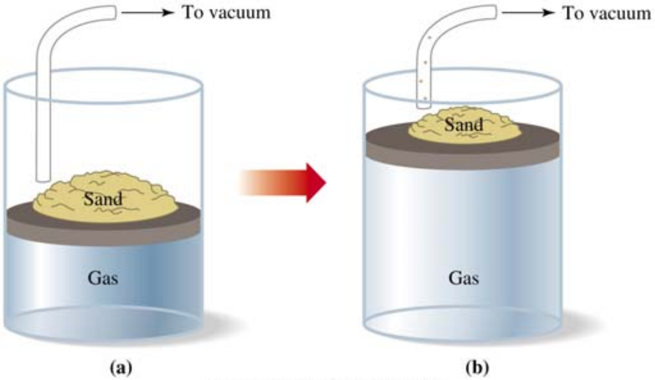
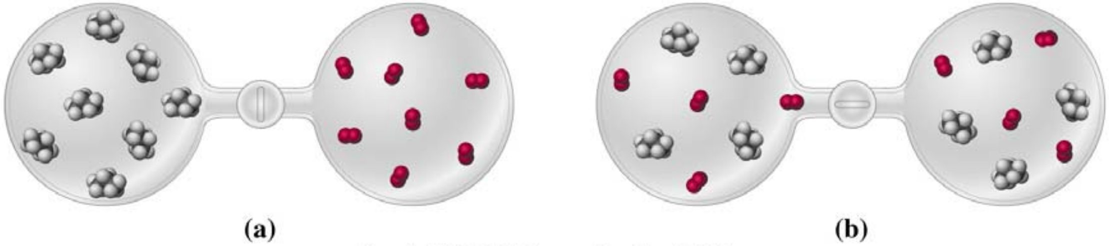
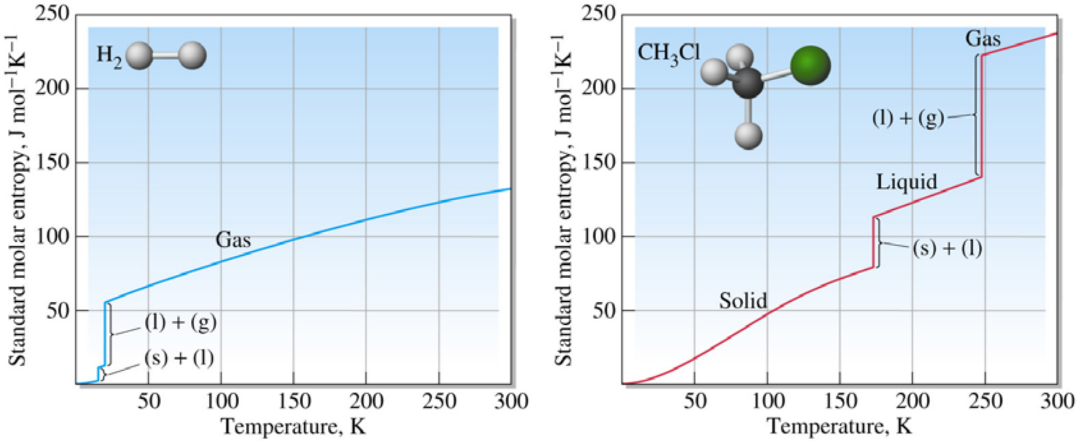
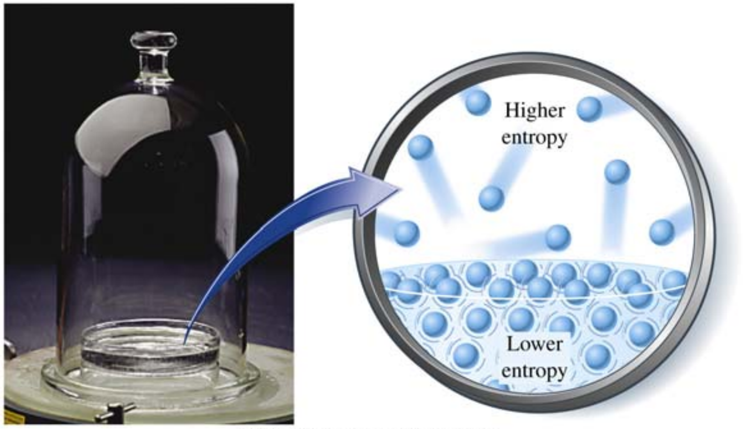
Chapter Seventeen

Thermodynamics: Spontaneity, Entropy, and Free Energy







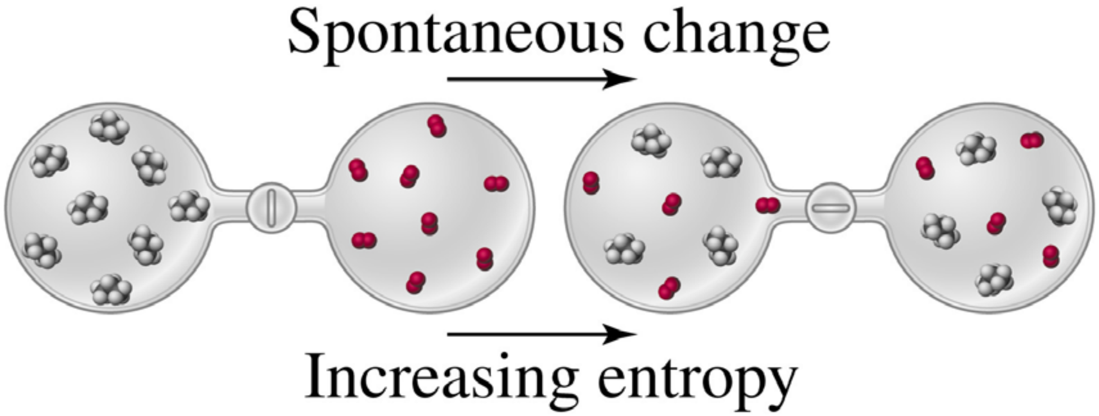


Introductory Concepts

Thermodynamics examines the relationship between ***heat (q)*** and ***work (w)***

Spontaneity is the notion of whether or not a process can take place unassisted

Entropy is a measure of how energy is spread out among the particles of a system



EOS

Introductory Concepts

Free energy is a thermodynamic function that relates enthalpy and entropy to spontaneity

Free energy is connected with the ability to do work

e.g., the chemical reaction in a battery generates electricity to light a flashlight bulb

EOS

Why Study Thermodynamics?

- With a knowledge of thermodynamics and by making a few calculations before embarking on a new venture, scientists and engineers can save themselves a great deal of time, money, and frustration.
  - "*To the manufacturing chemist thermodynamics gives information concerning the stability of his substances, the yield which he may hope to attain, the methods of avoiding undesirable substances, the optimum range of temperature and pressure, the proper choice of solvent….*" - from the introduction to *Thermodynamics and the Free Energy of Chemical Substances* by G. N. Lewis and M. Randall
- Thermodynamics tells us what processes are *possible*.
  - (Kinetics tells us whether the process is *practical*.)

Spontaneous Change

- A ***spontaneous*** process is one that can occur in a system left to itself; no action from outside the system is necessary to bring it about.
- A ***nonspontaneous*** process is one that cannot take place in a system left to itself.
- *If a process is spontaneous, the reverse process is nonspontaneous, and vice versa*.
- Example: gasoline combines spontaneously with oxygen.
- However, "spontaneous" signifies nothing about ***how fast*** a process occurs.
- A mixture of gasoline and oxygen may remain unreacted for years, or may ignite instantly with a spark.

Spontaneous Change

A **spontaneous process** is one that can occur in a system left to itself; no action from outside the system is necessary to bring the change about

Example: spontaneous combustion of damp hay or silo explosions from gases evolved from decomposing grain

If a **process is spontaneous**, the *reverse process is nonspontaneous* and vice versa

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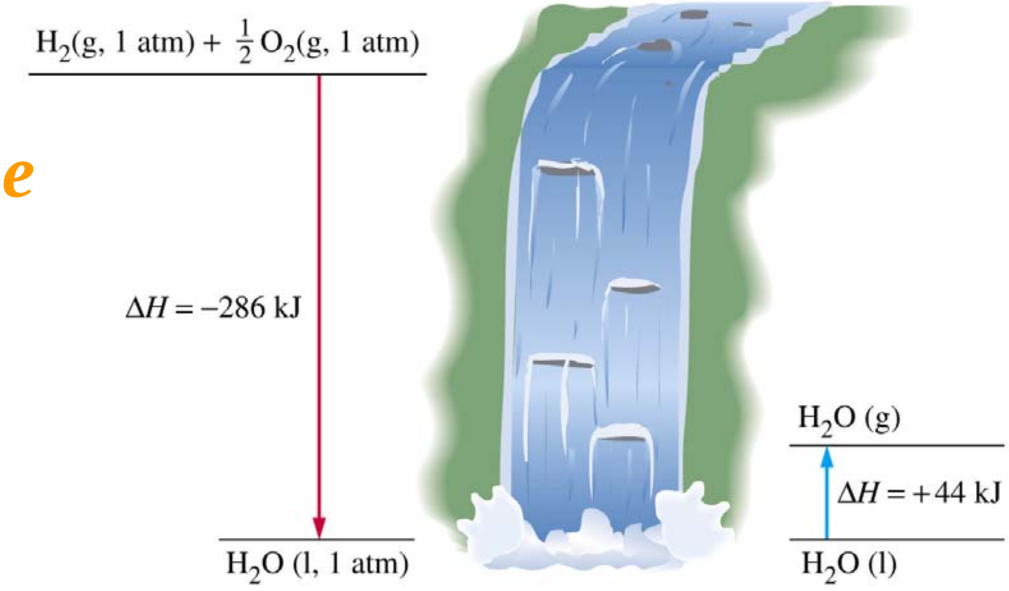
Spontaneous Change (cont'd)

- Thermodynamics determines the equilibrium *state* of a system.
- Thermodynamics is used to predict the proportions of products and reactants at equilibrium.
- Kinetics determines the *pathway* by which equilibrium is reached.
- A high activation energy can effectively block a reaction that is thermodynamically favored.
- Example: combustion reactions are thermodynamically favored, but (fortunately for life on Earth!) most such reactions also have a high activation energy.

Spontaneity

A *general* rule: that exothermic reactions are spontaneous and endothermic reactions are nonspontaneous works in many cases

However, ***enthalpy change*** is **not a sufficient criterion for predicting spontaneous change**



The formation of water at 25 °C and 1 atm: a spontaneous process that is exothermic

The vaporization of water at 25 °C and pressures up to 0.0313 atm: a spontaneous process that is endothermic

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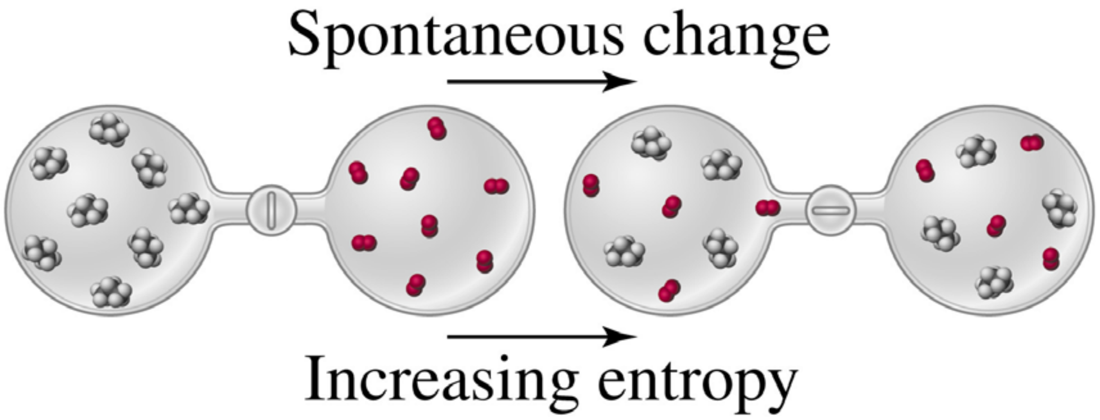
The Concept of Entropy

Consider mixing two gases: this occurs spontaneously, and the gases form a homogeneous mixture.

