Thermodynamics: Entropy and Free Energy

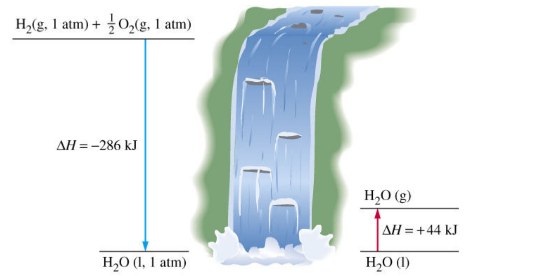
Terminology:

Spontaneity: The notion of whether or not a process can take place unassisted. (E.g. Rock rolling down hill; iron rusting; heat flow from hot to cold)

Entropy: A measure of how energy and matter is spread out (dispersed) among the atoms and molecules of a system and its surroundings.

Free Energy: A thermodynamic function that relates enthalpy and entropy to spontaneity.

Although heat (q) is a consideration in spontaneity, it is not the only factor in its determination.



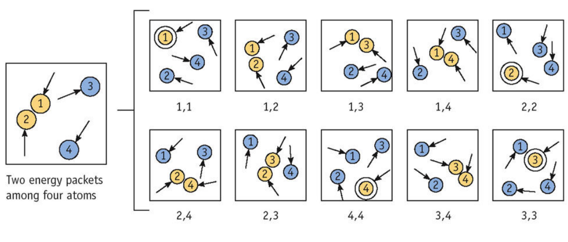
The formation of water at 25 °C and 1 atm: a spontaneous process that is exothermic

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

Dispersal of Energy

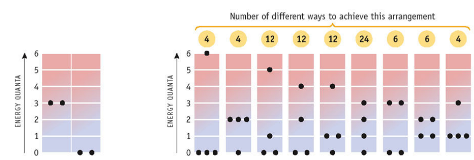
Statistical analysis of energy distribution of two quantized packets of energy

Beige = Quantum of energy; Blue = No energy.



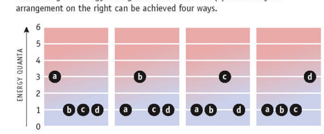
Note that energy is more likely to be distributed over multiple particles (6 of 10) than concentrated on one .

Energy distribution of 4 particles with a total of 6 quantized units of energy.



(a) Initially four particles are separated from each other. Two particles each have three quanta of energy, and the other two have none. A total of six quanta of energy will be distributed once the particles interact.

(b) Once the particles begin to interact, there are nine ways to distribute the six available quanta. Each of these arrangements will have multiple ways of distributing the energy among the four atoms. Part (c) shows why the arrangement on the right can be achieved four ways.



(c) There are four different ways to arrange four particles (a, b, c, and d) such that one particle has three quanta of energy and the other three each have one quantum of energy.

Most probable configuration is energy distributed over a large number of particles over a large number of states.

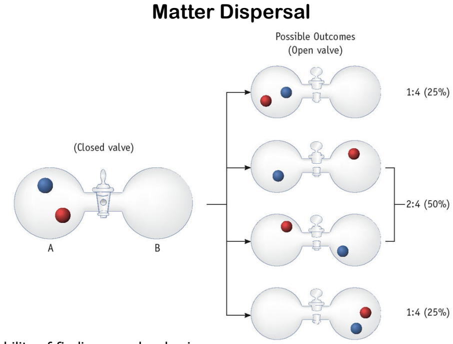
As the number of particles and the number of energy levels grows, one arrangement turns out to be vastly more probable than the others.

