Chapter 18

THERMODYNAMICS

THERMODYNAMICS

Branch of science that studies changes in energy which accompany physical or chemical changes

Can predict if reactions occur

Organized around 3 fundamental laws:
1st, 2nd, 3rd laws of thermodynamics

THERMODYNAMICS

First Law

Energy can be converted from one form to another; can’t be created or destroyed

Total energy of the universe is constant

Enthalpy, H (J or kJ) = heat of reaction at constant pressure

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Second Law

Spontaneous changes increase entropy of the universe

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Third Law

Entropy of a perfect crystalline substance at 0 K is zero

All molecular motion stops at 0 K

This represents perfect order

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Spontaneous Processes

Can we predict a spontaneous reaction?

alkane burning in oxygen
acid + base
iron rusting

Exothermic reactions often spontaneous

Not necessarily fast

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Spontaneous Processes

$2\ HgO\ (s) \rightarrow 2\ Hg\ (l) + O_2\ (g)$ $\Delta H° = 91\ kJ$

What other factors relevant?

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Entropy, S

Measures randomness or disorder of a system

High S → high disorder

Order/disorder related to probability (p)

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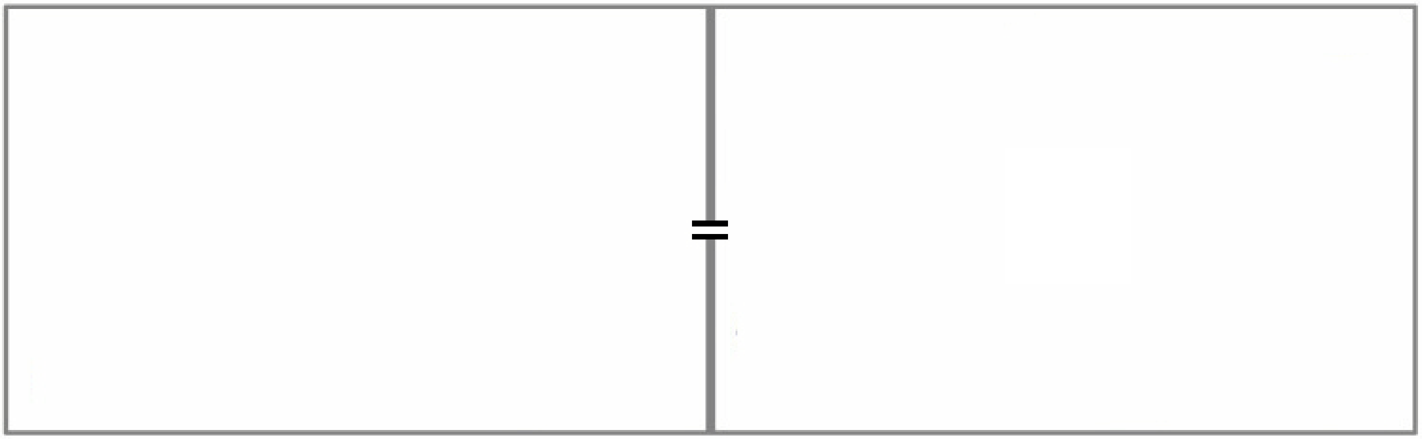
THERMODYNAMICS