There is essentially no enthalpy change involved, so why is the process spontaneous?



The driving force is a thermodynamic quantity called entropy, a mathematical concept that is difficult to portray visually

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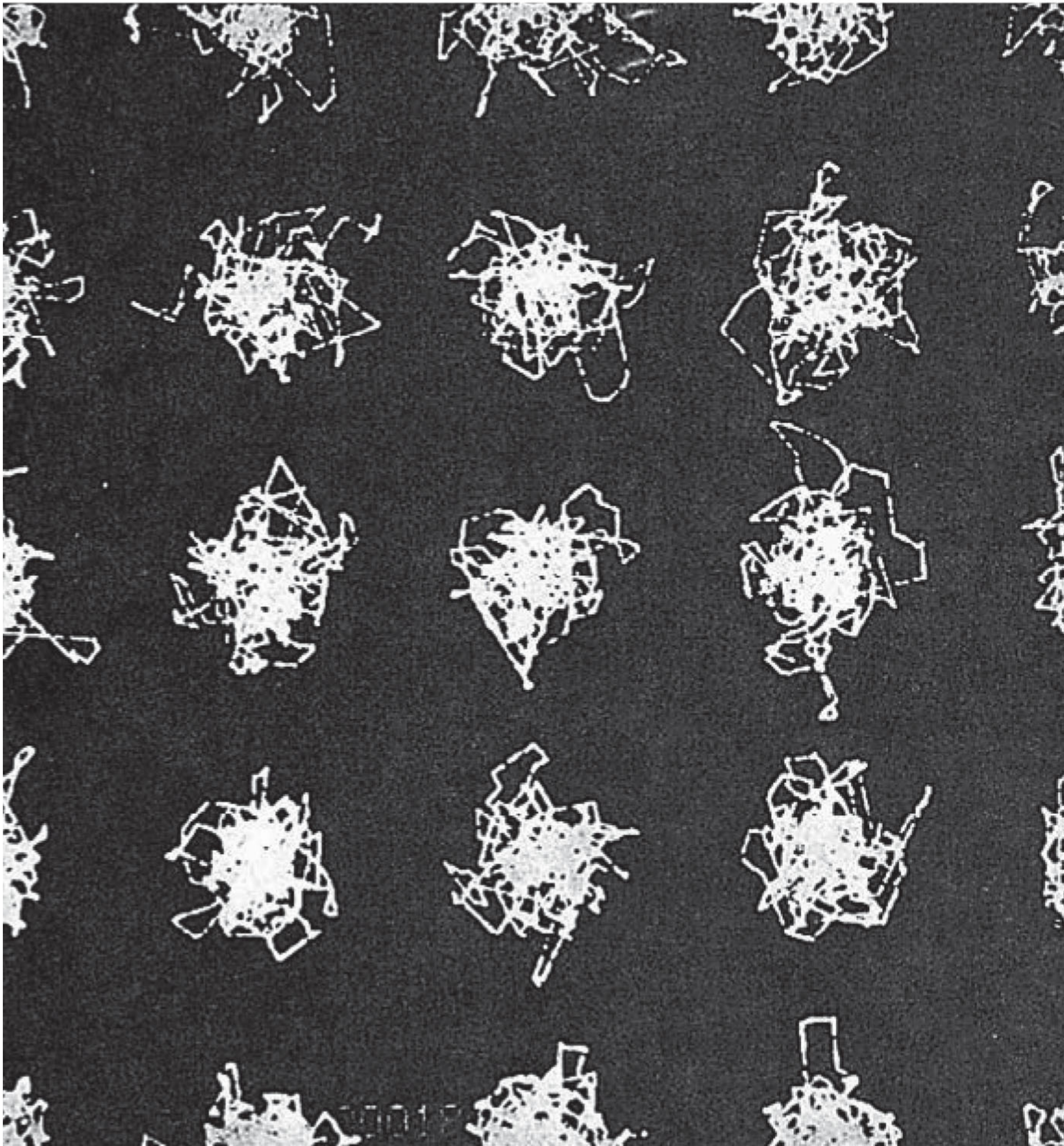
The Laws of Thermodynamics

- First Law of Thermodynamics
  - Energy is neither created or destroyed
    - $\Delta E = q + w$
- Second Law of Thermodynamics
  - In spontaneous processes the entropy of the universe increases
- Third Law of Thermodynamics
  - The entropy of a perfect crystal at zero Kelvin is zero (i.e. the crystal contains no disorder)

Random Motion in a Crystal

At 0 Kelvin

All motion ceases in a perfect crystal



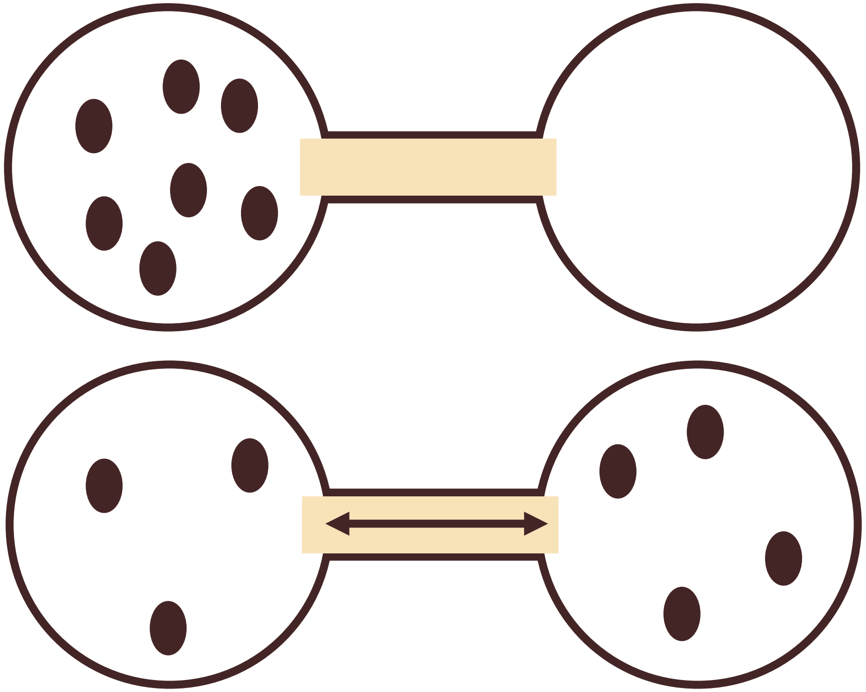
The Concept of Entropy (cont'd)

- The other factor that drives reactions is a thermodynamic quantity called ***entropy***.
- Entropy is a mathematical concept that is difficult to portray visually.
- The *total energy* of the system remains unchanged in the mixing of the gases …

- … but the number of *possibilities* for the *distribution* of that energy increases.

Entropy

The *total energy* of a system remains unchanged in the mixing of the gases but the number of possibilities for the *distribution* of that energy increases



This spreading of the energy and increase of entropy correspond to a greater physical disorder at the microscopic level

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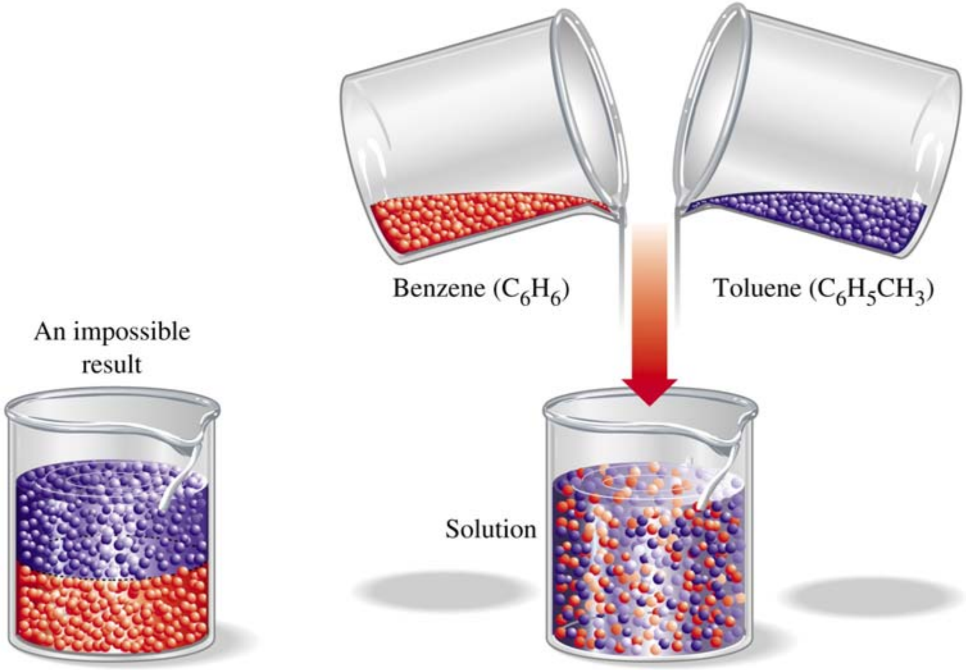
Entropy

There are ***two natural tendencies*** behind spontaneous processes: the tendency to ***achieve a lower energy state*** and the tendency toward ***a more disordered state***



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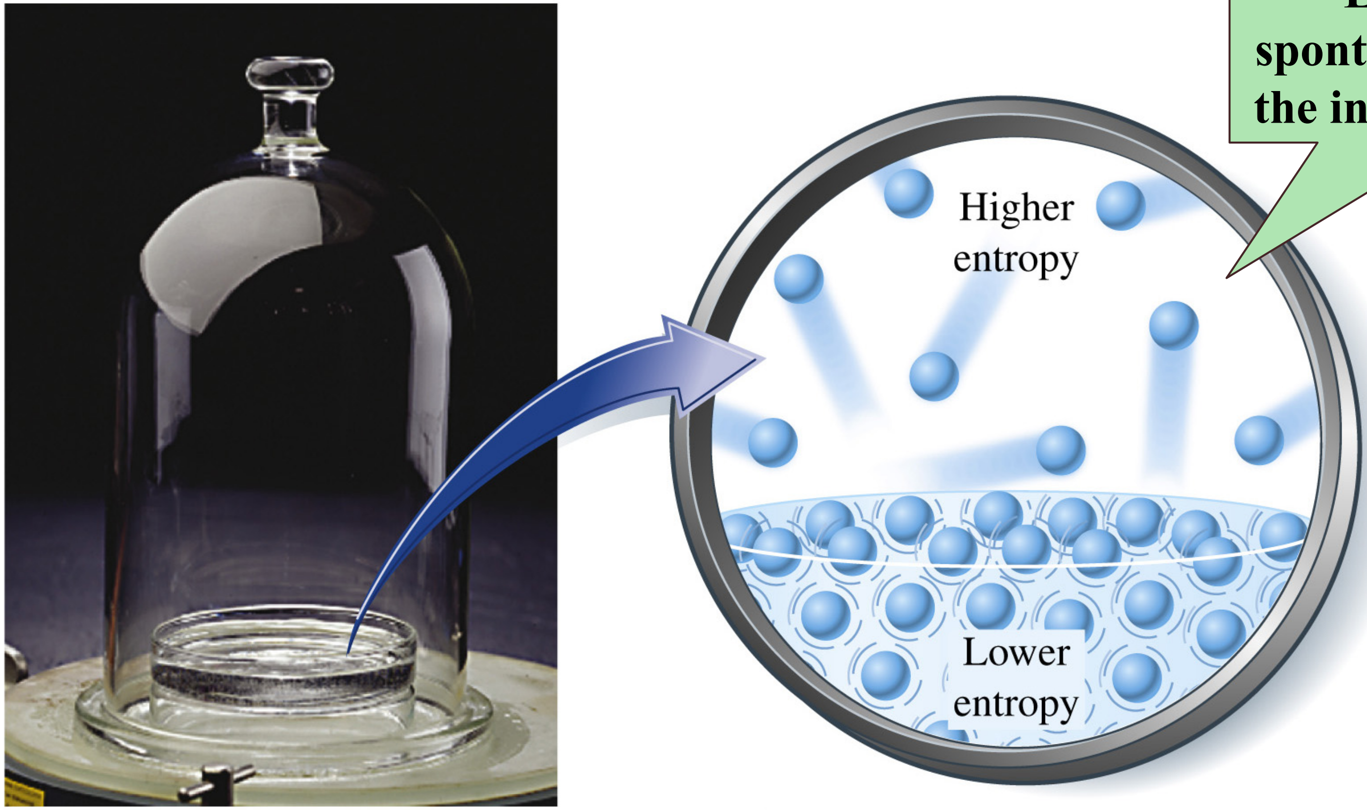
Increase in Entropy in the Vaporization of Water



Evaporation is spontaneous because of the increase in entropy.

