Chapter 2: Summary

Chapter 2 is a key and substantial chapter. It is mainly about **entropy**: its origin and definition from 2nd law, its basic properties (e.g., never decreases in isolation), its calculations, and its relations to other state functions. This chapter also covers many important theorems, relations, and other useful state functions (or thermodynamic potentials). You need to understand and be able to apply them.

1. Both heat engines and refrigerators run in cycles. Their efficiencies. In particular, heat engine's efficiency is

$$\eta_{\mathrm{E}} \equiv \frac{w}{Q_H} = 1 - \frac{Q_C}{Q_H},$$

where Q_C is the heat ejected to the cool source and Q_H is the heat absorbed from the hot source.

2. Carnot engine, Carnot theorem, Carnot relation and Carnot efficiency

$$\frac{Q_C}{Q_H} = \frac{T_C}{T_H} \quad \rightarrow \quad \eta_{\mathrm{CE}} = 1 - \frac{T_C}{T_H}.$$

Two equivalent statements of 2nd law (for heat engines and for refrigerators). Carnot's work led to the discovery of 2nd law from which entropy was defined (next item).

3. Entropy of a system is a state function. Its change is given by

$$\Delta S = \int \frac{đQ^{\mathrm{rev}}}{T}, \tag{1}$$

where $đQ^{\mathrm{rev}}$ is the heat absorbed in a reversible process.
For any spontaneous process, $\Delta S > 0$. Maximum entropy theorem.
Calculation of entropy change during an irreversible process can be done by theoretical construction of a reversible one with the same initial and final states.
Common three ways for calculating entropy: a) by definition Eq. (1), b) by the fundamental thermodynamic relation of Eq. (5) (next item), or c) by heat capacities and Maxwell relations.

4. The fundamental thermodynamic relation for a hydrostatic system,

$$dE = TdS - PdV, \tag{2}$$

implies

$$E = E(S, V), \quad T = \left(\frac{\partial E}{\partial S}\right)_V, \quad P = -\left(\frac{\partial E}{\partial V}\right)_S \tag{3}$$

and the corresponding Maxwell relation

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V. \tag{4}$$

Eq. (2) can also be rewritten as,

$$dS = \frac{1}{T}dE + \frac{P}{T}dV, \tag{5}$$

which implies

$$S = S(E, V), \quad \frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V, \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_E. \tag{6}$$

These relations are important for isolated systems where (E, V) are fixed. Statistical mechanics was established based on Boltzmann's formula for $S(E, V)$, topics of Chapter 3.

5. Helmholtz free energy $F \equiv E - TS$ and Gibbs free energy $G \equiv F + PV$. Their corresponding equations similar to Eqs. (2-4). (You need to write them down.)
For what processes are these two thermodynamic potentials useful for? In particular, the relations involving $F(T, V)$ are used in Chapter 4 on statistical mechanics of non-isolated systems with fixed (T, V).

6. Open systems: N now is not fixed but a variable. Additional chemical contribution to the fundamental thermodynamic relation

$$dE = TdS - PdV + \mu dN,$$

where $\mu = (\frac{\partial E}{\partial N})_{S,V}$ is the chemical potential. Similar addition to relations for dS, dF and dG.

7. Phase equilibrium condition for a substance: all intensive variables (P, T, μ) of the two phases are equal respectively.