Chapter 19 - Thermodynamics

The 0th, 1st, 2nd and 3rd Laws of Thermodynamics

"0th Law": Establishes the Thermodynamic Temperature Scale

The Kelvin temperature scale establishes absolute zero as the absence of thermal energy. Average Thermal Energy = k_BT

k_B is the Boltzmann Constant, Avogadro's Number x k_B = R

1st Law: The Conservation of Energy. $\Delta E = q + w$ (Chapter 6)

(Energy is neither created nor destroyed)

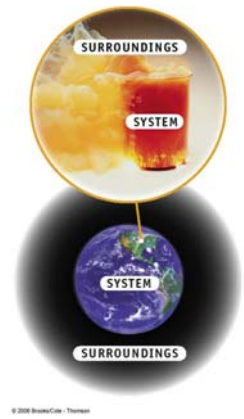
2nd Law: Entropy is Not Conserved

(A process is spontaneous when the entropy of the system plus the surroundings increase)

3rd Law: At Absolute Zero (T = 0 K), The Entropy is Zero (in a perfect crystal)

$S = k_B\ln(W)$; W is the number of arrangements in a given state of a system

W = 1 when T = 0 (for a perfect crystal & increases as T increases)



Review of Definitions (Ch 6):

System: A Part of the Universe Under Study

Surroundings: Everything Except the System

Universe: System plus Surroundings

In the laboratory the surroundings are regulated to measure energy exchange with the system. (A *Calorimeter* is a good example.)

2nd LAW: A process is spontaneous when the entropy of the universe increases

S_{univ} (final state) – S_{univ} (initial state) > 0

$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$

ΔS_{sys}

a) Chemical process

$$\Delta S^o_{sys} = \Sigma[nS^o_{(products)}] - \Sigma[mS^o_{(reactants)}]$$

$$\Delta S^o_{sys} = \Delta S^o_{rxn}$$

Entropy and Chemical Reaction: The Combustion of Propane

$C_3H_8\ (g) + 5O_2\ (g) \rightarrow 4H_2O\ (g) + 3CO_2\ (g)$

$\Delta S^o_{rxn} = \Sigma[S^o(\text{products})] - \Sigma[S^o(\text{reactants})]$

$\Delta S^o_{rxn} = [4S^o(H_2O, g) + 3S^o(CO_2, g)] - [S^o(C_3H_8, g) + 5S^o(O_2, g)]$

$\Delta S^o_{rxn} = [4(188.8) + 3\ (213.7)] - [(269.9) + 5(205.1)]$

$\Delta S^o_{rxn} = \Delta S^o_{sys} = [1396.3] - [1295.4] = 100.9$ J/K

Increase in moles of gas by reaction → Increase in entropy

Compound	ΔH^o_f (kJ/mol)	ΔG^o_f (kJ/mol)	S^o (J/K·mol)
C_3H_8 (*g*)	-103.8	-23.5	269.9
CO_2 (*g*)	-393.5	-394.4	213.7
H_2O (*l*)	-285.8	-237.1	69.9
H_2O (*g*)	-241.8	-228.6	188.8
O_2 (*g*)	0	0	205.1

ΔS_{surr}

$$\Delta S^0_{surr} = -q_{rev} / T$$

Assuming reversible process at constant T

$$\Delta S^0_{surr} = -\Delta H^0_{rxn} / 298.15\ K$$

$$\Delta S^0_{univ} = \Delta S^0_{rxn} + \Delta S^0_{surr}$$

Isothermal process

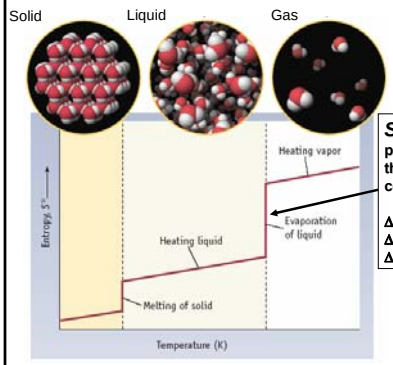
$$\Delta S = q_{rev}/T \quad \text{(constant T)}$$