The Concept of Entropy

- The spreading of the energy among states, and increase of entropy, often correspond to a greater physical disorder at the microscopic level (however, entropy is not “disorder”).
- There are two driving forces behind spontaneous processes: the tendency to achieve a lower energy state (enthalpy change) and the tendency for energy to be distributed among states (entropy).
- In many cases, however, the two factors work in opposition. One may increase and the other decrease or vice versa. In these cases, we must determine which factor predominates.

Entropy and the Second Law of Thermodynamics

The Second Law of Thermodynamics

- The second law of thermodynamics explains why spontaneous processes have a direction.
- In any spontaneous process, the entropy of the universe increases.
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$: the change in entropy of the universe is the sum of the change in entropy of the system and the change in entropy of the surroundings.
- Entropy is not conserved: ΔS_{univ} is increasing.

Entropy and the Second Law of Thermodynamics

The Second Law of Thermodynamics

- For a reversible process: $\Delta S_{\text{univ}} = 0$.
- For a spontaneous process (i.e. irreversible): $\Delta S_{\text{univ}} > 0$.
- Note: the second law states that the entropy of the universe must increase in a spontaneous process. It is possible for the entropy of a system to decrease as long as the entropy of the surroundings increases.
- For an isolated system, $\Delta S_{\text{sys}} = 0$ for a reversible process and $\Delta S_{\text{sys}} > 0$ for a spontaneous process.

Standard Free Energy Change, ΔG°

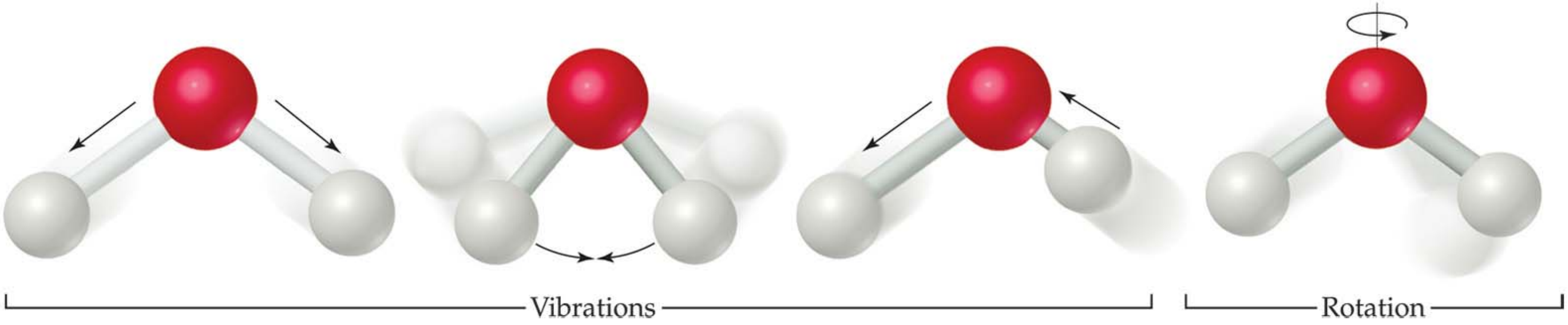
- The ***standard free energy change, ΔG°***, of a reaction is the free energy change when reactants and products are in their standard states.
- The ***standard free energy of formation, $\Delta G_f°$***, is the free energy change for the formation of 1 mol of a substance in its standard state from the elements in their standard states.

$$\Delta G° = \Sigma v_\mathrm{p}\, \Delta G_f°(\text{products}) - \Sigma v_\mathrm{r}\, \Delta G_f°(\text{reactants})$$

The form of this equation should appear very familiar by now!

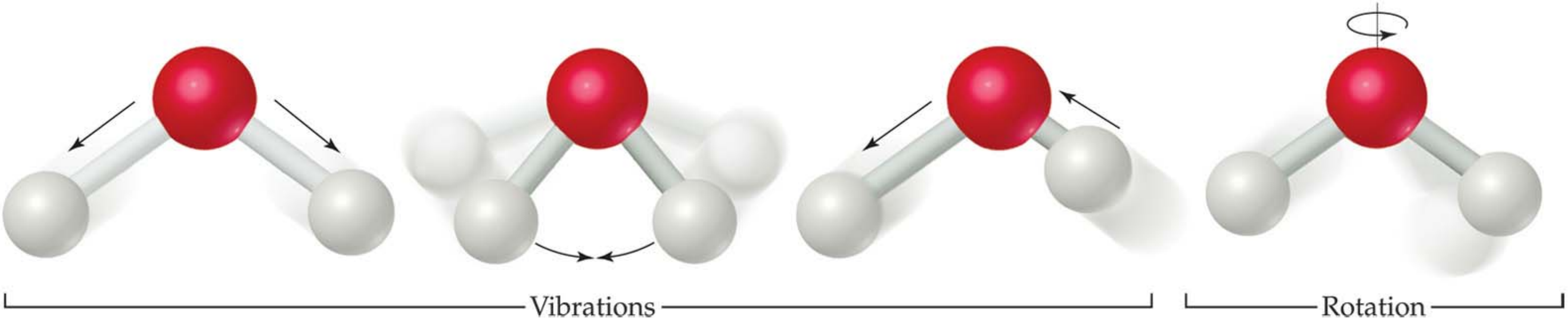
Entropy on the Molecular Scale

- Ludwig Boltzmann described the concept of entropy on the molecular level.
- Temperature is a measure of the average kinetic energy of the molecules in a sample.



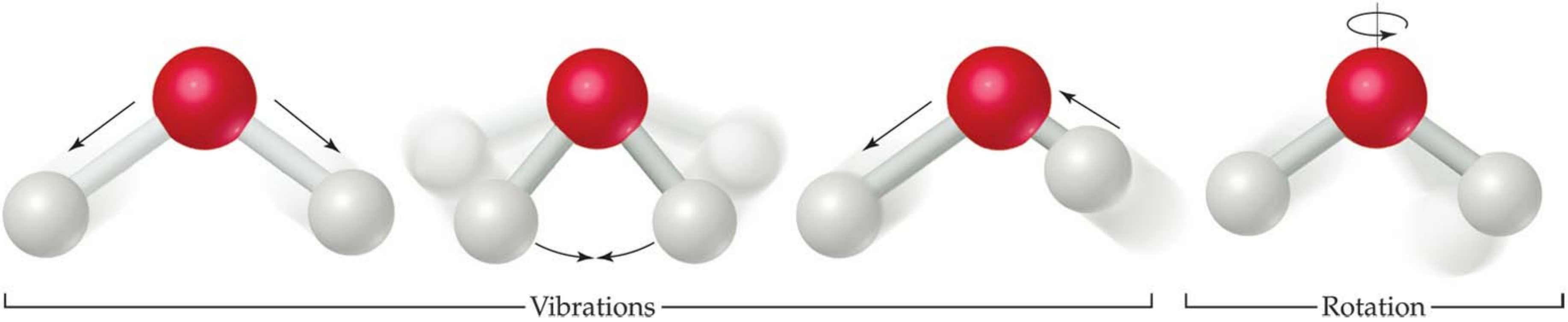
Entropy on the Molecular Scale

- 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 on about an axis or rotation about σ bonds.



Entropy on the Molecular Scale

- Boltzmann envisioned the motions of a sample of molecules at a particular instant in time.
  - This would be akin to taking a snapshot of all the molecules.
- He referred to this sampling as a microstate of the thermodynamic system.

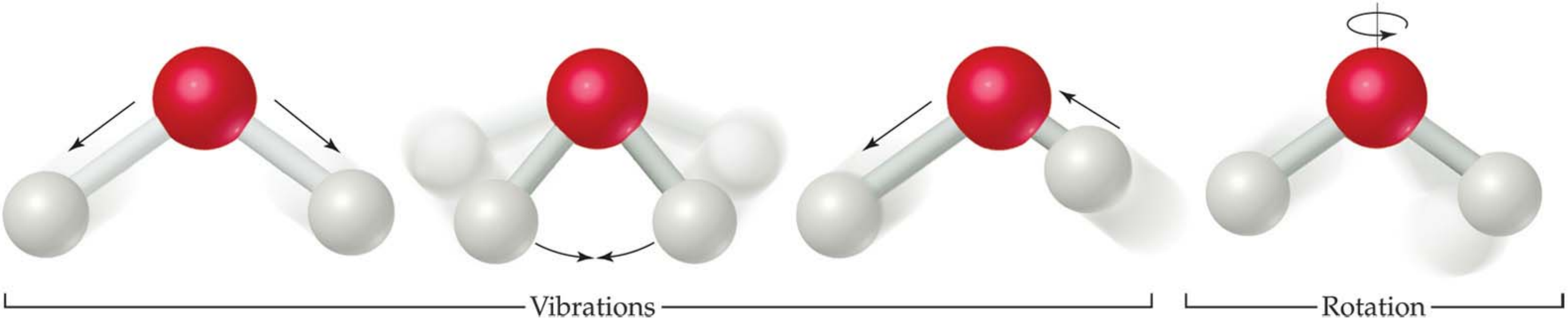


Entropy on the Molecular Scale

- Each thermodynamic state has a specific number of microstates, *W*, associated with it.
- Entropy is

$$S = k \ln W$$

where *k* is the Boltzmann constant, 1.38×10^{-23} J/K.



