Principles of Reactivity:
Entropy and Free Energy

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What is the difference between
system and surroundings?

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Spontaneous Reactions

Some reactions are product favored;
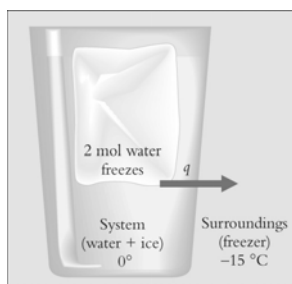**some are reactant favored**

Which one would have a larger K (equilibrium constant) value?

Thermodynamics is the science of energy transfer
which will help predict which way a reaction will go.

***Thermodymanics does not give any information about the speed
of a reaction!! Kinetics (Chapter 14) deals with that.***

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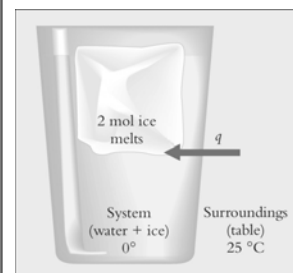**Fig 13-1**   **Pg 592**

Schematic view of the spontaneous process for a water-and-ice mixture in a freezer. The energy-releasing process, freezing, is spontaneous under these conditions.

2 mol water freezes q

System (water + ice) 0°

Surroundings (freezer) −15 °C

$$\Delta H = -n \ \Delta H_{fus} = -(2.00 \text{ mol})(6.01 \text{ kJ/mol}) = -12.0 \text{ kJ}$$

Fig 13-2   **Pg 592**

Schematic view of the spontaneous process for a water-and ice mixture on a table top, The energy-absorbing process, melting, is spontaneous under these conditions.

2 mol ice melts q

System (water + ice) 0°

Surroundings (table) 25 °C

$$\Delta H = n \ \Delta H_{fus} = (2.00 \text{ mol})(6.01 \text{ kJ/mol}) = 12.0 \text{ kJ}$$

Both processes are spontaneous, but have different ΔH values???

Therefore, just knowing ΔH (or ΔE) is not enough to determine if a reaction is spontaneous.

A reaction is considered spontaneous if $\Delta S_{universe}$ is positive or ΔG = negative

WHAT????

The sign of ΔG (free energy) determines if a reaction is spontaneous.

ΔG = **-** reaction is spontaneous in forward direction

ΔG = **+** reaction is nonspontaneous in forward
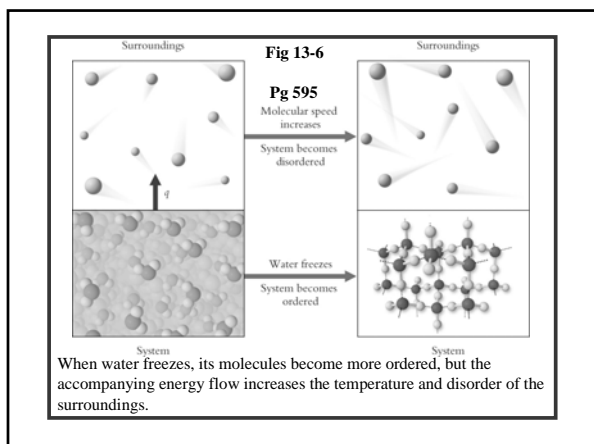

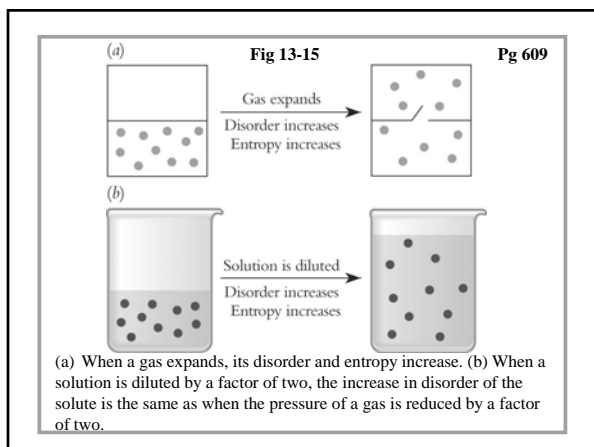**What is Entropy, ΔS?**

Entropy is the measure of disorder.

It is based on the assumption that at absolute 0 K, there is no disorder.