Examples of Energy Dispersal

- Heat energy in a coffee cup being distributed to the surroundings

- A rock rolling down a hill distributing its energy to the air and hillside

Matter Dispersal

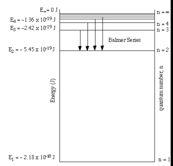


Probability of finding n molecules in the original flask when the valve is open is given by $(1/2)^n$

Matter Dispersal and Energy Dispersal

Related to quantum mechanics

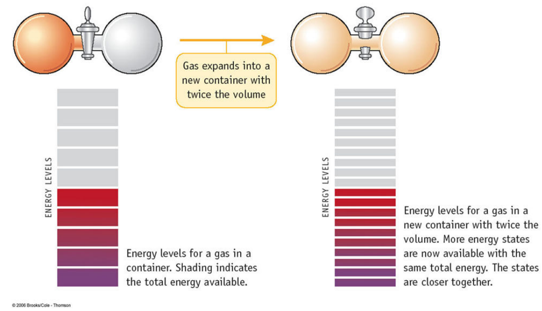
For larger n numbers (principal quantum number)
- Average radius increases
- Energy levels get closer together



Can be applied to macroscopic systems:
- n is related to the size of the system

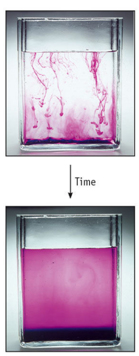
For a vessel holding a sample of gas:
- Increase in size corresponds to an increase in n number
- Energy levels get closer together
- Since available energy has not changed, the number of ways of distributing the total energy increases

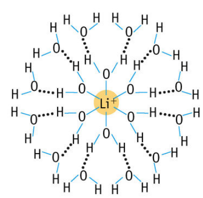
When matter is dispersed into a larger volume, energy is dispersed over more energy levels.



For gases at room temperature, the entropy-driven dispersal of matter is equivalent to an increase in disorder of the system.

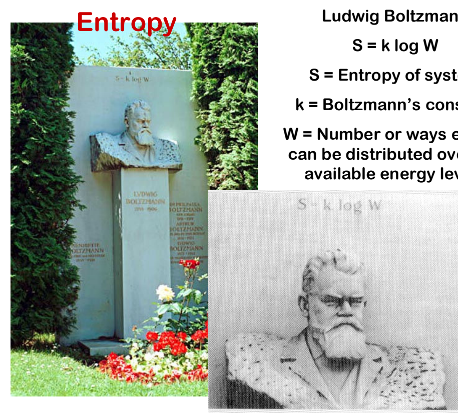
While dispersal of gases always increases disorder, the same is not always true for solutions





Decrease in disorder in the solvation of lithium hydroxide

Increase in disorder in the distribution of potassium permanganate



Ludwig Boltzmann

S = k log W

S = Entropy of system

k = Boltzmann's constant

W = Number or ways energy can be distributed over the available energy levels

Thermodynamics:

-Determines **if** a process is **possible and spontaneous** and the equilibrium state of the system (how far the reaction will proceed)

-Kinetics determines the rate of the process.

Review of Thermochemistry

For Pressure-Volume Work

$\Delta E = q + P\Delta V$ ΔE is the internal energy change of the system

$q_p = \Delta E - P\Delta V$ (at constant pressure)

q_p = Enthalpy change = ΔH

(negative = exothermic; positive = endothermic)

Laws of Thermodynamics:

1st Law: The energy of the universe is constant (conservation law)

2nd Law: The entropy of the universe is always increasing

3rd Law: The entropy of a perfect, pure crystal at 0K is zero. (Ludwig Boltzmann)

Entropy Equation

$$\Delta S = q_{rev}/T$$ Units: J/K mol

Absolute entropy is determined by cooling a pure crystal to near absolute zero and then adding small increments of heat while monitoring the temperature. The summation of the small increments gives the absolute entropy of the substance.

Since ΔE and ΔH are state functions, but q & w are not; to be reversible, the system must be an infinitesimal amount away from equilibrium.