Entropy on the Molecular Scale

Implications:

- more particles
  -> more states -> more entropy
- higher T
  -> more energy states -> more entropy
- less structure (gas vs solid)
  -> more states -> more entropy

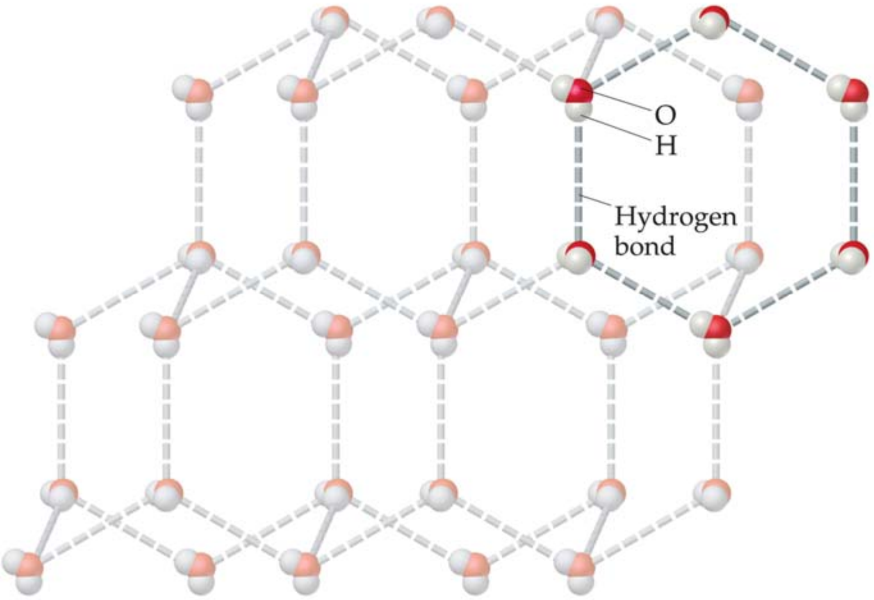
Entropy on the Molecular Scale

- The number of microstates and, therefore, the entropy tends to increase with increases in
  - Temperature.
  - Volume (gases).
  - The number of independently moving molecules.(The more atoms a molecule has the greater its entropy.)

Entropy and Physical States

- Entropy increases with the freedom of motion of molecules.
- Therefore,

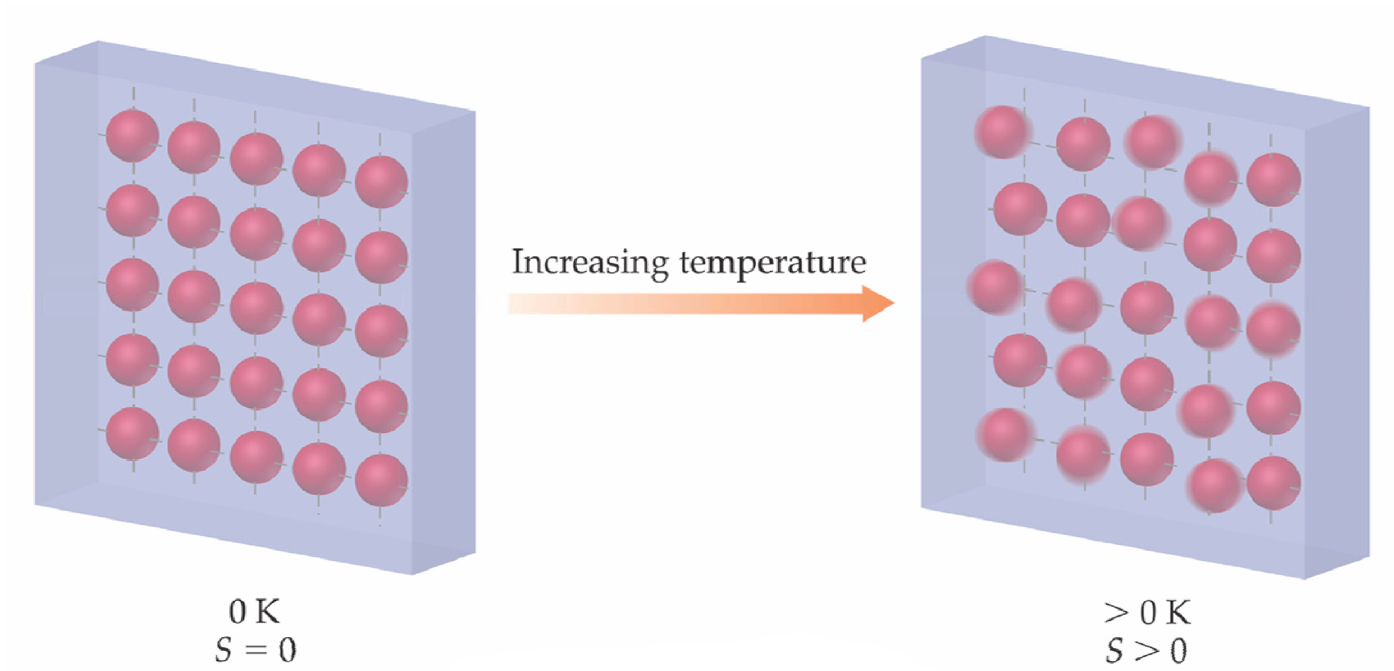
  $S(g) > S(l) > S(s)$



Third Law of Thermodynamics

The entropy of a pure crystalline substance at absolute zero is 0.

$$S = k\ lnW = k\ ln1 = 0$$



General Chemistry 4th edition, Hill, Petrucci, McCreary, Perry

Assessing Entropy Change

- The difference in entropy (*S*) between two states is the ***entropy change* (Δ*S*).**
- *The greater the number of configurations of the microscopic particles (atoms, ions, molecules) among the energy levels in a particular state of a system, the greater is the entropy of the system.*
- Entropy generally increases when:
  - Solids melt to form liquids.
  - Solids or liquids vaporize to form gases.
  - Solids or liquids dissolve in a solvent to form nonelectrolyte solutions.
  - A chemical reaction produces an increase in the number of molecules of *gases*.
  - A substance is heated.

Which Substance Has The Highest Entropy?

- $SnCl_{4(l)}$ or $SnCl_{4(g)}$
- $O_{2(g)}$ or $O_{3(g)}$
- $NO_{2(g)}$ or $N_2O_{4(g)}$

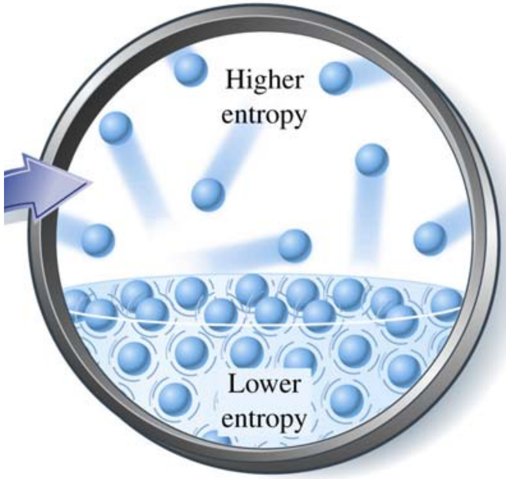
Entropy (*S*)

The ***greater the number of configurations*** of the microscopic particles (atoms, ions, molecules) among the energy levels in a particular state of a system, ***the greater the entropy*** of the system

Entropy (**S**) is a **state function**:
it is path independent

➔ $S_{\text{final}} - S_{\text{init}} = \Delta S$

$$\Delta S = q_{\text{rev}}/T$$



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Standard Molar Entropies

- According to the ***Third Law of Thermodynamics***, the entropy of a pure, perfect crystal can be taken to be zero at 0 K.
- The ***standard molar entropy***, $\boldsymbol{S°}$, is the entropy of one mole of a substance in its standard state.
- Since entropy increases with temperature, standard molar entropies are positive—even for elements. Entropy changes for a reaction can be calculated the same way we used for ΔH.

$$\Delta S = \Sigma v_{\mathrm{p}}\, S°(\text{products}) - \Sigma v_{\mathrm{r}}\, S°(\text{reactants})$$

S° for each component is found in a table.

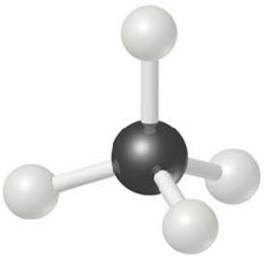
Note for pure elements:

$$S° \neq 0$$

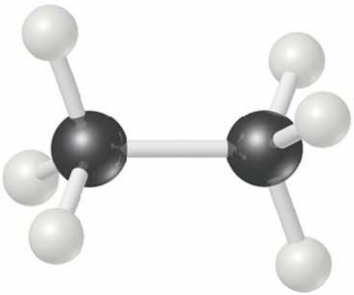
$$\Delta H° = 0$$

Standard Entropies

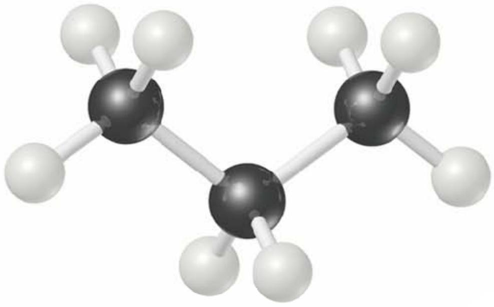
Larger and more complex molecules have greater entropies.



Methane, CH_4
$S° = 186.3\ J\ mol^{-1}\ K^{-1}$



Ethane, C_2H_6
$S° = 229.6\ J\ mol^{-1}\ K^{-1}$



Propane, C_3H_8
$S° = 270.3\ J\ mol^{-1}\ K^{-1}$

Standard Entropies

- These are molar entropy values of substances in their standard states.
- Standard entropies tend to increase with increasing molar mass.

