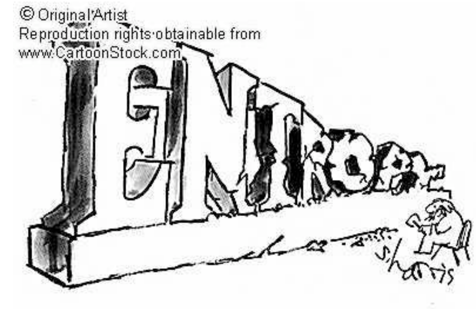
Ch. 17: Thermodynamics: Entropy and Free Energy

Entropy

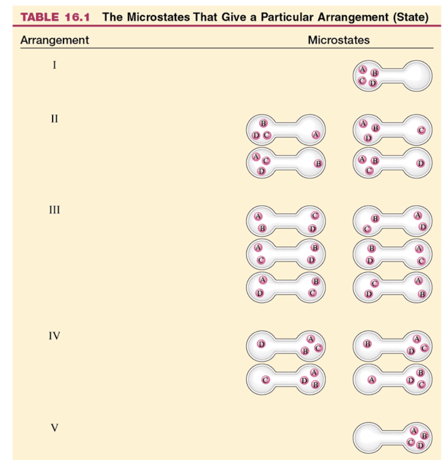


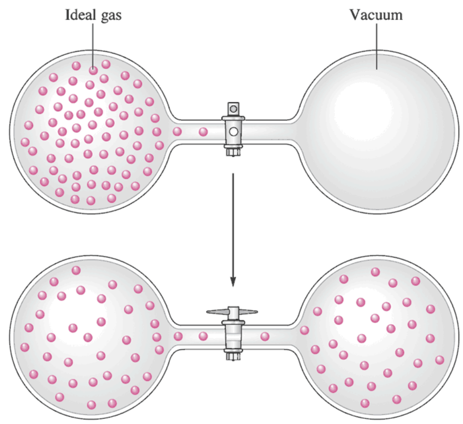
I.
  A. This, like enthalpy,
  B. Thus,

II. A reaction is (more on this later) if:
  A. (H, enthalpy)
  B. (S, entropy)

III.

IV. Why does entropy happen?
  A. It's harder to keep things in order (look at my room).
  B. Therefore,





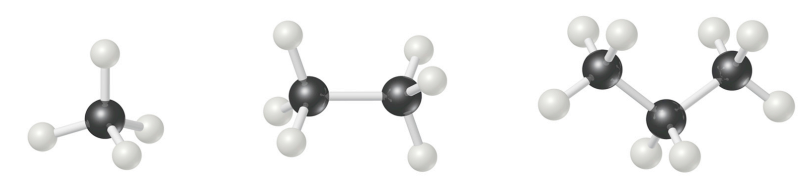
V. Entropy of states of matter:
  A.

VI. Entropy increases generally when:
  A.
  B.
  C.
  D.

VII.

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



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 — $S° = 270.3\ J\ mol^{-1}\ K^{-1}$

The Laws of Thermodynamics

I. First Law
  A.
  B. a.k.a. of Energy
  C. Gives rise to
  D. Side note: heat flows from

II. Second Law
  A.
  B.

III. Third Law
  A.

Ch. 17: Thermodynamics: Entropy and Free Energy

Spontaneity

I. Many chemical reactions spontaneously happen.

A. A reaction is

B. This has   Even if a reaction happens slowly, it is considered spontaneous.

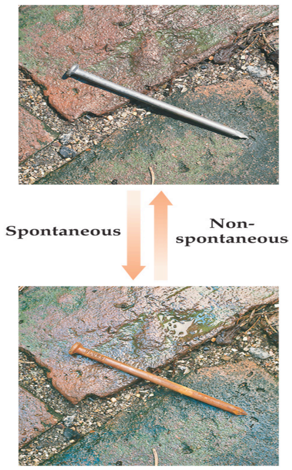
II. A reaction is <u>spontaneous</u> if:

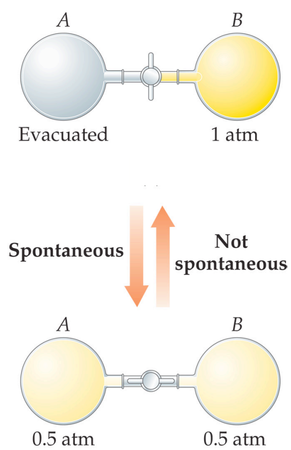
A.   (H, enthalpy)

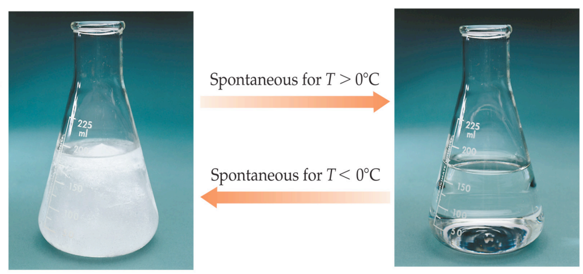
B.   (S, entropy)

III. Thus,

IV.







