10/12 Lecture outline

• Arbitrary system $\mathcal{O}$ undergoing arbitrary cyclic process. Couple to lots of little Carnot engines/refrigerators, $\mathcal{C}$, whose heat output is $\mathcal{O}$'s input. In combined system, would violate Kelvin's statement unless

$$\oint \frac{đQ}{T_{ext}} \leq 0.$$

And for a reversible cycle, $T_{ext} = T$, and can reverse to get similar inequality with $đQ \to -đQ$, so

$$\oint \frac{đQ_R}{T} = 0.$$

• So $đQ_R/T = dS$ is a state variable!

• So $S(B) - S(A) = \int_A^B đQ_R/T$ over any reversible path.

• Thus $\int_A^B đQ/T \leq S(B) - S(A)$, equality iff reversible.

• Entropy of thermally isolated ($đQ = 0$) system never decreases. Thermally isolated system is in state of maximum entropy, consistent with external constraints.

• Examples: reversible isothermal expansion of ideal gas; free expansion of ideal gas; general process with ideal gas; systems of different temperatures put in thermal contact.