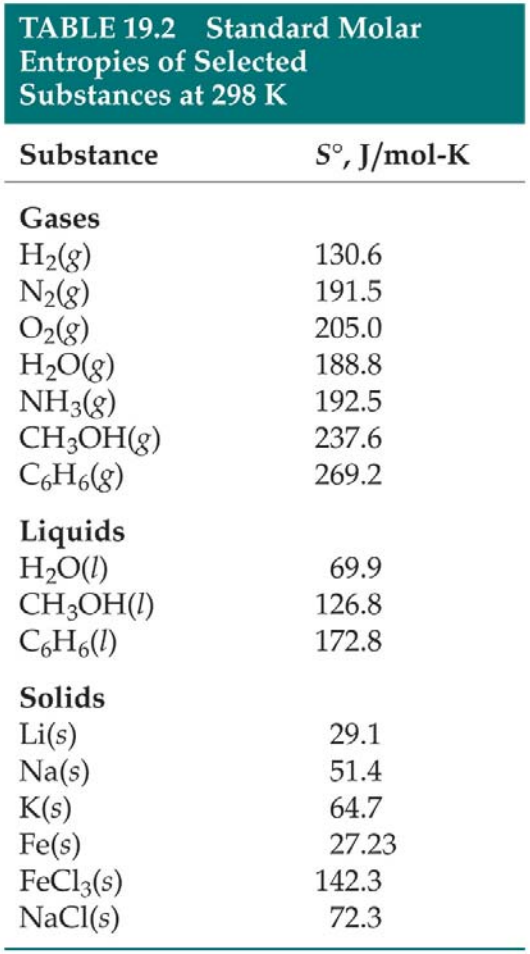


TABLE 19.2 Standard Molar Entropies of Selected Substances at 298 K

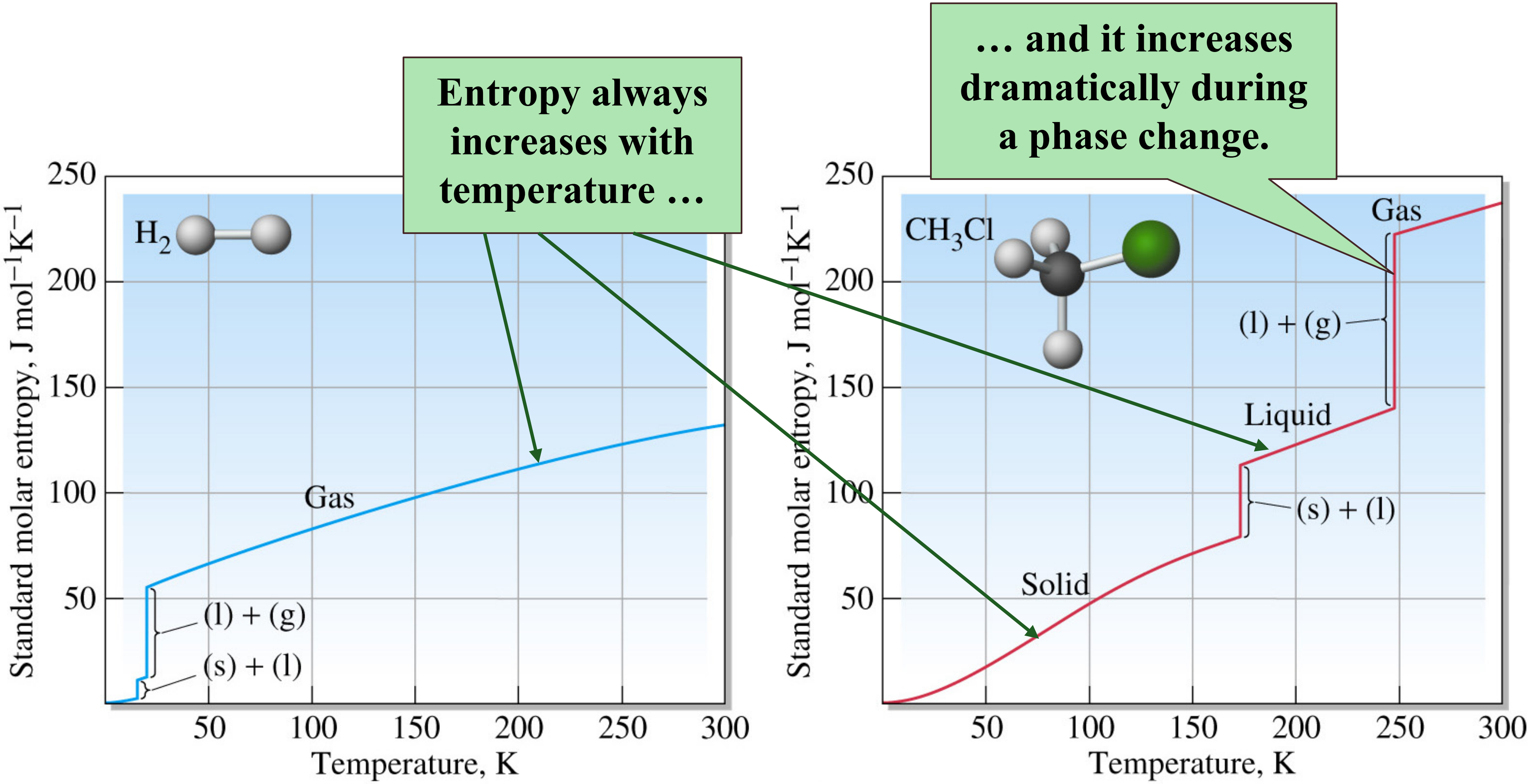
Substance	$S°$, J/mol-K
Gases	
$H_2(g)$	130.6
$N_2(g)$	191.5
$O_2(g)$	205.0
$H_2O(g)$	188.8
$NH_3(g)$	192.5
$CH_3OH(g)$	237.6
$C_6H_6(g)$	269.2
Liquids	
$H_2O(l)$	69.9
$CH_3OH(l)$	126.8
$C_6H_6(l)$	172.8
Solids	
$Li(s)$	29.1
$Na(s)$	51.4
$K(s)$	64.7
$Fe(s)$	27.23
$FeCl_3(s)$	142.3
$NaCl(s)$	72.3

Calculating Standard Entropy Changes ΔS^0

$$\Delta S^0 = \Sigma\, S^0_{(products)} - \Sigma\, S^0_{(reactants)}$$

- Calculate the entropy change which occurs when 1 mole of ethanol is burned:
  - $CH_2H_5OH_{(g)} + 3O_{2(g)} \rightarrow 2\ CO_{2(g)} + 3\ H_2O_{(g)}$
    - ➢ $\Delta S^0 = [(2)\ S^0CO_2 + (3)S^0H_2O] - [\ (1)\ S^0CH_2H_5OH + (3)S^0O_2]$
    - ➢ = [(2mol)213.74J/Kmol) + (3mol)(188.84J/Kmol)] –
    - ➢ [(1mol)(282.70J/Kmol) + (3mol)(205.07J/molK
    - ➢ ΔS^0 = 96.09J/K Does this number make sense?

Entropy as a Function of Temperature



Entropy always increases with temperature …

… and it increases dramatically during a phase change.

Example 17.2

Predict whether each of the following leads to an increase or decrease in the entropy of a system. If in doubt, explain why.

(a) The synthesis of ammonia:

$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$

(b) Preparation of a sucrose solution:

$C_{12}H_{22}O_{11}(s) \xrightarrow{H_2O(l)} C_{12}H_{22}O_{11}(aq)$

(c) Evaporation to dryness of a solution of urea, $CO(NH_2)_2$, in water:

$CO(NH_2)_2(aq) \rightarrow CO(NH_2)_2(s)$

Entropy Change

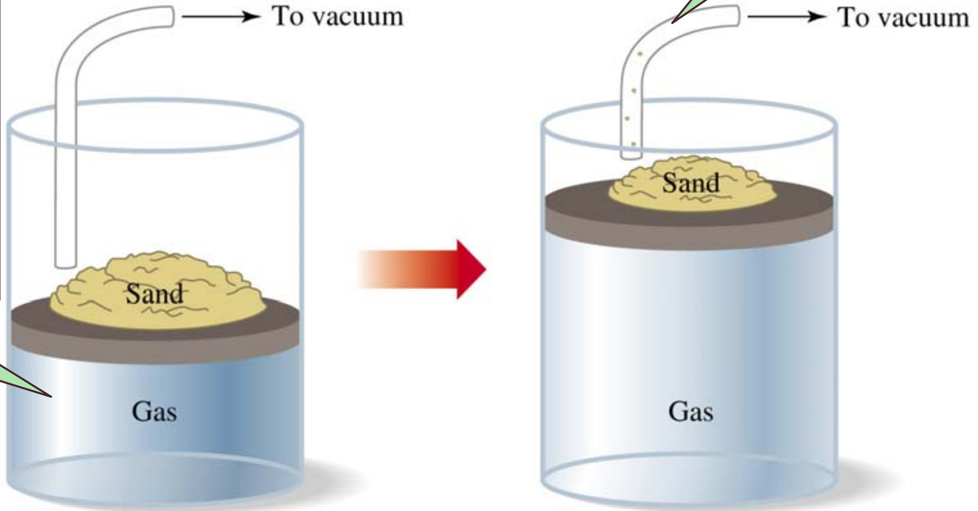
- Sometimes it is necessary to obtain ***quantitative*** values of entropy changes.

$$\Delta S = q_{rxn}/T$$

- where q_{rxn} is *reversible* heat, a state function.

The expansion can be reversed by allowing the sand to return, one grain at a time.

A *reversible* process can be reversed by a very small change, as in the expansion of this gas. A reversible process is never more than a tiny step from equilibrium.



(a) (b)

Practical uses: surroundings & system

Entropy Changes in Surroundings

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

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

Practical uses: surroundings & system

Entropy Changes in Surroundings

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

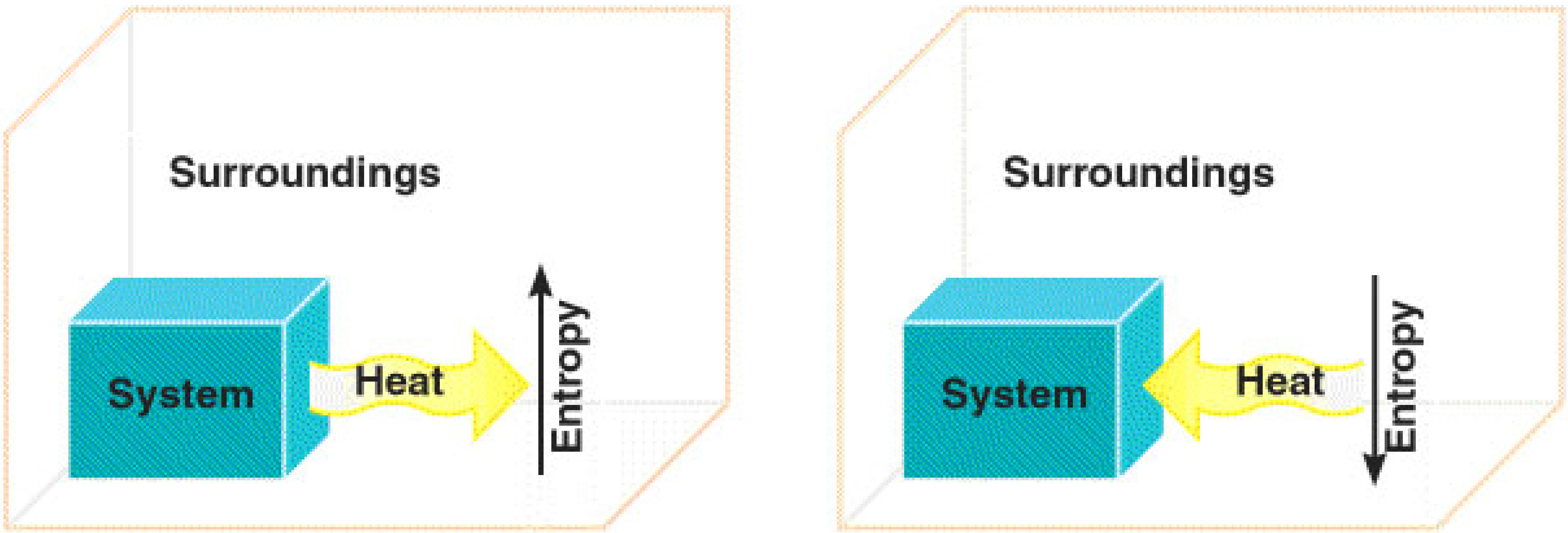
$$\Delta S_{surr} = \frac{-q_{sys}}{T}$$

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

$$\Delta S_{surr} = \frac{-q_{sys}}{T} = \frac{-\Delta H^\circ}{T}$$

Fig. 18.4

Exothermic and Endothermic Processes



(a) (b)

Link S and ΔH: Phase changes

$$\Delta S_{surr} = \frac{-q_{sys}}{T} = \frac{-\Delta H^\circ_{sys}}{T}$$

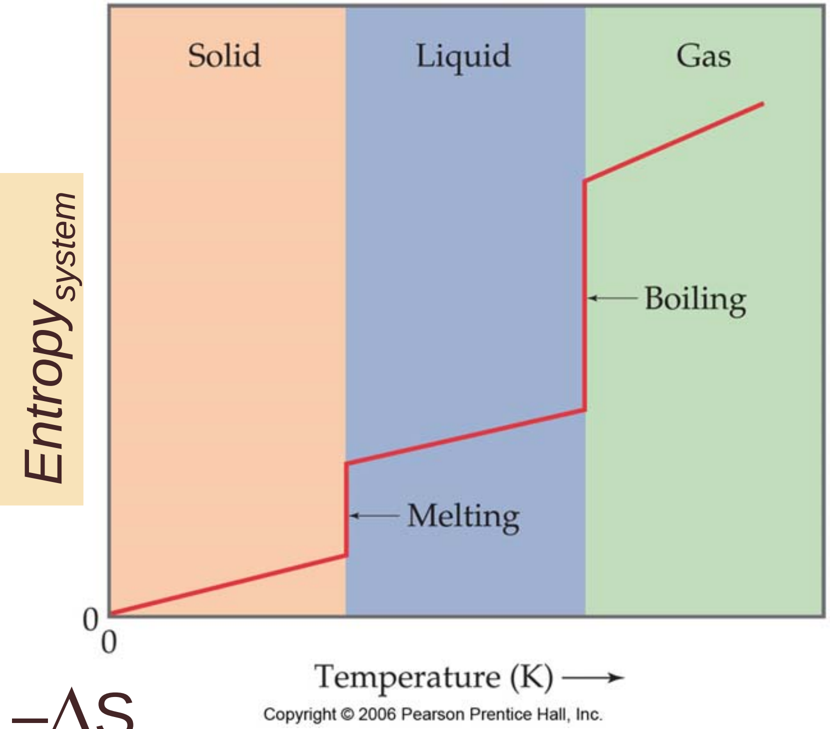
A phase change is isothermal (no change in T).