The more positive the number is for entropy, S, the more disordered it is

Which one of these has the highest disorder?

solid, liquid or gas

Fig 13-6

Pg 595

Surroundings

Molecular speed increases

System becomes disordered

Surroundings

Water freezes

System becomes ordered

System

System

When water freezes, its molecules become more ordered, but the accompanying energy flow increases the temperature and disorder of the surroundings.

(a)

Fig 13-15

Pg 609

Gas expands

Disorder increases
Entropy increases

(b)

Solution is diluted

Disorder increases
Entropy increases

(a) When a gas expands, its disorder and entropy increase. (b) When a solution is diluted by a factor of two, the increase in disorder of the solute is the same as when the pressure of a gas is reduced by a factor of two.

Which of the following reactions leads to a decrease in entropy of the system?

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

B) $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$

C) $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

D) $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

E) $PCl_5(s) \rightarrow PCl_3(l) + Cl_2(g)$

Useful Generalizations About Entropy

- When comparing the same or very similar substances, entropies of gases are much larger than those of liquids, which are larger than for solids

- Entropies of more complex molecules are larger than those of simpler molecules, especially in a series of closely related compounds

- Entropies of ionic solids become larger as the attractions among the ions become weaker

- Entropy usually increase when a pure liquid or solid dissolves in a solvent.

Laws of Thermodynamics

| First Law	The total energy of the universe is constant
Second Law	The total entropy of the universe is always increasing
Third Law	The entropy of a pure, perfectly formed crystalline substance at absolute zero is zero

Entropy can be defined in terms of heat flow:

$$\Delta S = q/T$$ <u>At a constant temperature</u>

Where q = heat (units = J/mol)
T = temperature (in Kelvin)

When heat flows at constant temperature, the entropy change is equal to the heat transferred (q_T) divided by the temperature In kelvins.

You can also use Hess' Law to determine the entropy change for a system

What is the ΔS_{system} for the reaction:

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(l)$$
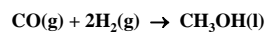
$$\Delta S = -332.2 \text{ J/K}$$

More or less disorder for the forward reaction?
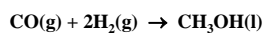

Calculating the Entropy Change in the Surroundings

$$\Delta S_{surroundings} = \frac{q_{surroundings}}{T} = -\frac{\Delta H_{system}}{T}$$

If $\Delta H° = -1202$ kJ and $\Delta S° = -217$ J·K^{-1} for the combustion of 2 moles of magnesium, the change in entropy of the surroundings at 298 K is

A) 217 J·K^{-1}

B) -217 J K^{-1}

C) -4.03×10^3 J·K^{-1}

D) 5.54×10^3 J·K^{-1}

E) 4.03×10^3 J·K^{-1}

Calculating the Entropy Change for System and Surroundings

$$\Delta S^{\circ}_{universe} = \Delta S^{\circ}_{system} + \Delta S^{\circ}_{surroundings}$$

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(l)$$

$\Delta S^{\circ}_{system} = -332.2 \text{ J/K}$

$\Delta S^{\circ}_{surroundings} = 430 \text{ J/K}$

Add them

$\Delta S^{\circ}_{universe} = 98 \text{ J/K}$

The Second Law

- Three possibilities:
  - If $\Delta S_{univ} > 0$…..process is spontaneous
  - If $\Delta S_{univ} < 0$…..process is spontaneous in opposite direction.
  - If $\Delta S_{univ} = 0$….equilibrium

- Here's the catch: We need to know ΔS for both the system and surroundings to predict if a reaction will be spontaneous!

Example

- Is the following reaction spontaneous at 298 K? (Is $\Delta S^{\circ}_{univ} > 0$?)

$$2Fe(s) + 3H_2O(g) \longrightarrow Fe_2O_3(s) + 3H_2(g)$$
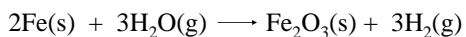
$$\Delta S^{\circ}_{rxn} = \Delta S^{\circ}_{system} = -141.5 \text{ J/K}$$

$$\Delta S^{\circ}_{surr} = -\Delta H^{\circ}_{sys}/T = -\Delta H^{\circ}_{rxn}/T$$

$$\Delta H^{\circ}_{rxn} = \Delta H^{\circ}_f(Fe_2O_3(s)) + 3\Delta H^{\circ}_f(H_2(g))$$
$$- 2\Delta H^{\circ}_f(Fe(s)) - 3\Delta H^{\circ}_f(H_2O(g))$$

Example (cont.)

