

**Preamble:** As requested by some of you, this is a short and totally not-objective view of how to navigate the two texts this week.

**Generic advice:** Read the whole assignment for *either* B&B or G&T. Read closely ... which for me involves taking notes, looking at images and captions, and being sure I can get between equations and can follow examples. Write down anything that confuses you.

Then take a break. (Nap, eat, exercise, let the sun set and rise again, ... )

Then read from the other textbook, with your notes next to you. Linger on things that confused you, are new, or really interest you. Skim or skip other things.

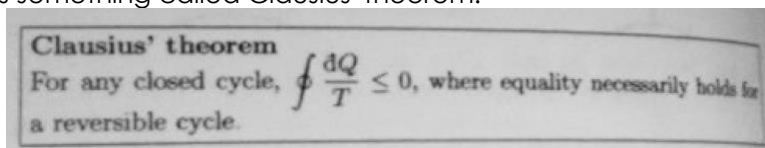
### My observations about reading this week:

#### 1. Topics that are common to both books:

- These statements of the second law: Kelvin-Planck and Clausius. Also, the assertion that entropy,  $S$ , exists; and  $S_{\text{universe}}$  is a nondecreasing function for any process, with  $S$  remaining constant only for a reversible process. (Subtle: Reversible means we consider the system *and* its surroundings as isolated from everything else.)
- Proofs that these three statements are interconnected; either with examples that show one implies the other or rigorous proofs.
- Both books talk about the entropy of an ideal gas, and processes in which entropy changes.
- Both do engines, heat pumps and fridges (though G&T kindly uses " $\eta$ " for the efficiency of an engine and "COP" for the measure of goodness of a heat pump or fridge, whereas B&B use " $\eta$ " for all three.)
- Both books do a good job with the definition of entropy and its changes (B&B Ch. 14 and G&T 2.15). Both talk about having a big bath and a small system (G&T Ex. 2.16 and B&B Ex. 14.1)
- Both books derive the fundamental thermodynamic relation:  $dU = T dS - p dV$ .

#### 2. Topics that might be unique to one book:

- B&B is more rigorous this week. For example:
  - 13.4 proves the equivalence of Clausius and Kelvin's statements of the 2nd law
  - 13.3 states and proves Carnot's theorem (that its efficiency of  $\eta = 1 - T_L/T_H$  is the maximum possible for any engine working between two temps,  $T_L$  and  $T_H$ ).
  - 13.7 proves something called Clausius' theorem.




This is beautiful but perhaps not too useful to us. E.g. The example that follows it, work done by a Carnot cycle between two finite baths, can be done in a different way (see G&T Eq. 2.109).

- G&T Ex. 2.19 talks about the maximum work and they give you a problem on it. It is done in B&B Example 13.5.
- G&T 2.16 talks about the ideal gas and thermodynamic temperature scales as being equivalent. (If you accept this, no need to read it :-)

### 3. Generic things Amy likes about one book or the other

- Entropy changes are an important topic and I like the range of example in both books. The free (aka Joule) expansion is treated in both, but I like the shorter version in B&B 14.4.
- I lean toward G&T 2.13 and 2.17 for the thermodynamic definitions of T and P, because they talk you through examples of boxes with a partition between the halves.



↑ diathermal, fixed

Similar argument with moveable partition

$$\Delta S = 0 \Rightarrow \left. \frac{\partial S_A}{\partial E_A} \right|_{V_A, N_A} = \left. \frac{\partial S_B}{\partial E_B} \right|_{V_B, N_B}$$

$$\equiv \frac{1}{T_A} \equiv \frac{1}{T_B}$$

$$\Rightarrow \left( \frac{\partial S_i}{\partial V_i} \right)_{E_i, N_i} = \frac{P_i}{T_i} \quad i = A, B$$

But if you are comfortable starting with the fundamental thermodynamic relation:  $dE = T dS - p dV$

and taking partial derivatives .. you can come to the same conclusion by reading B&B 14.3

$$T = \left( \frac{\partial E}{\partial S} \right)_V \quad ; \quad P/T = \left( \frac{\partial S}{\partial V} \right)_E$$

Here, N is just assumed to be constant.

- I like B&B Ch. 13, the engines chapter. It is welcome to see both the Carnot Cycle in Fig. 13.1 in the PV plane and Fig. 13.2 in the T, S plane. It is helpful to have little figures with engines and heat baths repeated several times to show different setups, including some rigorous proofs.

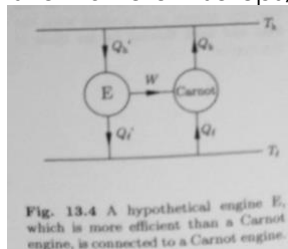


Fig. 13.4 A hypothetical engine E, which is more efficient than a Carnot engine, is connected to a Carnot engine.

- G&T does a lot more of supporting the reader with examples around engines. B&B is terse, emphasizes theory, and leaves the examples to the end-of-chapter problems.
- Both books derive the fundamental thermodynamic relation. I like B&B's box in section 14.3

<b>Summary</b>	
$dU = dQ + dW$	always true
$dQ = T dS$	only true for reversible changes
$dW = -p dV$	only true for reversible changes
$dU = T dS - p dV$	always true
For irreversible changes:	$dQ \leq T dS, \quad dW \geq -p dV$

- I like the fact that G&T section 2.18 pitches this relation both as  $dE = \dots$  and as  $dS = \dots$  and also that they include the term in the chemical potential  $dE = T dS - p dV + \mu dN$  (2.128)

#### 4. Problematic

- For the 3rd law of thermo: G&T 2.20 is only 1 page. Do we want more? If so, Ch. 18 of B&B treats it But ...

• In B&B 18.1, Amy doesn't understand the words "internal degrees of freedom in equilibrium" in Planck's and Simon's formulation of the 3rd law. These words are slightly misleading, suggesting that a particle changes its internal state ... exchanging microscopic quantities with other particles in the kind of 'equilibrium' we already know about.

A better form of **Planck** statement of 3rd law "When temperature falls to absolute zero, the entropy of any pure crystalline substance tends to a universal constant (which can be taken to be zero)"

A better statement of **Nernst-Simons**: "The change in entropy which occurs when a homogeneous system undergoes an isothermal reversible process approaches zero as the temperature approaches absolute zero."

- A Better plan? As an alternative to B&B Ch. 18, read Wikipedia:  
[https://en.wikipedia.org/wiki/Third\\_law\\_of\\_thermodynamics](https://en.wikipedia.org/wiki/Third_law_of_thermodynamics)