For water:

ΔH_{fusion} = 6 kJ/mol

ΔH_{vap} = 41 kJ/mol

If we do this reversibly: $\Delta S_{surr} = -\Delta S_{sys}$



The Second Law of Thermodynamics

- Entropy can be used as a sole criterion for spontaneous change …
- … but the entropy change of both the ***system*** and its ***surroundings*** must be considered.
- ***The Second Law of Thermodynamics*** establishes that all spontaneous processes increase the entropy of the ***universe*** (system *and* surroundings). "*Direction of time*"
- If entropy increases in both the system and the surroundings, the process is spontaneous.

The Second Law of Thermodynamics

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

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

The Second Law of Thermodynamics

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

For a spontaneous process: $\Delta S_{\text{universe}} > 0$

Since heat is exchanged with the surroundings: $q_{\text{surr}} = -q_{\text{p}} = \Delta H_{\text{sys}}$

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

Therefore: $$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T}$$

Multiply by $-T$: $-T\Delta S_{\text{univ}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$

Free Energy and Free Energy Change

- What is the significance of: $-T\Delta S_{\text{univ}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$?
- The entropy change of the *universe*—our criterion for spontaneity—has now been defined entirely in terms of the *system*.
- The quantity $-T\Delta S_{\text{univ}}$ is called the ***free energy change* (ΔG)**.
- For a process at constant temperature and pressure:

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

Free Energy and Free Energy Change

- If $\Delta G < 0$ (negative), a process is ***spontaneous***.
- If $\Delta G > 0$ (positive), a process is ***nonspontaneous***.
- If $\Delta G = 0$, neither the forward nor the reverse process is favored; there is no net change, and the process is at ***equilibrium***.

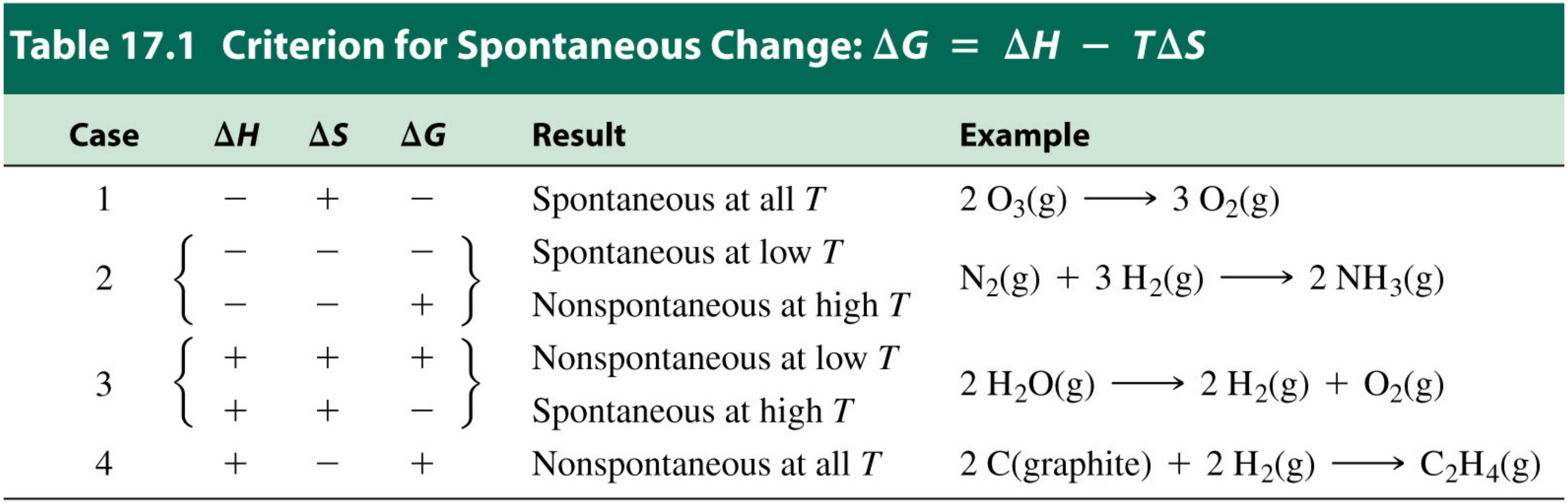
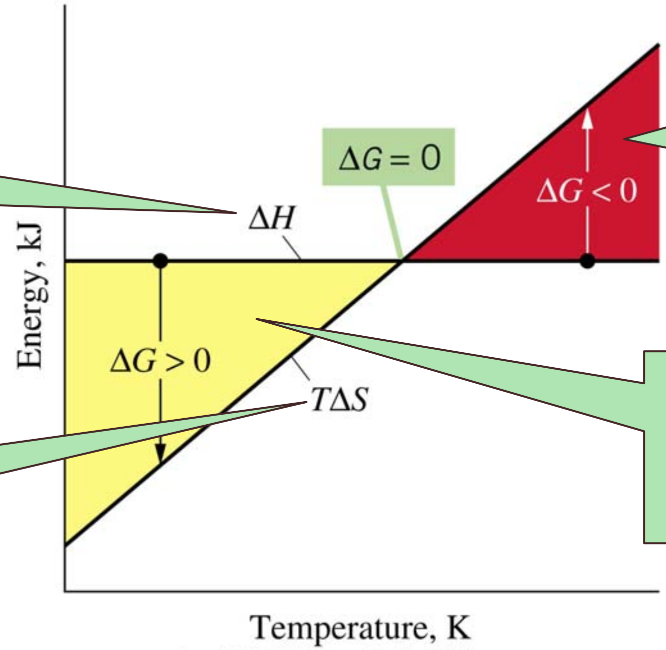


Table 17.1 Criterion for Spontaneous Change: $\Delta G = \Delta H - T\Delta S$

Case	ΔH	ΔS	ΔG	Result	Example
1	−	+	−	Spontaneous at all T	$2\ O_3(g) \longrightarrow 3\ O_2(g)$
2	−	−	−	Spontaneous at low T	$N_2(g) + 3\ H_2(g) \longrightarrow 2\ NH_3(g)$
	−	−	+	Nonspontaneous at high T	
3	+	+	+	Nonspontaneous at low T	$2\ H_2O(g) \longrightarrow 2\ H_2(g) + O_2(g)$
	+	+	−	Spontaneous at high T	
4	+	−	+	Nonspontaneous at all T	$2\ C(graphite) + 2\ H_2(g) \longrightarrow C_2H_4(g)$

Case 3 illustrated



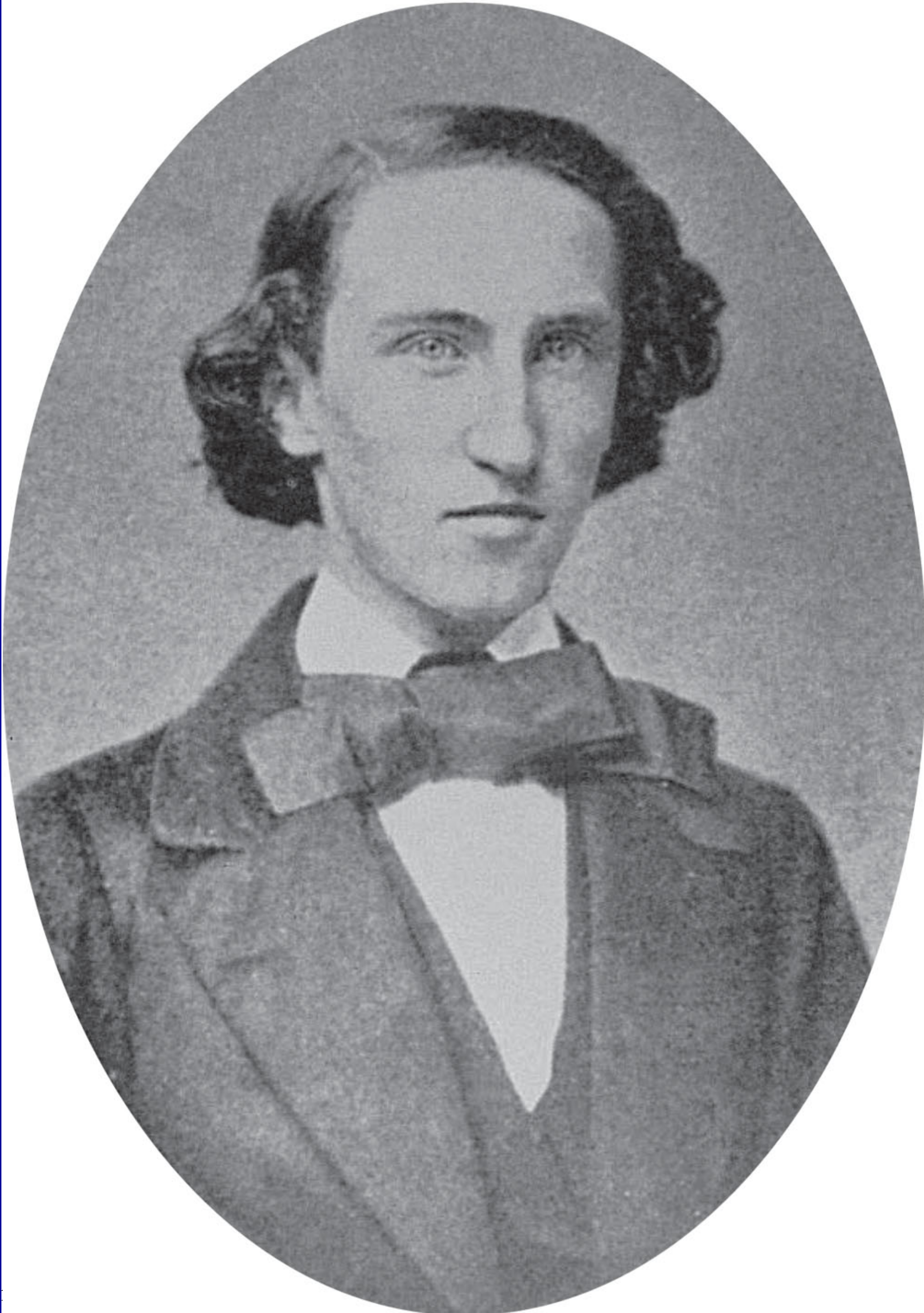
ΔH is (+) and is more-or-less constant with T.

At high T, the size of $T\Delta S$ is large, and $-T\Delta S$ predominates.

At low T, the size of $T\Delta S$ is small, and ΔH (+) predominates.

Since ΔS is (+), the slope $T\Delta S$ is also (+).

