Chemistry and Chemical Reactivity
6th Edition

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CHAPTER 19

Principles of Reactivity: Entropy and Free Energy

Lectures written by John Kotz

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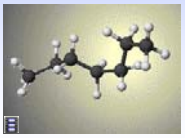
Entropy and Free Energy

How to predict if a reaction can occur, given enough time?

THERMODYNAMICS

How to predict if a reaction can occur at a reasonable rate?

KINETICS



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Thermodynamics

- Both product- and reactant-favored reactions can proceed to equilibrium in a **spontaneous** process.

  $AgCl(s) \leftrightarrows Ag^+(aq) + Cl^-(aq)$
  $K = 1.8 \times 10^{-10}$

  Reaction is not product-favored, but it moves spontaneously toward equilibrium.
- Spontaneous does not imply anything about time for reaction to occur.

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Entropy, S

One property common to spontaneous processes is that the final state is more **DISORDERED** or **RANDOM** than the original.

Spontaneity is related to an increase in randomness.

The thermodynamic property related to randomness is **ENTROPY, S**.

Reaction of K with water

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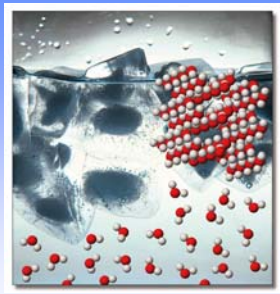

The entropy of liquid water is greater than the entropy of solid water (ice) at 0˚ C.

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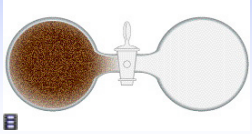
Directionality of Reactions

Probability suggests that a spontaneous reaction will result in the dispersal of energy or of matter or both.

Matter Dispersal



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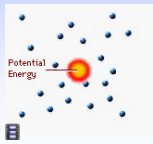
Directionality of Reactions

Probability suggests that a spontaneous reaction will result in the dispersal of energy or of matter or both.

Energy Dispersal



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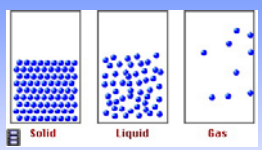
Entropy, S



	S^o (J/K•mol)
H_2O(liq)	69.95
H_2O(gas)	188.8

S (gases) > S (liquids) > S (solids)

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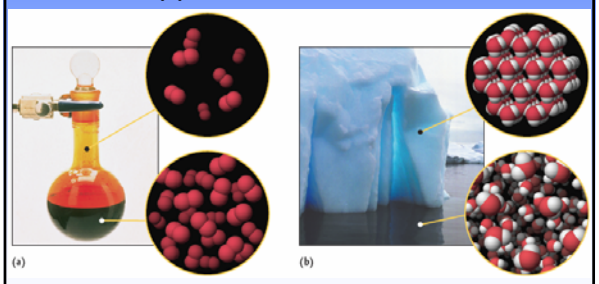
Entropy and States of Matter



$S^\circ(Br_2\ liq) < S^\circ(Br_2\ gas)$ $S^\circ(H_2O\ sol) < S^\circ(H_2O\ liq)$

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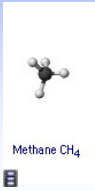
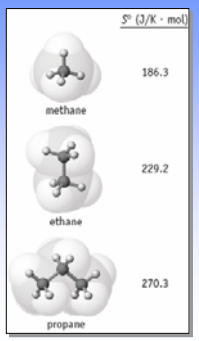
Entropy, S

Increase in molecular complexity generally leads to increase in S.





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Standard Molar Entropies

Table 19.1 Some Standard Molar Entropy Values at 298 K

Element	Entropy, S° (J/K mol)	Compound	Entropy, S° (J/K mol)
C(graphite)	5.6	$CH_4(g)$	186.3
C(diamond)	2.377	$C_2H_6(g)$	229.2
C(vapor)	158.1	$C_3H_8(g)$	270.3
Ca(s)	41.59	$CH_3OH(\ell)$	127.2
Ar(g)	154.9	CO(g)	197.7
$H_2(g)$	130.7	$CO_2(g)$	213.7
$O_2(g)$	205.1	$H_2O(g)$	188.84
$N_2(g)$	191.6	$H_2O(\ell)$	69.95
$F_2(g)$	202.8	HCl(g)	186.2
$Cl_2(g)$	223.1	NaCl(s)	72.11
$Br_2(\ell)$	152.2	MgO(s)	26.85
$I_2(s)$	116.1	$CaCO_3(s)$	91.7

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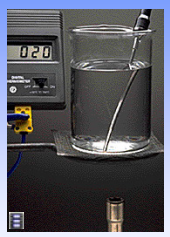
Entropy Changes for Phase Changes



For a phase change,

$\Delta S = q/T$

where q = heat transferred in phase change

For H_2O (liq) → H_2O(g)

$\Delta H = q = +40{,}700$ J/mol

$$\Delta S = \frac{q}{T} = \frac{40{,}700\ \text{J/mol}}{373.15\ \text{K}} = +109\ \text{J/K}\bullet\text{mol}$$

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Entropy and Temperature

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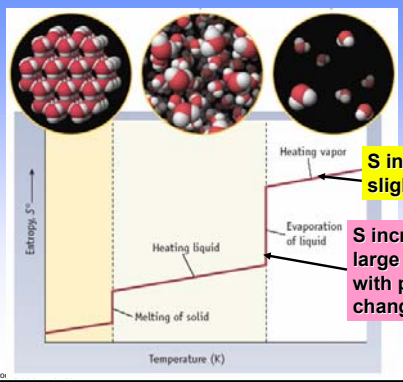

S increases slightly with T

S increases a large amount with phase changes

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Calculating ΔS for a Reaction

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$\Delta S^o = \Sigma S^o$ (products) - ΣS^o (reactants)

Consider $2\ H_2(g) + O_2(g) \text{--->} 2\ H_2O(liq)$

$\Delta S^o = 2\ S^o(H_2O) - [2\ S^o(H_2) + S^o(O_2)]$

ΔS^o = 2 mol (69.9 J/K•mol) -
[2 mol (130.7 J/K•mol) +
1 mol (205.3 J/K•mol)]

ΔS^o = -326.9 J/K

Note that there is a **decrease in S** because 3 mol of gas give 2 mol of liquid.

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