Phase change → isothermal

$$\Delta S_{sys} = \Delta S_{fus} = \Delta H_{fus}/T_{fus}$$

$$\Delta S_{sys} = \Delta S_{vap} = \Delta H_{vap}/T_{vap}$$

Entropy and Phase Changes



S changes abruptly with a phase change, indicating the abrupt change in configurations

$\Delta S_{vap} = \Delta H_{vap}/T$
$\Delta S_{vap} = (40.7\ kJ/mol)/(373\ K)$
$\Delta S_{vap} = 109\ J/(mol{\cdot}K)$

$\Delta S_{sys} = \Delta S_{vap}$

ΔS_{uni} determines when a process is spontaneous

$\Delta S^o_{sys} = \Delta S^o_{fus} = \Delta H^o_{fus} / T_{fus}$
$= 6007\ J/mol / 273\ K =$
$= 21.99\ J/(K\ mol)$

What is ΔS^o_{melt} at 260 K(-13°C)?

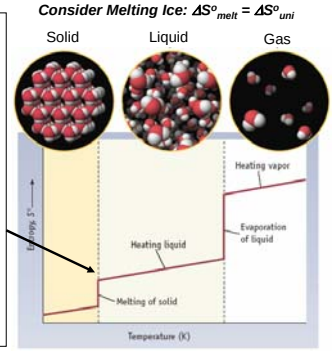
$\Delta S^o_{sur} = -\Delta H^o_{sys}/260 = -6007 / 260$
$\Delta S^o_{sur} = -23.10\ J/K$

$\Delta S^o_{melt} = \Delta S^o_{sys} + \Delta S^o_{sur} < 0$?
$\Delta S^o_{melt} = 21.99 - 23.10 = -1.11\ J/K$

$\Delta S_{univ} < 0$ → Not Spontaneous

The withdrawal of energy from the surroundings ($-\Delta H^o_{sys}$ = -6007 kJ) produces a decrease in entropy of the surroundings that exceeds the increase in entropy produced in the system.

Consider Melting Ice: $\Delta S^o_{melt} = \Delta S^o_{uni}$



What is ΔS^o_{melt} at 280 K (7°C)?

$\Delta S^o_{sys} = \Delta S^o_{fus} = \Delta H^o_{fus} / T_{fus} = 6007\ J/mol / 273\ K = 21.99\ J/(K\ mol)$

$\Delta S^o_{surr} = -\Delta H^o_{fus}/280 = (-6007\ J)/(280\ K) = -21.45\ J/K$

$\Delta S^o_{melt} = 21.99 - 21.45 = 0.55\ J/K$

$\Delta S^o_{univ} > 0$ → Spontaneous

The withdrawal of energy from the surroundings ($-\Delta H^o_{sys}$ = -6007 kJ) produces a decrease in entropy of the surroundings that *is less than* the increase in entropy produced in the system.

For Ice Melting: $\Delta H^o_{sys} > 0$ and $\Delta S^o_{sys} > 0$ (Type 3)

Table 19.2 Predicting Whether a Process Will Be Spontaneous

Type	ΔH^o_{sys}	ΔS^o_{sys}	Spontaneous Process?
1	Exothermic process	Less order	Spontaneous under all conditions
	$\Delta H^o_{sys} < 0$	$\Delta S^o_{sys} > 0$	$\Delta S^o_{univ} > 0$.
2	Exothermic process	more order	Depends on relative magnitudes of ΔH and ΔS.
	$\Delta H^o_{sys} < 0$	$\Delta S^o_{sys} < 0$	More favorable at *lower* temperatures.
3	Endothermic process	Less order	Depends on relative magnitudes of ΔH and ΔS.
	$\Delta H^o_{sys} > 0$	$\Delta S^o_{sys} > 0$	More favorable at *higher* temperatures.
4	Endothermic process	More order	Not spontaneous under any conditions
	$\Delta H^o_{sys} > 0$	$\Delta S^o_{sys} < 0$	$\Delta S^o_{univ} < 0$