Gibbs
1839-1903
Professor of Mathematical Physics
Yale University



Gibbs Free Energy ΔG

$$\Delta G^0_{sys} = \Delta H^0_{sys} - T\Delta S^0_{sys}$$

- If Gibbs Free Energy is negative, a reaction will be spontaneous.(Thermodynamically favored)
- If Gibbs Free Energy is zero, the reaction is at equilibrium(poised to change spontaneity)
- If Gibbs Free Energy is positive, the reaction is nonspontaneous.
- Gibbs Free Energy represents the maximum work (w_{max}) available
- Note: $\Delta G^0_{rxn} = \Sigma\Delta G^0_f(\text{products}) - \Sigma\Delta G^0_f(\text{reactants})$

Standard Free Energy Changes

Standard free energies of formation, $\Delta G_f°$ are analogous to standard enthalpies of formation, $\Delta H_f°$.

$$\Delta G_f^\circ = \Sigma\Delta G^\circ_{reactants} - \Sigma\Delta G^\circ_{products}$$

$\Delta G°$ can be looked up in tables,

or

calculated from $S°$ and $\Delta H°$.

Free Energy Changes

Very key equation:

$$\Delta G = \Delta H^{\circ}_{sys} - T\Delta S_{system}$$

This equation shows how ΔG° changes with temperature.

(We assume S° & ΔH° are independent of T.)

Free Energy and Temperature

- There are two parts to the free energy equation:
  - $\Delta H°$— the enthalpy term
  - $T\Delta S°$ — the entropy term

- The temperature dependence of free energy comes from the entropy term.

Free Energy Change and Equilibrium

- At equilibrium, $\Delta G = 0$ (reaction is neither spontaneous nor nonspontaneous).
- Therefore, at the equilibrium temperature, the free energy change expression becomes:

$$\Delta H = T\Delta S \qquad \text{and} \qquad \Delta S = \Delta H/T$$

- ***Trouton's rule*** states that the entropy change is about the same when one mole of a substance is converted from liquid to vapor (at the normal boiling point).
- $\Delta S°_{\text{vapn}}$ for many substances is about 87 J mol^{-1} K^{-1}.
- This rule works best with nonpolar substances.
- It generally fails for liquids with a more ordered structure, such as those with extensive hydrogen bonding.

Vaporization Energies

Trouton's rule implies that **about the same amount of disorder** is generated in the passage of **one mole of substance from liquid to vapor** when comparisons are made **at the normal boiling point**

$$\Delta S°_{\text{vapn}} = \Delta H°_{\text{vapn}}/T_{\text{bp}} \approx 87 \text{ J mol}^{-1} \text{ K}^{-1}$$

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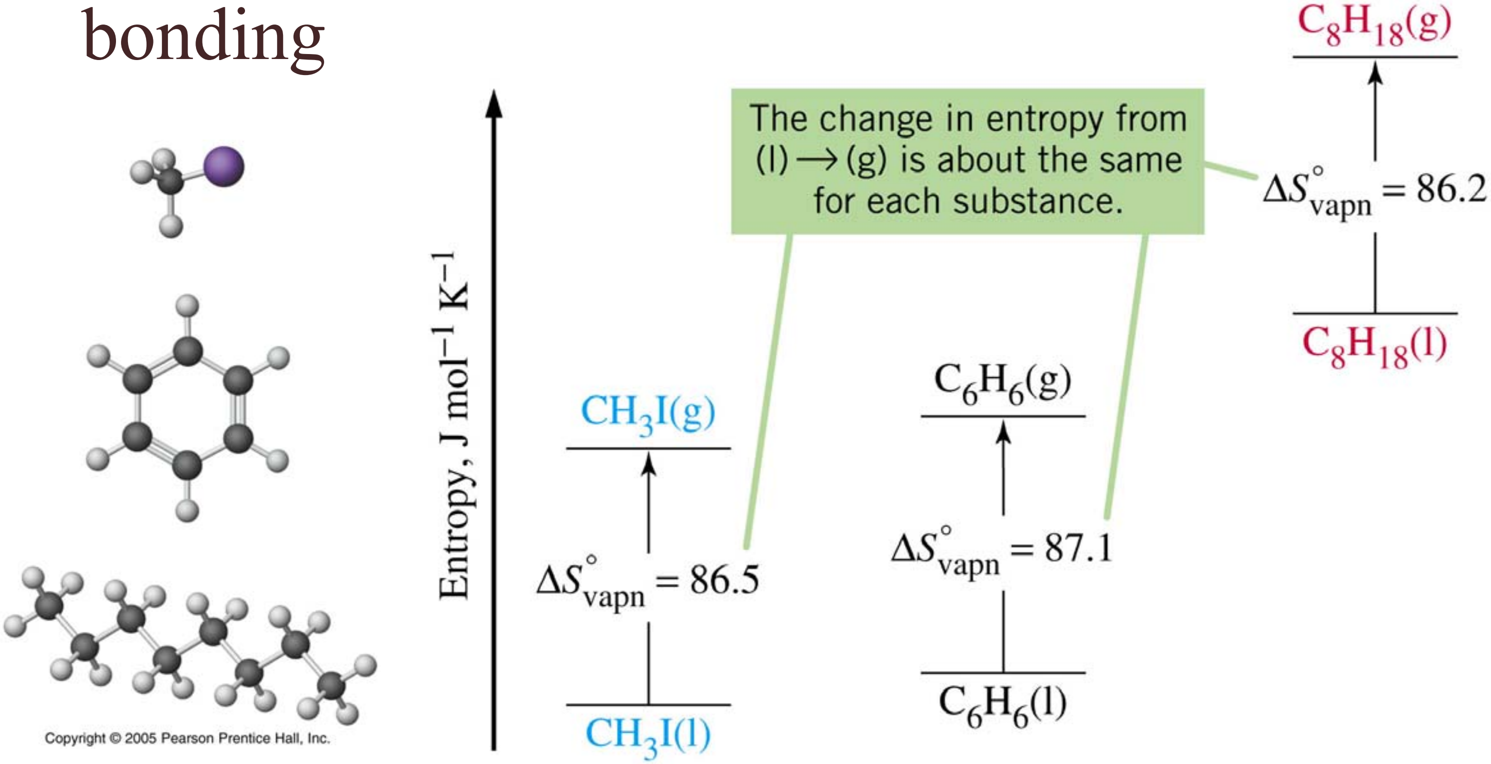
Trouton’s Rule

This rule works best with nonpolar substances and generally fails for liquids with a more ordered structure, such as those with extensive hydrogen bonding



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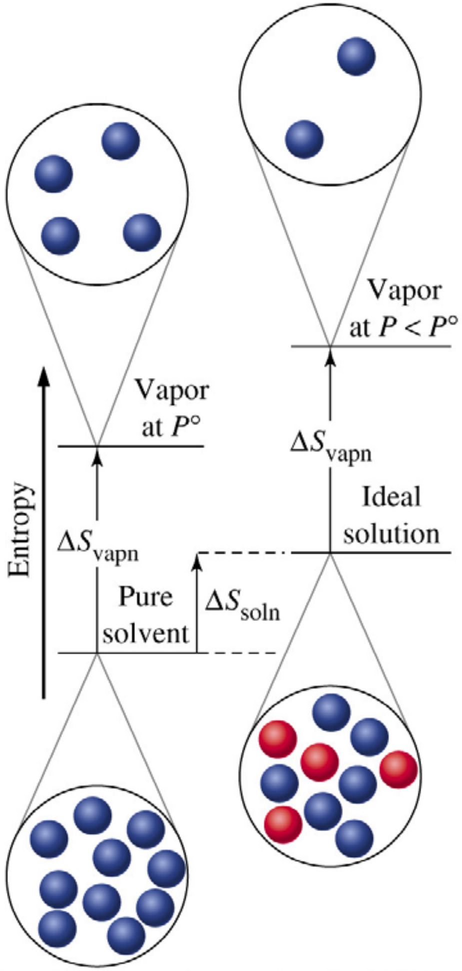
Raoult's Law Revisited

$$P_{\text{solv}} = x_{\text{solv}} \cdot P^{\text{o}}_{\text{solv}}$$

Because the mole fraction of solvent in a solution (x_{solv}) is less than 1, the **vapor pressure of the solvent (P_{solv}) in an ideal solution is lower than that of the pure solvent ($P^{\text{o}}_{\text{solv}}$)**



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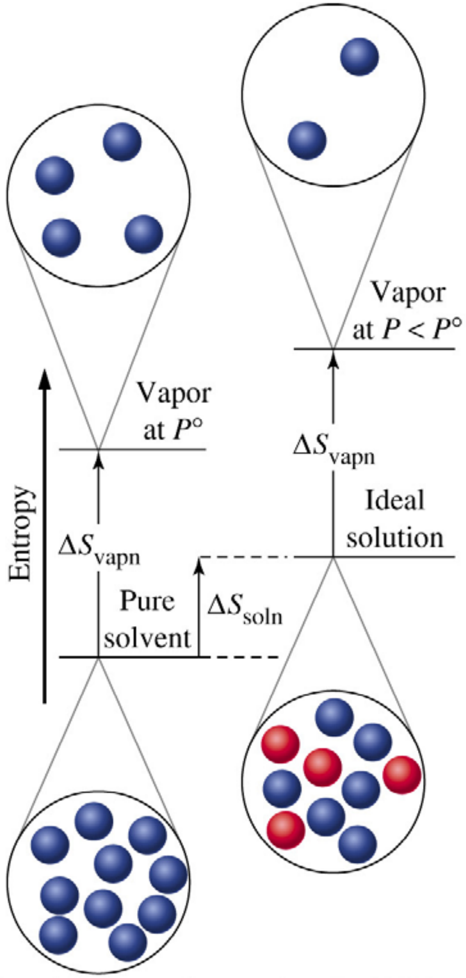
Raoult’s Law Revisited

A **solution has a higher entropy** than the pure solvent

Because a solution has a higher entropy than the pure solvent, the **vapor from the solution** must also have a **higher entropy** than the **vapor from the pure solvent**

The entropy of the vapor increases if molecules can roam more freely, that is, they are at a *lower* pressure



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Relationship of ΔG^o and K_{eq}

$\Delta G = 0$ is a criterion for equilibrium at a single temperature, the one temperature at which the equilibrium state has ***all reactants and products in their standard states***

ΔG and ΔG^o are related through the reaction quotient, Q

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

Under the conditions of $\Delta G = 0$ and $Q = K_{eq}$, the equation above becomes

$$\Delta G^o = -RT \ln K_{eq}$$

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Calculating Equilibrium Constants

- Rearranging Equation (17.12):

$$\Delta G^\circ = -RT\ ln\ K_{eq}$$

$$ln\ K_{eq} = -\frac{\Delta G^\circ}{RT}$$

- The units of ΔG° and R must be consistent; both must use kJ or both must use J.

The Equilibrium Constant, K_{eq}

Activities are the dimensionless quantities needed in the equilibrium constant expression K_{eq}

For *pure* ***solid*** *and* ***liquid*** *phases*: activity, ***a*****, = 1**

For ***gases***: ***Assume ideal gas*** behavior, and replace the activity by the numerical value of the gas ***partial pressure in atm***.