T is in the denominator because at higher temperatures the addition of heat has less of an effect on the entropy. (The proportional increase (with temperature) in the number of energy levels is greater at lower temperatures)

Reaction spontaneity: Driven by two factors

Enthalpy ΔH (heat of the reaction)

Spontaneity is favored by exothermic ($-\Delta H$)

Entropy, S
Spontaneity favored by increase in entropy ($+\Delta S$)

Reversible processes are in equilibrium

Spontaneous processes are not reversible

Enthalpy and entropy are both "state functions"

Factors That Increase the Entropy of a System:

Phase change Solid<Liquid<Gas (Randomness of particles and separation)

Nonelectrolyte solutions of solids or liquids in a solvent (random mixing of particles)

A reaction that increases the molecules of a gas

A substance is heated

The number of atoms in a substance (greater vibrational modes)

The molar mass of a substance. (Generally)

Question:

Indicate whether each of the following processes is spontaneous or nonspontaneous. Comment on cases in which a clear determination cannot be made.

a. The decay of a piece of wood buried in soil.

b. The formation of sodium, $Na_{(s)}$, and chlorine, $Cl_{2(g)}$, by vigorously stirring an aqueous solution of sodium chloride, $NaCl_{(aq)}$.

c. The formation of lime, $CaO_{(s)}$, and carbon dioxide, $CO_{2(g)}$ at 1 atm pressure, from limestone, $CaCO_{3(s)}$, at 600°C.

d. The ionization of hydrogen chloride when $HCl_{(g)}$ dissolves in liquid water.

Answer:

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d. The ionization of hydrogen chloride when $HCl_{(g)}$ dissolves in liquid water.

a. Spontaneous

b. Nonspontaneous

c. Uncertain

d. Spontaneous

Question:

Predict whether each of the following leads to an increase or decrease in the entropy of a system or if more information is needed.

a. $NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)}$

b. $2KClO_{3(s)} \rightarrow 2KCl_{(s)} + 3O_{2(g)}$

c. $CO_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + H_{2(g)}$

Answer:

a. Decrease

b. Increase

c. Uncertain

From the 2nd Law of Thermodynamics:

$$\Delta S_{univ} = \Delta S_{surr} + \Delta S_{sys}$$
$$\Delta S^o_{univ} = \Delta S^o_{surr} + \Delta S^o_{sys} \quad \text{(1molal; 1bar)}$$

If ΔS^o_{univ} >0; spontaneous
=0; equilibrium
<0; nonspontaneous

$\Delta S^o_{sys} = \Sigma m S^o_{prod} - \Sigma n S^o_{react}$

(system includes reactant and product mass dispersal)

Since the system exchanges energy with its surroundings:

$\Delta S^o_{surr} = q_{surr}/T = -\Delta H^o_{sys}/T$

$\Delta H^o = \Sigma m \Delta H_f^o{}_{prod} - \Sigma n \Delta H_f^o{}_{react}$

where m and n are the coefficients of the balanced equation.

Watch Units: Enthalpy is usually given in kJ/mol, and entropy in J/K mol

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Table 19.2 Predicting Whether a Process Will Be Spontaneous

Type	ΔH^o_{sys}	ΔS^o_{sys}	Spontaneous Process?
1	Exothermic process	Less order	Spontaneous under all conditions
	$\Delta H^o_{sys} < 0$	$\Delta S^o_{sys} > 0$	$\Delta S^o_{univ} > 0$.
2	Exothermic process	more order	Depends on relative magnitudes of ΔH and ΔS.
	$\Delta H^o_{sys} < 0$	$\Delta S^o_{sys} < 0$	More favorable at *lower* temperatures.
3	Endothermic process	Less order	Depends on relative magnitudes of ΔH and ΔS.
	$\Delta H^o_{sys} > 0$	$\Delta S^o_{sys} > 0$	More favorable at *higher* temperatures.
4	Endothermic process	More order	Not spontaneous under any conditions
	$\Delta H^o_{sys} > 0$	$\Delta S^o_{sys} < 0$	$\Delta S^o_{univ} < 0$

Summary of Entropy Change Equations

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

$\Delta S^o_{sys} = \Sigma m S^o_{prod} - \Sigma n S^o_{react}$

$$\Delta S^o_{univ} = \Delta S^o_{surr} + \Delta S^o_{sys}$$

$-\Delta H^o_{sys}/T$

$\Delta H^o = \Sigma m \Delta H_f^o{}_{prod} - \Sigma n \Delta H_f^o{}_{react}$

Example:

Is the direct reaction of hydrogen and chlorine to give hydrogen chloride gas predicted to be spontaneous?
$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$
Answer the question by calculating the values for ΔS^o_{sys} and ΔS^o_{surr} (at 298) and then summing them to determine ΔS^o_{univ}

Answers:

ΔS^o_{sys} = 2 S° (HCl) – [S° (H_2) + S° (Cl_2)]
ΔS^o_{sys} = (2mol)(186.2J/molK) – [(1mol)(130.7J/molK) + (1mol)(223.08J/molK)] = 18.6J/K

$\Delta S^o_{surr} = -\Delta H^o_{sys}/T$ = - (-184,620J/298K) = 619.5J/K

$\Delta S^o_{univ} = \Delta S^o_{sys} + \Delta S^o_{surr}$ = 18.6J/K + 619.5J/K = 638.1J/K

Example:

Iron is produced in a blast furnace by reducing iron oxide using carbon. For this reaction,
$2Fe_2O_{3(s)} + 3C_{(graphite)} \rightarrow 4Fe_{(s)} + 3CO_{2(g)}$
the following parameters are determined: ΔH^o_{rxn} = +467.9kJ and ΔS^o_{rxn} = +560.7J/K. Show that it is necessary that this reaction be carried out at a high temperature

At 298K, ΔS^o_{surr} = -(467,900J/K)/298K = -1,570J/K

$\Delta S^o_{univ} = \Delta S^o_{sys} + \Delta S^o_{surr}$ = 560.7J/K – 1570J/K = -1010J/K

Since the entropy change is negative, the reaction is not spontaneous as written. If the temperature is raised high enough ΔS^o_{surr} will be less of a factor and the ΔS^o of the system will be great enough to make the overall ΔS^o_{univ} >0.

Gibbs Free Energy

Defined as: The maximum energy available to do useful work.

G = H – TS

In kJ/mol

Allows calculations solely based on the system and not the surroundings

Negative Gibbs free energy values for reactions are spontaneous

Derivation of the Gibbs Free Energy Equation:

From the 2nd Law of Thermodynamics:

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

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

Substituting:

$\Delta S_{univ} = -\Delta H_{sys}/T + \Delta S_{sys}$ multiplying through by T

$T\Delta S_{univ} = -\Delta H_{sys} + T\Delta S_{sys}$ multiplying through by -1

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

$-T\Delta S_{univ}$ is given the special symbol ΔG and is known as **Gibbs Free Energy**

The final form of the equation is:

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

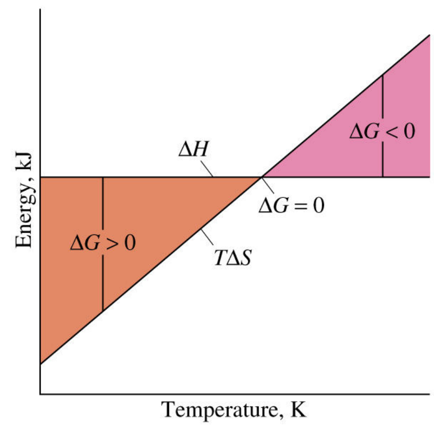
Sign of ΔG and Spontaneity

ΔG < 0 Spontaneous

ΔG> 0 Nonspontaneous (Spontaneous in reverse direction)

ΔG = 0 At Equilibrium (K = 1)

Sign of Enthalpy	Sign of Entropy	Spontaneous?
-	+	Yes
+	-	No
+	+	Depends on T (Entropy driven)
-	-	Depends on T (Enthalpy driven)



Calculating ΔG°, ΔH°, ΔS° from Tabulated Data for a Reaction (° = standard state):

$\Delta G^o = \Sigma m \Delta G_f^o{}_{prod} - \Sigma n \Delta G_f^o{}_{react}$

$\Delta S^o = \Sigma m S^o{}_{prod} - \Sigma n S^o{}_{react}$

$\Delta H^o = \Sigma m \Delta H_f^o{}_{prod} - \Sigma n \Delta H_f^o{}_{react}$

where m and n are the coefficients of the balanced equation.

