10/18 Lecture outline

• Efficiency of reversible engine, continued. Last time: Carnot engine with ideal gas. Now don't assume ideal gas. Also, don't assume earlier definition of temperature. Do Carnot cycle again, for isotherms Θ_2 and Θ_1, with heats Q_1 and Q_2, both taken incoming. $\eta = W/Q_2 = 1 + Q_1/Q_2$. Show $Q_1/Q_2 = -|Q_1|/|Q_2|$ is same for all C-cyclic engines. E.g. $nQ_1 = mQ_1'$, then use $C = nC_1 - mC_1'$ and Kelvin implies $W = nQ_2 - mQ_2' < 0$. Reversing gives $Q_2/Q_2' = m/n = Q_1/Q_1'$, so $Q_1/Q_2 = Q_1'/Q_2' = f(\Theta_1, \Theta_2)$. Also consider Q_2/Q_3 and Q_1/Q_3 to get $f(\Theta_1, \Theta_3) = f(\Theta_1, \Theta_2)f(\Theta_2, \Theta_3)$, so $\eta = 1 - \phi(\Theta_1)/\phi(\Theta_2)$. Define temperature by $\eta \equiv 1 - \Theta_1/\Theta_2$.

Now consider series of C-cycles, between Θ_{n+1} and Θ_n, where each does equal work W. Define $x = \Theta_n/Q_n$, and show it's independent of n. Then $\Theta_{n+1} - \Theta_n = xW$ is independent of n. Taking $xW = 1K$, this system gives the Kelvin temperature scale. It agrees with previous definition, based on ideal gas, $\Theta = T$ (!).

• Arbitrary system undergoes cyclic process. Absorbs heat Q_1 from reservoir at temperature T_1 and Q_2 from one at temperature T_2. Carnot says $(1+Q_1/Q_2) \leq (1-T_1/T_2)$. E.g. $T_1 = T_C$, $T_2 = T_H$, and $Q_1 = -|Q_C| < 0$, $Q_2 = Q_H > 0$. So $(Q_1/T_1) + (Q_2/T_2) \leq 0$, with equality holding iff the cycle is reversible.

• 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 $đQ_R/T \equiv dS$ is a state variable!

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

• Thus $\int_1^2 đQ/T \leq S_2 - S_1$, equality iff reversible. LHS depends on process, RHS is some definite value.

• Entropy of thermally isolated ($đQ = 0$) system never decreases, $S_f - S_i \geq 0$. Thermally isolated system is in state of maximum entropy, consistent with external constraints. If not thermally isolated, $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$.

- Examples. Heat engine, $\Delta S_{total} \geq 0$ gives Carnot statement. $W = W_{max}$ iff $\Delta S = 0$, iff reversible. Also apply to $W = 0$ to get Clausius' statement.
- Carnot cycle in $T - S$ diagram.
- Ideal gas: $\Delta S = C_V \ln(T_f/T_i) + nR\ln(V_f/V_i) = C_P \ln(T_f/T_i) - nR\ln(P_f/P_i)$.
- Example: free expansion of ideal gas, $\Delta S = nR\ln(V_f/V_i) \sim$ wasted energy.