Entropy, S



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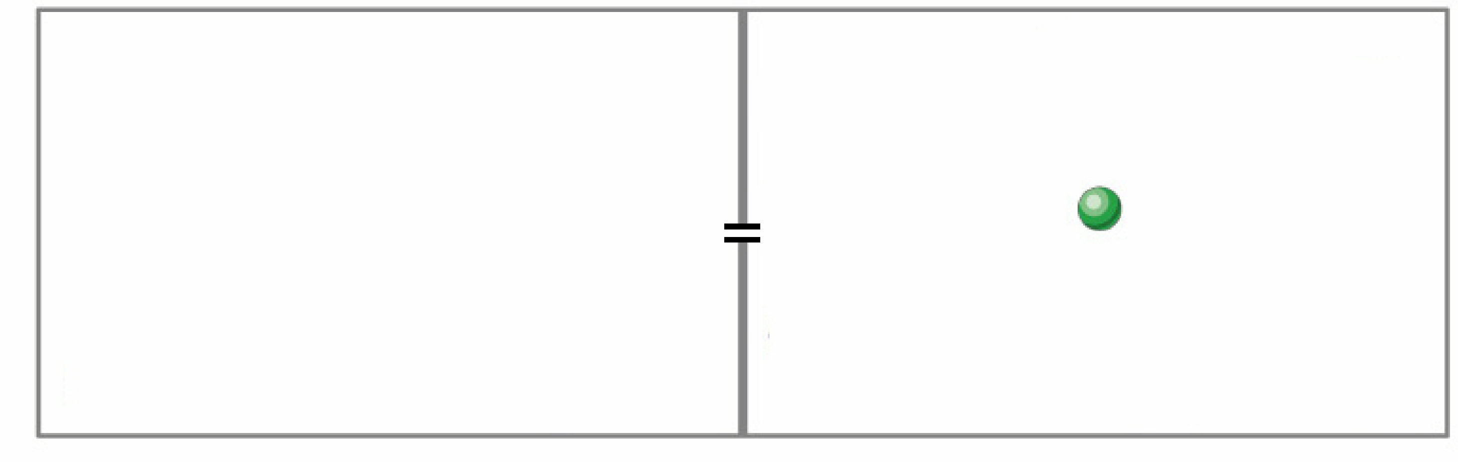
Entropy, S



p = ½ atom being on either side

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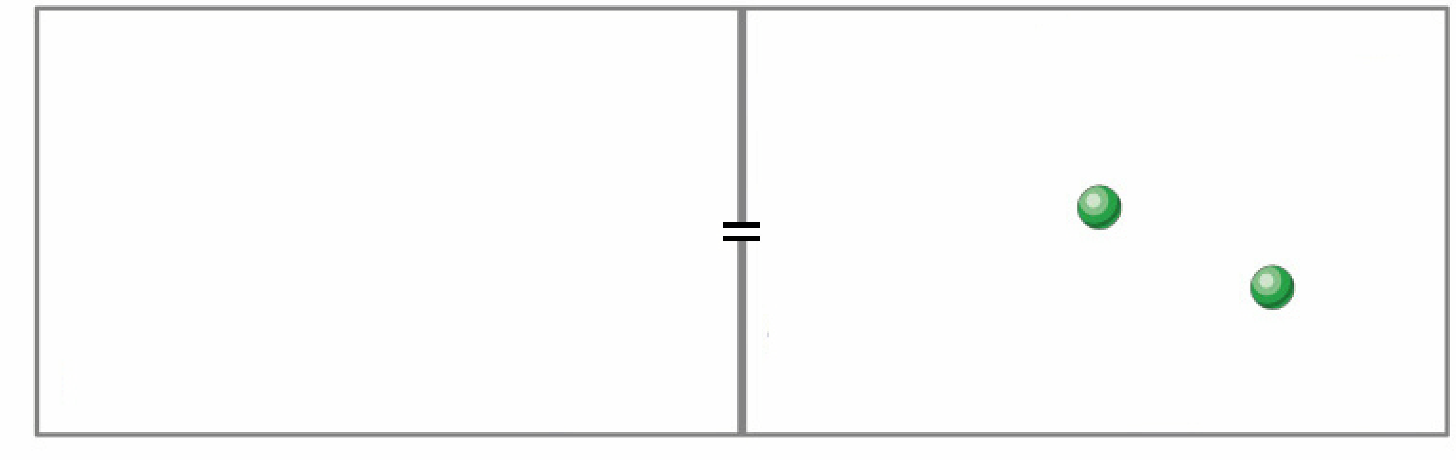
Entropy, S



$p = \frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$ atoms being on same side

$= (\frac{1}{2})^2$

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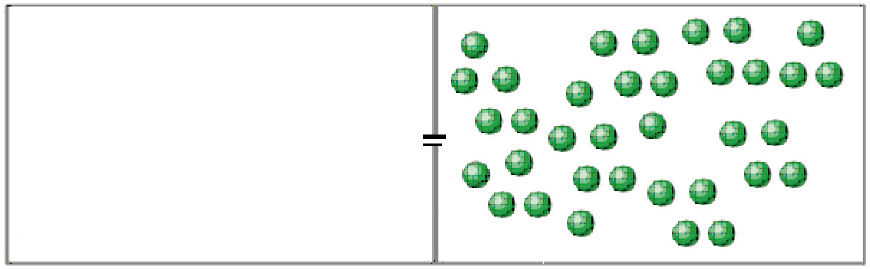
Entropy, S

What is probability of N atoms going into same side?