Note that the enthalpy of formation and the Gibbs free energy of formation for an element in its standard state is zero, but **the entropy is not**!

Question:

Using data from Appendix L to calculate the standard molar entropy change at 25°C for the following reaction. Note that this is a reaction given in an earlier question for which we could not predict whether entropy increases or decreases.

$CO_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + H_{2(g)}$

Answer:

Using data from Appendix L to calculate the standard molar entropy change at 25°C for the following reaction. Note that this is a reaction given in an earlier question for which we could not predict whether entropy increases or decreases.

$CO_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + H_{2(g)}$

[213.6J/molK(1mol)+ 130.6J/molK(1mol)] – [197.6J/molK(1mol) + 188.7J/molK(1mol)] =

ΔS^o = -42.1 J/K mol

Question:

The following reaction is one of those that my occur in the high-temperature, catalyzed oxidation of $NH_{3(g)}$. Use data from appendix L to calculate the standard molar entropy change for this reaction at 25°C.

$NH_{3(g)} + O_{2(g)} \rightarrow N_{2(g)} + H_2O_{(g)}$ (not balanced)

Answer:

The following reaction is one of those that my occur in the high-temperature, catalyzed oxidation of $NH_{3(g)}$. Use data from appendix L to calculate the standard molar entropy change for this reaction at 25°C.

$NH_{3(g)} + O_{2(g)} \rightarrow N_{2(g)} + H_2O_{(g)}$ (not balanced)

$4NH_{3(g)} + 3O_{2(g)} \rightarrow 2N_{2(g)} + 6H_2O_{(g)}$

[2(191.5) + 6(188.7)]-[4(192.3) + 3(205.0)] =

ΔS^o = 131.0 J/K

Example:

Using values of ΔH^o_f and S^o to find ΔH^o_{rxn} and ΔS^o_{rxn}, respectively, calculate the free energy change, ΔG^o_{rxn}, for the formation of 2mol of $NH_{3(g)}$ from the elements at standard conditions (and 25°C)

$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$

Answer:

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

ΔH^o = (2)(-45.90) – [(1)(0) + (3)(0)] = -91.80kJ

ΔS^o = (2)(192.77) – [(1)(191.56) + (3)(130.7)] = -198.12J/K

ΔG^o = -91.80kJ – (298K)(-.19812kJ/K) = -32.8kJ

Example:

Calculate the standard free energy change for the oxidation (react with oxygen) of 1.00mol of $SO_{2(g)}$ to form $SO_{3(g)}$ using standard Gibbs free energy of formation information.

Answer:

$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$

ΔG^o_f = (2)(-371.04kJ/mol) – [(2)(-300.13kJ/mol) + (1)(0kJ/mol)] = -141.82kJ

For 1 mol of SO_2 it is half this amount or

-70.91kJ/mol SO_2

Example:

Oxygen was first prepared by Joseph Priestly (1733-1804), by heating HgO. Use the thermodynamic data in Appendix L to estimate the temperature required to just decompose $HgO_{(s)}$ into $Hg_{(l)}$ and $O_{2(g)}$.

Answer:

$HgO_{(s)} \rightarrow Hg_{(l)} + ½\, O_{2(g)}$

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

ΔH^o = [(1/2)(0)+(1)(0)] – (1)(-90.83kJ/mol) = 90.83kJ/mol

ΔS^o = [(1/2)(205.07J/K)+(1)(76.02)] – (1)(70.29J/K) = 108.265J/K

0 = 90.83 – T(.108265)

T = 839K

ΔG^o, K, and Product Favorability

Calculating ΔG^o_{rxn} from ΔG^o_f values assumes complete conversion to products

