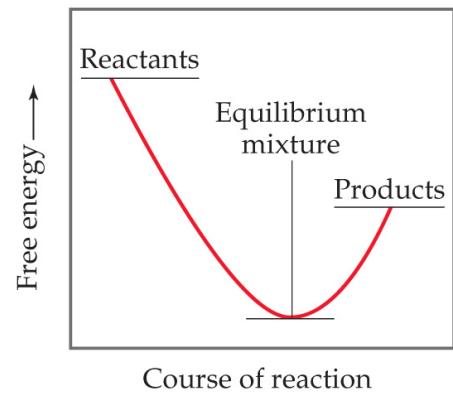
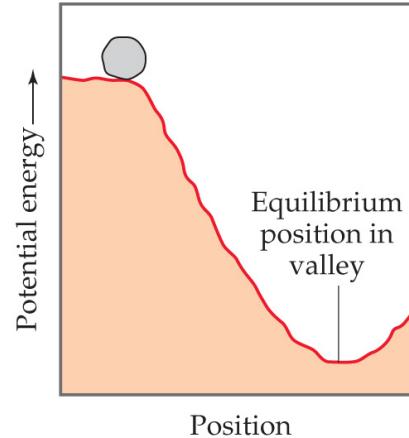
1. If ΔG is negative, the forward reaction is spontaneous.
2. If ΔG is 0, the system is at equilibrium.
3. If ΔG is positive, the reaction is spontaneous in the reverse direction.



Standard Free Energy Changes

Analogous to standard enthalpies of formation are standard free energies of formation, ΔG_f° :

where n and m are the stoichiometric coefficients.



Free Energy Changes

Table 19.3 How Signs of ΔH and ΔS Affect Reaction Spontaneity

ΔH	ΔS	$-\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Characteristics	Example
-	+	-	-	Spontaneous at all temperatures	$2 O_3(g) \longrightarrow 3 O_2(g)$
+	-	+	+	Nonspontaneous at all temperatures	$3 O_2(g) \longrightarrow 2 O_3(g)$
-	-	+	+ or -	Spontaneous at low T ; nonspontaneous at high T	$H_2O(l) \longrightarrow H_2O(s)$
+	+	-	+ or -	Spontaneous at high T ; nonspontaneous at low T	$H_2O(s) \longrightarrow H_2O(l)$

- How does ΔG change with temperature?
- $\Delta G = \Delta H - T\Delta S$
- Since reactions are spontaneous if $\Delta G < 0$, the sign of enthalpy and entropy and the magnitude of the temperature matters to spontaneity.

Free Energy and Equilibrium

Under any conditions, standard or nonstandard, the free energy change can be found this way:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

(Under standard conditions, concentrations are 1 M, so $Q = 1$ and $\ln Q = 0$; the last term drops out.)



Free Energy and Equilibrium

- At equilibrium, $Q = K$, and $\Delta G = 0$.
- The equation becomes

$$0 = \Delta G^\circ + RT \ln K$$

- Rearranging, this becomes

$$\Delta G^\circ = -RT \ln K$$

or

$$K = e^{-\Delta G^\circ / RT}$$