$p = (\frac{1}{2})^N$

If $N = 100 \Rightarrow p = (\frac{1}{2})^{100} \Rightarrow 8 \times 10^{-31}$



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Entropy, S

Ordered states : low p
Disordered states: high p

S° at 1 atm, 25 °C

Values in table 18.1, appendix 2

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Entropy, S

S for H_2O (l) = 70 J/K.mol at 25°C

S for H_2O (g) = 189

$S_{solid} < S_{liquid} < S_{gas}$

solvent + solute → solution

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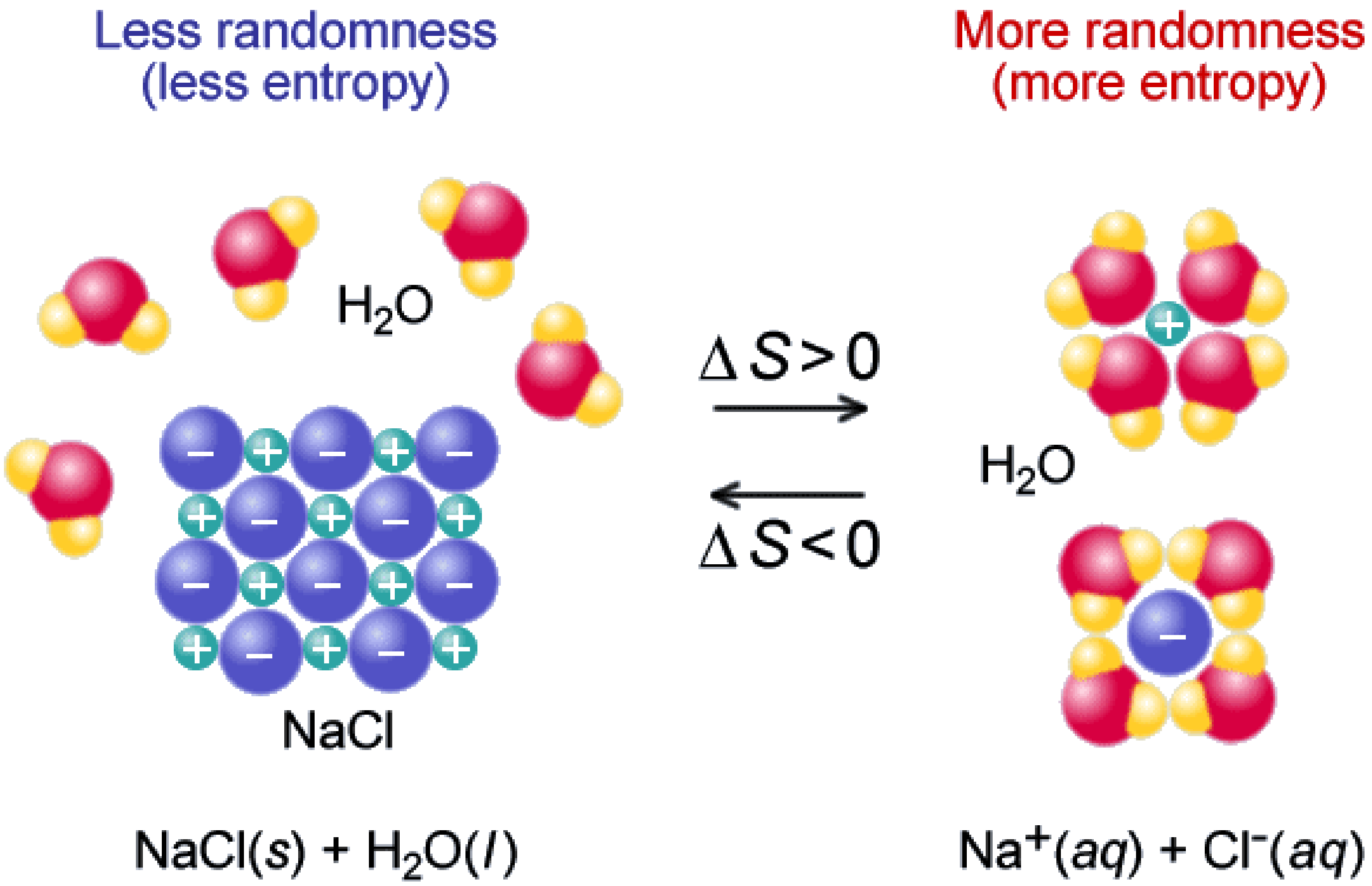
Dissolution of NaCl increases entropy