Gibbs Energy: G = H – TS

A State Function of the System that Predicts Spontaneity

For an Isothermal Process, Initial → Final State: $\Delta G^o_{sys} = \Delta H^o_{sys} - T\Delta S^o_{sys}$

$$\Delta S^o_{uni} = \Delta S^o_{sys} + \Delta S^o_{sur}$$

$$\Delta S^o_{uni} = \Delta S^o_{sys} + \Delta H^o_{sur}/T$$

$$-T\Delta S^o_{uni} = -T\Delta S^o_{sys} + \Delta H^o_{sys}$$

Rename "$-T\Delta S^o_{uni}$" as ΔG^o_{sys}

$$\Delta G^o_{sys} = \Delta H^o_{sys} - T\Delta S^o_{sys}$$

The process does not have to be at standard state:

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

$\Delta G < 0$ spontaneous, $\Delta G > 0$ nonspontaneous, $\Delta G = 0$ equilibrium

Chapter 19 – Entropy

Molecular Properties of Entropy (1st & 2nd Laws of Thermo)
- ***The Magnitude of Entropy Grows with Number of Microscopic States:***
- ***(1) $S^o(g) > S^o(l) > S^o(s)$***
- ***(2) Molar Entropy of a molecule increases with complexity and temperature***
- ***(3) Spreading of Energy and/or Molecules increases S***

Thermodynamic and Statistical Definitions of Entropy (0th, 1st, 2nd, 3rd Laws of Thermo)
- ***(1) Thermodynamic: $\Delta S = q_{rev}/T$***
- ***(2) Statistical: $S = k_B \ln W$ (W is the number of configurations), S is 0 at 0 K and S increases with T (S is always positive)***
- ***(3) $\Delta S^o_{sys} = \Sigma[S^o(\text{products})] - \Sigma[S^o(\text{reactants})]$***
- ***(4) $\Delta S^o_{surr} = -\Delta H^o_{sys}/T$***
- ***(5) $\Delta S^o_{uni} = \Delta S^o_{sys} + \Delta S^o_{sur}$; $\Delta S^o_{uni} > 0$ (spontaneous)***

A Calculation of ΔS_{uni}, The Definition of ΔG_{sys}, Calculations with ΔG_{sys}, ΔH_{sys} & ΔS_{sys}
- ***(1) Equilibrium Condition of a Phase Change: Ice is Stable below 0 °C; not above 0 °C***
- ***(2) ΔG^o_{rxn}, Chemical Reactions at Standard Conditions: Propane Example***
- ***(3) Definition of ΔG as a State Variable, $\Delta H - T\Delta S$***
- ***(4) Calculations with ΔG***
  - ***(a) As a State Variable, $\Delta H - T\Delta S$***
  - ***(b) T-Dependence: (i) $\Delta H > 0$ $\Delta S > 0$, (ii) $\Delta H < 0$ $\Delta S < 0$, (iii) $\Delta H > 0$ $\Delta S < 0$, (iv) $\Delta H < 0$ $\Delta S > 0$***
  - ***(c) For Cases (i) and (ii), T at which the process becomes Spontaneous/Nonspont.***

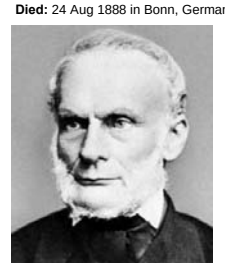
ΔG^o and K, ΔG and Q
- ***(1) $\Delta G = \Delta G^o + RT\ln Q$***
- ***(2) Q = 1 when all products and reactants are at standard state***
- ***(3) $\Delta G = \Delta G^o$***
- ***(4) At Equilibrium $\Delta G = 0$ and Q = K, $\Delta G^o = -RT\ln K$***

Sadi Nicolas Léonard Carnot

Born: 1 June 1796 in Paris, France
Died: 24 Aug 1832 in Paris, France

Rudolf Julius Emmanuel Clausius

Born: 2 Jan 1822 in Koslin, Prussia
Died: 24 Aug 1888 in Bonn, Germany



$$\Delta S_{sys} = \frac{q_{rev}}{T} \qquad \Delta S_{sys} = \frac{\Delta H_{sys}}{T}$$

Clausius stated the 1st and 2nd Laws as we know them today:
1. *The energy of the universe is constant.*
2. *The entropy of the universe tends to a maximum.*