$\Delta G = \Delta G^o + RT\ lnQ$ R = 8.3145J/molK

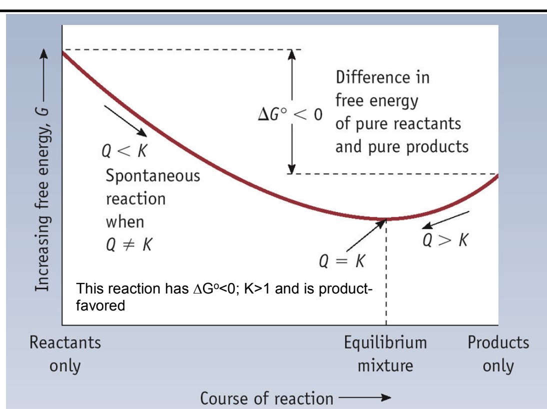
$Q = [C]^c[D]^d/[A]^a[B]^b$ when $aA + bB \leftrightarrow cC + dD$

When system is at equilibrium:
$\Delta G = 0$ and Q = K (see diagram on next slide)

$\Delta G^o_{rxn} = -RT\ lnK$

Can be used to determine K from Gibbs free energy of formation information

Or determine the Gibbs free energy from equilibrium information.



For: $\Delta G_{rxn} = \Delta G^o_{rxn} + RTlnQ$

When:

ΔG_{rxn} <0 then Q<K
Reactants → Products until equilibrium is reached

ΔG_{rxn} >0 then Q>K
Products → Reactants until equilibrium is reached

ΔG_{rxn} = 0 then Q=K
Reaction is at equilibrium

Example:

Determine the value of ΔG^o_{rxn} for the reaction $C_{(graphite)}$ + $CO_{2(g)} \rightarrow 2\ CO_{(g)}$ from the thermodynamic data in Appendix L. Use this result to calculate the equilibrium constant at 298K.

Answer:

$\Delta G^o_{rxn} = -RT \ln K$
ΔG^o = 2(-137.168kJ/mol) – [(1)(0) + (1)(-394.359kJ/mol)] = 120.023kJ/mol
120,023J/mol = -(8.3145J/mol K)(298K)lnK
ln K = -48.44 $K = 9.17 \times 10^{-22}$

Example:

The formation constant for $[Ag(NH_3)_2]^+$ is 1.6×10^7. Use this value to calculate ΔG^o for the reaction

$Ag^+_{(aq)} + 2NH_{3(aq)} \rightarrow [Ag(NH_3)_2]^+_{(aq)}$.

Answer:

$\Delta G^o_{rxn} = -RT \ln K$

ΔG^o_{rxn} = -(8.3145J/molK)(298K)ln(1.6×10^7)

= -41.1kJ/mol

Equilibrium Under Nonstandard Conditions

Liquid water is in equilibrium with water vapor at 1atm pressure and 100°C. As we have seen, ΔG for this (or any) equilibrium process is zero. Moreover, because the liquid and vapor are both in their standard states, we can write

$H_2O_{(l,\ 1atm)} \leftrightarrow H_2O_{(g,\ 1atm)}$ $\Delta G^o_{373} = 0$

We can write the same equation for the vaporization of water at 25°C and determine ΔG^o_{298} from tabulated standard free energies of formation ΔG^o_{298} = +8.590kJ

The positive value of ΔG^o_{298} shows that the process is nonspontaneous. This ***does not mean that water will not vaporize*** at 25°C, just that it will not produce a vapor at 1atm pressure; equilibrium is displaced to the left. The equilibrium vapor pressure of water at 25°C is 23.8mmHg (0.0313atm), a fact that can be represented by the following equation:

$H_2O_{(l,\ 0.0313atm)} \leftrightarrow H_2O_{(g,\ 0.0312atm)}$ $\Delta G_{298} = 0$

To summarize, $\Delta G^o = 0$ 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***. At equilibrium at every other temperature, some or all of the reactants and products must be in a nonstandard state. For these nonstandard conditions, the criterion for equilibrium is that $\Delta G = 0$ (not $\Delta G^o = 0$)