Entropy: A Summary

- A popular statement of the Second Law of Thermodynamics is:
  "The Entropy of the Universe is increasing."
- More formal statements include:
  - Clausius: It is impossible to devise a continuously cycling engine (the system) that transfers heat from a colder to a hotter body without doing work on the system.
  - Kelvin: It is impossible to devise a continuously cycling engine that produces no effect other than the extraction of heat from a reservoir at one temperature and the performance of an equal amount of mechanical work.

- Continued:
  - Caratheodory: In the neighbourhood of every equilibrium state of a closed system, there are states that cannot be reached from the first state along any adiabatic path by any spontaneous process or reversible limit of a spontaneous process.
    - This means that reversible adiabats do not cross each other. (Neither do reversible isotherms.)
- The Second Law gives the condition for spontaneity of a process.
  - Spontaneous processes maximize entropy.
- In Chapter 15, entropy may be defined as:

$$S = k_B \ln \Omega$$

- Entropy may also be defined as:

$$dS = \frac{đq_{rev}}{T}$$

- Recall that $dU = đq + đw$ or $\Delta U = q + w$.
- Entropy is a state function, so if the path of the process is not convenient for the calculation of the change in entropy, a convenient alternate path may be selected.
  - Any two points in pV space may be joined by a combination of up to two of the following:
    - A reversible adiabat
    - A reversible isotherm
    - A reversible isobar
    - A reversible isochor

Calculation of entropy on various paths.

- Reversible adiabat

$$đq_{rev} = 0; \quad \frac{đq_{rev}}{T} = 0; \quad dS = 0$$

- Reversible isotherm

$$đq_{rev} = dU - đw; \quad dS = \frac{dU + pdV}{T}$$

- Reversible isobar

$$đq_{rev} = C_p dT; \quad dS = \frac{C_p}{T} dT$$

- Reversible isochore

$$đq_{rev} = C_V dT; \quad dS = \frac{C_V}{T} dT$$

- The change in internal energy may be expressed in terms of entropy:

$$dU = TdS - pdV$$

  where T and S are a conjugate pair of variables. (We have previously encountered p and V as a conjugate pair).

  - This equation is also known as the master equation of thermodynamics.

Thermodynamic Potentials

- There are four thermodynamic potentials:
  - U internal energy
  - H enthalpy
  - A Helmholtz free energy
  - G Gibbs free energy
- They are related through the pairs of conjugate variables.
  - $H = U + PV$; $dH = dU + pdV + Vdp = TdS + Vdp$
  - $A = U - TS$; $dA = dU - TdS - SdT = -SdT - pdV$
  - $G = U - TS + PV$;
    $dG = dU - TdS - SdT + pdV + Vdp = -SdT + Vdp$

  (These are also known as Legendre transforms).

Thermodynamic Potentials as State Functions

- State functions have exact differentials
  - This means that cross derivatives are equal
  - Consider U.

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right) = \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)$$

  - But $dU = TdS - pdV$. Therefore:

$$\left(\frac{\partial U}{\partial S}\right)_V = T; \left(\frac{\partial U}{\partial V}\right)_S = -p$$

- and

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

- Similarly from the expressions for dH, dA, and dG may be shown respectively:

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p$$

- These are known as the Maxwell relations.

The Third Law

- A popular statement of the Third Law of Thermodynamics is:
  “It is impossible to reach absolute zero.”
- More formal statements include:
  - In any system in internal equilibrium undergoing an isothermal process between two states, the entropy change of the process approaches zero as the temperature of the system approaches zero.
  - The entropy of any system vanishes in the state for which

$$T = \left(\frac{\partial U}{\partial S}\right)_V = 0$$

Recommended Reading

- The rest of Chapter 15
- In Chapter 16
  - Section 16.1 about statements of the Second Law
  - Section 16.2 about reversible processes and cycles
  - Section 16.3
  - Section 16.4 about the Carnot cycle.
- In Chapter 17
  - Section 17.1 about H, A and G.
  - Section 17.3 and 17.4 about calculating ΔS for reversible and irreversible processes.