CHAPTER 4
THERMODYNAMICS: THE SECOND LAW
CHAPTER OUTLINE

HW: Questions are below. Solutions are in separate file on the course web site.

Sect. **Material**

1. Spontaneous Processes
2. Entropy (S): A Measure of Disorder
3. Entropy Changes in Reversible Processes
4. Trouton's Rule
5. The Second Law of Thermodynamics + Examples
6. The Third Law of Thermodynamics
7. Entropy Changes in Chemical Reactions
8. The Gibbs Energy (G)
9. Gibbs Energy of Formation
10. Double Strand Formation in DNA
11. Enzyme Denaturation
12. Hydrophobic Interactions in Proteins
13. Glucose Metabolism

Chapter 4 - Homework

4.1 Suppose you put a cube of ice of mass 100 g into a glass of water at 0 ^{o}C. When the ice melts, 33. kJ of energy is absorbed from the surroundings as heat. What is the change of entrop of:
(a) the sample (the ice)
(b) the surroundings (the glass of water)

4.2 A sample of aluminum [M = 27] of mass 1.25 kg is cooled at constant pressure from 27 ^{o}C to -13 ^{o}C. Calculate the energy which must be removed as heat and the change in entropy of the sample.
Note: The constant pressure molar heat capacity of aluminum is 24.35 J/mol-K

4.3 A sample of $CO_2(g)$ [M = 44] occupies 15. L at -23 ^{o}C and 1.00 atm is compressed isothermally. To what volume must the gas be compressed to reduce its entropy by 10.0 J/K?

4.4 Whenever a gas expands, the gas undergoes an increase in entropy. A sample of $CH_4(g)$ [M = 16] of mass 25. g at -23 ^{o}C and 185 kPa expands isothermally until the pressure is 2.5 kPa. Calculate the entropy change when the gas expands (a) reversibly, (b) irreversibly.

4.5 Calculate the change in molar entropy when an 80 g sample of argon [M = 40] is compressed from 2.0 L to 500 cm^3 and simultaneously heated from 300 K to 400 K.
Note: The constant volume molar heat capacity is $C_{V,m}$ = 12.5 J/mol

4.6 The enthalpy of vaporizaton of trichloromethane, $CHCl_3$, is 29.4 kJ/mol at its normal boiling point, 62 ^{o}C.
(a) Calculate the entropy of vaporization of trichloromethane at its normal boiling point.
(b) What is the entropy change of the surroundings?

4.7 Calculate the standard reaction entropy (at 298 K) of the following two reactions:

(a) $2\ CH_3CHO(g) + O_2(g) \rightarrow 2\ CH_3COOH(l)$

(b) $2\ AgCl(s) + Br_2(l) \rightarrow 2\ AgBr(s) + Cl_2(g)$

Molar Entropies

Compound	**S^0**
$CH_3CHO(g)$	250.3 J/mol-K
$O_2(g)$	205.1
CH_3COOH	159.8

$AgCl(s)$	96.2
$Br_2(l)$	152.2
$AgBr(s)$	107.1
$Cl_2(g)$	223.1

4.8 A quantity of 0.35 moles of a Perfect Gas at 16 ^oC is expanded from 1.2 L to 7.4 L. Calculate w, q, ΔU, ΔH, ΔS and ΔG if the process is carried out: (a) isothermally and reversibly, and (b) isothermally and irreversibly against an external pressure of 1.0 bar.

4.9 Calculate ΔH, ΔU and ΔS when 1 mol of water undergoes the following process:

$$H_2O(liq, 25\ ^oC) \rightarrow H_2O(gas, 100\ ^oC)$$

The molar heat of vaporization of water at 100 ^oC is 40.7 kJ/mol. The constant pressure molar heat capacity of water is 75.3 J/mol-K

4.10 Use the data below to calculate ΔG^o for the following reaction:

$$\beta\text{-D-Glucose(s)}\ [C_6H_{12}O_6(s)] \rightarrow 2C_2H_5OH(l) + 2CO_2(g)$$

using: (a) Enthalpies of formation and standard entropies, and (b) Gibbs energies of formation.

Compound	**$\Delta_f H^o$**	**S^o**	**$\Delta_f G^o$**
β-D-Glucose(s)	-1268.0 kJ/mol	212.0 J/mol-K	-910.0 kJ/mol
$C_2H_5OH(l)$	-277.7	160.7	-174.8
$CO_2(g)$	-393.5	213.7	-394.4

4.11 As an approximation, one may assume that proteins exist in either the native or denatured state. The standard molar enthalpy and entropy for the denaturation of a certain protein are 512 kJ/mol and 1600 J/mol-K. At what temperature does the denaturation of this protein become spontaneous? Is the reaction spontaneous at temperatures above OR below this temperature?

4.12 The Enthalpy of Fusion of Benzene is 9.87 kJ/mol.
The Entropy of Fusion of Benzene is 35.4 J/mol-K
The normal melting point of benzene is 6 ^oC.

Calculate ΔG for the melting of two moles of benzene at:
(a) -25 ^oC, (b) 6 ^oC, (c) 25 ^oC
In each case, indicate whether the process is spontaneous, non-spontaneous, at equilibrium.