Gibbs Free Energy (G)

I. Definition

A.

B. Dependent on

C. Equation:

D. For standard (   ) states,

1. This shows that

E.

F.

II. The Significance of the Signs

Property	Positive (+)	Negative (-)
ΔH		
ΔS		
ΔG		

III. A Special Case!

A.

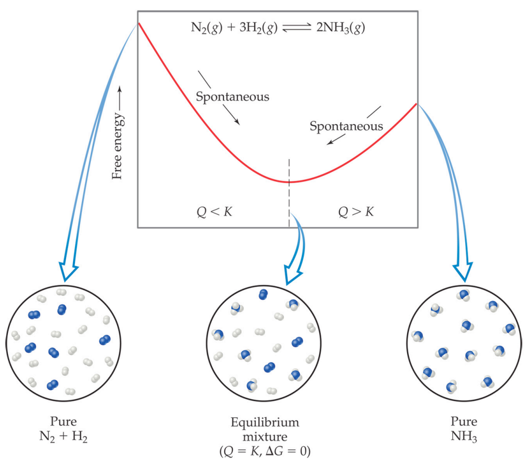
B. The equation changes:

1. You can find the temperature at a given point if the system is at equilibrium

2. Ex: What is the boiling point of a solution where the ΔH_{vap}=23.5kJ/mol and ΔS=34.5J/Kmol?

a. At boiling, there is equilibrium between liquid and gas phase.

b.



IV. Spontaneous or not? Use $\Delta G = \Delta H - T\Delta S$

ΔG	ΔH	ΔS	Spontaneous?

V. Example:

$2\ C_4H_{10}(g) + 13\ O_2(g) \text{ ------> } 8\ CO_2(g) + 10\ H_2O(l)$

The reaction represented above is spontaneous at 25 °C. Assume that all reactants and products are in their standard states.

(a) Predict the sign of $\Delta S°$ for the reaction and justify your prediction.

(b) What is the sign of $\Delta G°$ for the reaction? How would the sign and magnitude of $\Delta G°$ be affected by an increase in temperature to 50 °C? Explain your answer.

(c) What must be the sign of $\Delta H°$ for the reaction at 25°C? How does the total bond energy of the reactants compare to that of the products?

(d) When the reactants are placed together in a container, no change is observed even though the reaction is known to be spontaneous. Explain this observation.

Thermo. Calculations

I. Calculating ΔH (four ways):

- A.
- B.
  1. v. 1:
  2. v. 2:
- C.

II. Calculating ΔS:

- A.
- B. When calculating with S AND G or H,
- C.
- D. Ex. Calculate $\Delta S°$ for the rxn:
  $2NiS_{(s)} + 3O_{2(g)} \text{-->} 2SO_{2(g)} + 2NiO_{(s)}$
- E. Ex. Calculate $\Delta S°$ for the rxn:
  $Al_2O_{3(s)} + 3H_{2(g)} \text{-->} 2Al_{(s)} + 3H_2O_{(g)}$

III. Calculating ΔG (five ways)

- A.
- B.
- C.
  1. Just like $\Delta H°_f$,
  2. Ex: Calculate $\Delta G°$ for the reaction:
     $2CH_3OH + 3O_2 \text{-->} 2CO_2 + H_2O$
- D.
  1.
  2. Usually used
- E.

IV. Practice:

A. Calculate ΔH, ΔS, and ΔG for the following reaction: Use the appropriate appendices in your book to find individual values: $2SO_2\ (g) + O_2(g) \longrightarrow 2SO_3\ (g)$

B. Consider the ammonia synthesis rxn: $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$
Where $\Delta G° = -33.3$ kJ/mol of N_2 consumed at 25° C.
Calculate the value for the equilibrium constant

C. Example 2: Calculate the value of $\Delta G°$ for the following reaction at 389K where at equilibrium, $[NH_3]$=2.0M, $[H_2]$=1.25M, and $[N_2]$=3.01M. $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$

V. AP Practice: $C_2H_2(g) + 2\ H_2(g) \dashrightarrow C_2H_6(g)$

Information about the substances

Substance	S° (J/mol K)	$\Delta H°_f$ (kJ/mol)	Bond	Bond Energy (kJ/mol)
$C_2H_2(g)$	200.9	226.7	C-C	347
$H_2(g)$	130.7	0	C=C	611
$C_2H_6(g)$	--------	-84.7	C-H	414
			H-H	436

(a) If the value of the standard entropy change, $\Delta S°$, for the reaction is -232.7 joules per mole Kelvin, calculate the standard molar entropy, S°, of C_2H_6 gas.

(b) Calculate the value of the standard free-energy change, $\Delta G°$, for the reaction. What does the sign of $\Delta G°$ indicate about the reaction above?

(c) Calculate the value of the equilibrium constant, K, for the reaction at 298 K.

(d) Calculate the value of the C≡C bond energy in C_2H_2 in kilojoules per mole.

Free Energy and Equilibrium

I. When a reaction is
A.
B.

II. When the reaction is   When...
A.
B.
C.