$\Delta H^\circ_{rxn} = -100 \text{ kJ}$

$\Delta S^\circ_{surr} = -\Delta H^\circ_{sys}/T = 348 \text{ J/K}$

$\Delta S^\circ_{univ} = \Delta S^\circ_{sys} + \Delta S^\circ_{surr}$
$= -141.5 \text{ J/K} + 348 \text{ J/K}$
$= 207.5 \text{ J/K}$

$\Delta S^\circ_{univ} > 0$; therefore, reaction is spontaneous

Entropy and Phase Changes

- Phase Change: Reaction in which a substance goes from one phase of state to another.
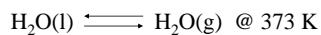
- Example:
$$H_2O(l) \longrightarrow H_2O(g) \ @ \ 373 \text{ K}$$
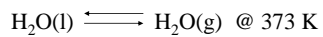
- Phase changes are equilibrium processes such that:
$$\Delta S_{univ} = 0$$

S and Phase Changes (cont.)

$H_2O(l) \rightleftharpoons H_2O(g) \ @ \ 373 \text{ K}$

- Now, $\Delta S^\circ_{rxn} = S^\circ(H_2O(g)) - S^\circ(H_2O(l))$
$= 195.9 \text{ J/K} - 86.6 \text{ J/K}$
$= 109.1 \text{ J/K}$

- And, $\Delta S^\circ_{surr} = -\Delta H_{sys}/T$
$= -40.7 \text{ kJ}/373 \text{ K}$
$= -109.1 \text{ J/K}$

- Therefore, $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$

Example

- Determine the temperature at which liquid bromine boils:

$$Br_2(l) \rightleftharpoons Br_2(g)$$

- Now, $\Delta S°_{rxn} = S°(Br_2\ (g)) - S°(Br_2(l))$
  - $= 245.38\ J/K - 152.23\ J/K$
  - $= 93.2\ J/K$

Example (cont.)

- Now, $\Delta S°_{surr} = -\Delta S°_{sys} = -93.2\ J/K = -\Delta H_{sys}/T$

- Therefore, calculate ΔH_{sys} and solve for T!

- Now, $\Delta H°_{rxn} = \Delta H°_f(Br_2(g)) - \Delta H°_f(Br_2(l))$ [0]
  - $= 30.91\ kJ - 0$ (standard state)
  - $= 30.91\ kJ$

- Such that, $-93.2\ J/K = -30.91\ kJ/T$
  - $T_{boiling} = 331.6\ K$

ΔG allows spontaneity to be calculated based on the *system*.

Free Energy of Formation

Free energy of formation is the change in Gibbs
Free energy when 1 mol of a compound is formed
from the elements

Hess' Law

$$\Delta G^\circ_{reaction} = \sum \Delta G^\circ_{f\ products} - \sum \Delta G^\circ_{f\ reactants}$$

Using Hess' Law to solve for ΔG only
works at 298 K.

Gibbs Free Energy

The Gibbs Free Energy equation allows ΔG
to be calculated at other temperatures

$$\Delta G^\circ_{system} = \Delta H^\circ_{system} - T\Delta S^\circ_{system}$$

Gibbs Free Energy

The Gibbs Free Energy equation allows ΔG
allows spontaneity to be at different temperatures

$$\Delta G^\circ_{system} = \Delta H^\circ_{system} - T\Delta S^\circ_{system}$$

ΔH	ΔS	Temp	ΔG	Spontaneous Direction
-	+	All	-	Forward
-	-	Low	-	Forward
		High	+	Reverse
+	+	Low	+	Reverse
		High	-	Forward
+	-	All	+	Reverse

How is ΔG related to Q?

Wait, what is Q?

$$\Delta G = \Delta G^{\bullet} + RT \ln Q$$

At equilibrium, ΔG is equal to 0.

Estimate the normal boiling point of Br_2(l), given the molar enthalpy and molar entropy of vaporization of 30.7 kJ·mol–1 and 93.0 J·K–1·mol–1, respectively.

A) 303°C

B) 57°C

C) 30°C

D) 330°C

E) 100°C

How are ΔG and the equilibrium constant related?

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

If you increase K, ΔG becomes more negative

**If a reaction is product-favored,
it is considered to be spontaneous**

**If a reaction is reactant-favored,
it is considered to be nonspontaneous**

Temperature and the Equilibrium Constant

The effect of temperature on K depends on the sign of **ΔH**

Sign of ΔH	Temperature	K
+ (endothermic)	increase	increase
- (exothermic)	increase	decrease