For *solutes in* ***aqueous solution***: Assume intermolecular or interionic attractions are negligible and replace solute activity by the ***numerical value of the solute molarity***

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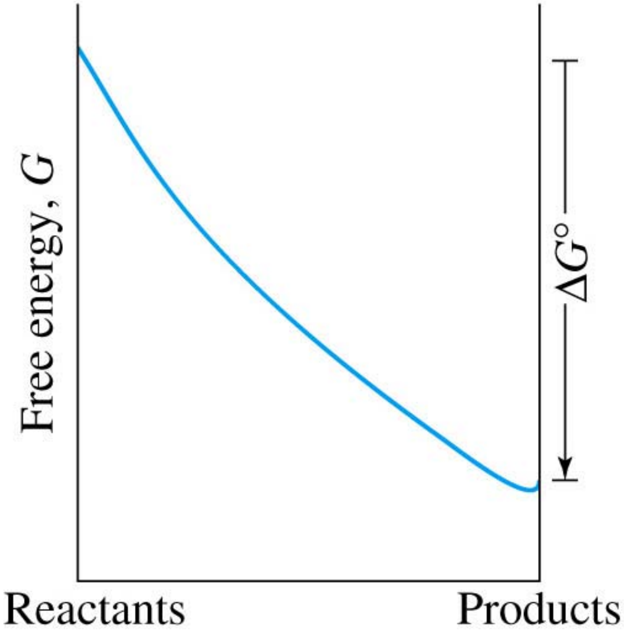
The Significance of the Sign and Magnitude of ΔG°

$\Delta G_{prod} << \Delta G_{reac}$

ΔG^{o} is a *large, negative* quantity and equilibrium is very **far to the right**

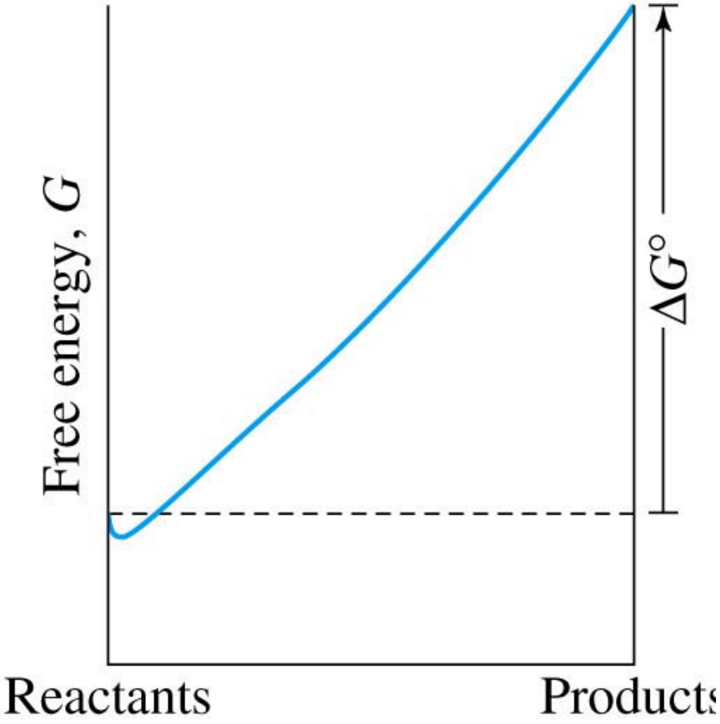


EOS

The Significance of the Sign and Magnitude of $\Delta G°$

$\Delta G_{\text{prod}} >> \Delta G_{\text{reac}}$

$\Delta G°$ is a *large, positive* quantity and equilibrium is very **far to the left**

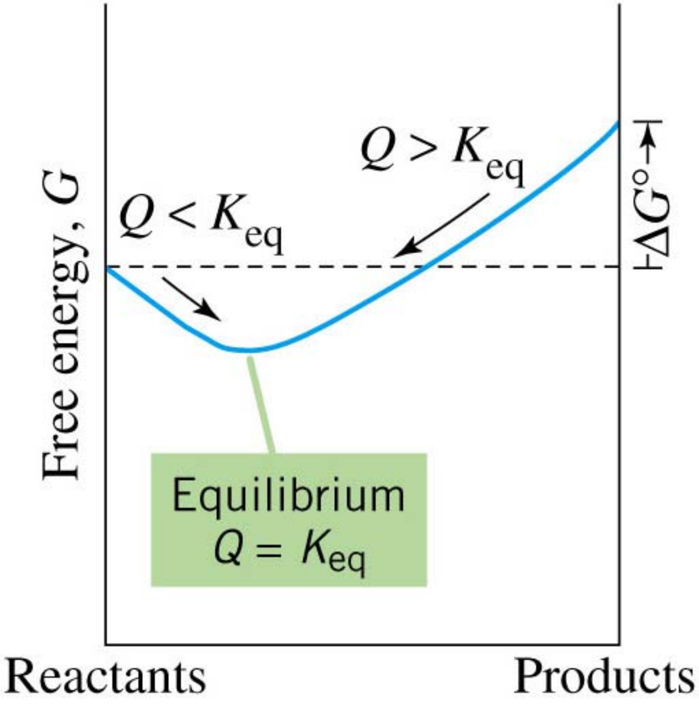


EOS

The Significance of the Sign and Magnitude of $\Delta G°$

$$\Delta G_{prod} \approx \Delta G_{reac}$$

the equilibrium lies more toward the center of the reaction profile



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Coupled Reactions

- A nonspontaneous reaction may be ***coupled*** with a spontaneous reaction.
- The decomposition of copper(I) oxide is quite nonspontaneous at room temperature:

$$Cu_2O(s) \rightleftharpoons 2\,Cu(s) + \tfrac{1}{2}\,O_2(g) \qquad \Delta G^\circ_{298} = +149.9\text{ kJ}$$

- By coupling this decomposition with the formation of CO from carbon,

$$C(\text{graphite}) + \tfrac{1}{2}\,O_2(g) \rightleftharpoons CO(g) \qquad \Delta G^\circ_{298} = -137.2\text{ kJ}$$

we can reduce the nonspontaneity of Cu_2O and make the overall reaction occur slightly above room temperature:

$$Cu_2O(s) + C(\text{graphite}) \rightleftharpoons 2\,Cu(s) + CO(g) \qquad \Delta G^\circ_{298} = +12.7\text{ kJ}$$

The Dependence of ΔG^o and K_{eq} on Temperature

To obtain equilibrium constants at different temperatures, it will be assumed that ΔH and ΔS do not change much with temperature

the **25 °C values of ΔH^o and ΔS^o** along with the **desired temperature** are substituted

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

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The Dependence of ΔG° and K_{eq} on Temperature

To obtain K_{eq} at the desired temperature, the following equation is used …

$$ln\ K_{eq} = \frac{-\Delta H^{\circ}}{RT} + \text{ constant} \qquad \textbf{\textit{or}}$$

$$ln\ \frac{K_2}{K_1} = \frac{\Delta H^{\circ}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

This is the van’t Hoff equation

Equilibrium with Vapor

ΔH^o for either sublimation or vaporization is used depending on the other component (gaseous – solid/liquid equilibria.)

Partial pressures are exchanged for *K*'s

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H^o_{vap}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

This is the Clausius–Clapeyron equation

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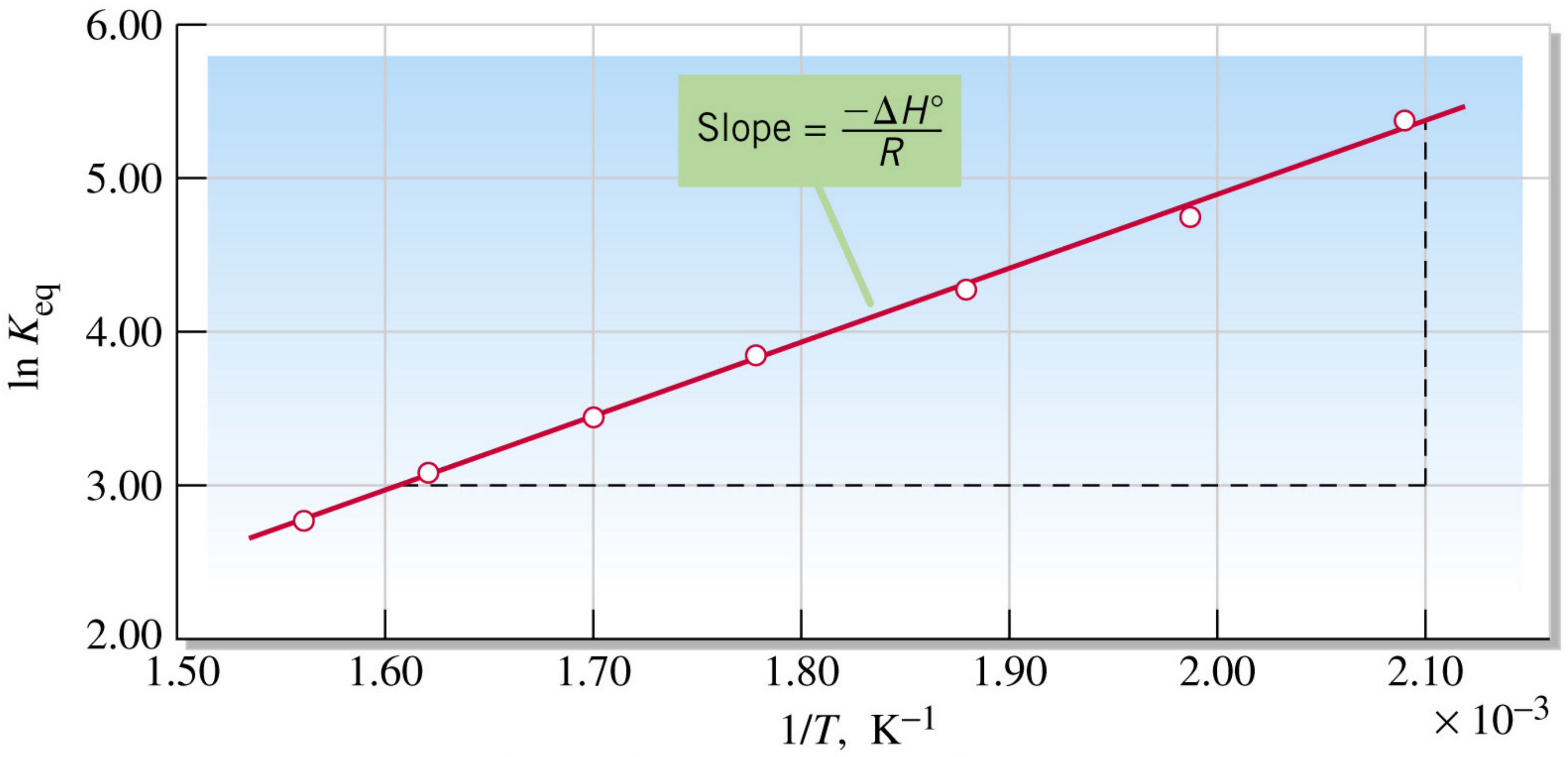
Temperature Dependence of K_{eq}



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Summary of Concepts

- **Le Chatelier's Principle** predicts that when an equilibrium reaction is stressed, the driving force for the reaction will change in such a way as to remove the stress.
- **Gibb's Free Energy** measures the driving force for a reaction and is also a measure of reaction spontaneity.
- The **equilibrium constant, K**, reflects a point in a reaction where there is no more tendency to react in either direction. (the driving force is zero)
- The **reaction quotient, Q**, measures the progress of a reaction and becomes greater or less than K when an equilibrium reaction is stressed (i.e. no longer at equilibrium)

Summary of Concepts

- A spontaneous change is one that occurs by itself without outside intervention
- The third law of thermodynamics states that the entropy of a pure, perfect crystal at 0 K can be taken to be zero
- The direction of spontaneous change is that in which *total* entropy increases

- The free energy change, ΔG, is equal to $-T\Delta S$, and it applies just to the system itself

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Summary (cont'd)

- The standard free energy change, ΔG^o, can be calculated by substituting standard enthalpies and entropies of reaction and a Kelvin temperature into the Gibbs equation, or, by combining standard free energies of formation
- The condition of equilibrium is one for which $\Delta G = 0$

EOS

Summary (cont’d)

- The value of ΔG^{o} is in itself often sufficient to determine how a reaction will proceed
- Values of $\Delta G^{o}{}_{f}$, $\Delta H^{o}{}_{f}$, and ΔS are generally tabulated for 25 °C. To obtain values of K_{eq} at other temperatures, the van’t Hoff equation must be used
- The Clausius–Clapeyron equation connects solid/vapor or liquid/vapor equilibria to varying temperature

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