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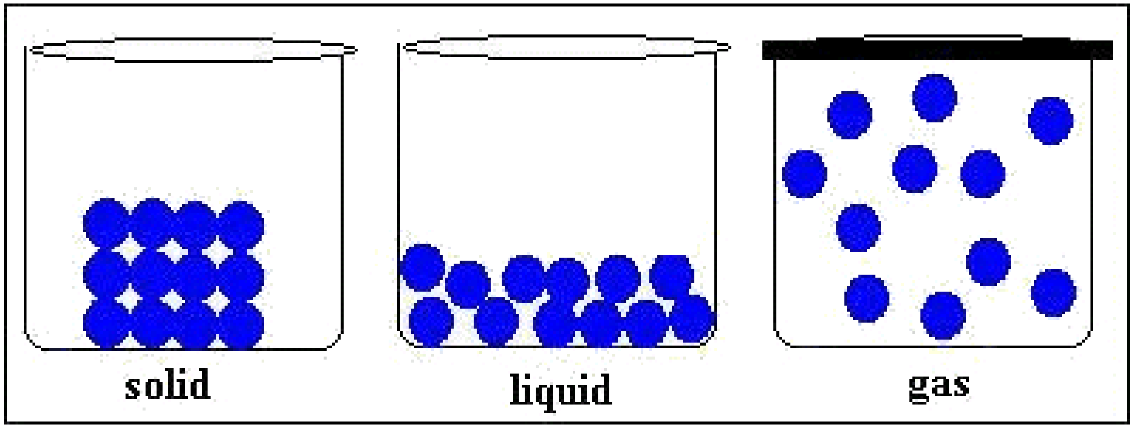
Change in Entropy, ΔS

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

When $S_{final} > S_{initial} \Rightarrow \Delta S > 0$

S increases when s → l   l → g



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Calculating ΔS

$$a\,A + b\,B \rightarrow c\,C + d\,D$$

$$\Delta S^\circ = [c\,S^\circ_{(C)} + d\,S^\circ_{(D)}] - [a\,S^\circ_{(A)} + b\,S^\circ_{(B)}]$$

S° values from tables

When products are gases ΔS° is +

When products are s or l, ΔS° is -

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Free Energy ΔG

S or H alone can’t predict spontaneity

ΔH° (-) or ΔS° (+) often spontaneous

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

When $\Delta G^\circ < 0$ spontaneous forward

When $\Delta G^\circ > 0$ spontaneous reverse

When $\Delta G^\circ = 0$ system at equilibrium

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Calculating ΔG

$a\ A + b\ B \rightarrow c\ C + d\ D$

$$\Delta G^\circ = [c\Delta G_f^\circ{}_{(C)} + d\Delta G_f^\circ{}_{(D)}] - [a\Delta G_f^\circ{}_{(A)} + b\Delta G_f^\circ{}_{(B)}]$$

ΔG_f° free energy of formationvalues from tables in append. 2

Large (-) ΔG° means spontaneous

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How do ΔH & ΔS affect ΔG?

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

1. If ΔH° and ΔS° (+)
   ΔG° (-) only when T is large

2. If ΔH° (+) and ΔS° (-)
   ΔG° always (+)
   forward reaction not spontaneous

THERMODYNAMICS

How do ΔH & ΔS affect ΔG?

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

3. If ΔH° (-) and ΔS° (+)
   ΔG° always (-)
   forward reaction spontaneous

4. If ΔH° and ΔS° (-)
   ΔG° (-) only when T is small

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Equilibrium and ΔG

$\Delta G^\circ = -2.303\ RT \log K$ (or $-RT\ln K$)

$R = 8.31$ J/K.mol

As ΔG° becomes more (-): K increases

THERMODYNAMICS

Equilibrium and ΔG

$$\Delta G^\circ = -2.303\ RT \log K$$

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

$$\Delta H^\circ - T\Delta S^\circ = -2.303\ RT \log K$$