140a Lecture 6, 1/24/19

⋆ Week 3 reading: Blundell+Blundell, chapters 11, 12, 13.

• Last time: Examples of ΔW for ideal gas. Isothermal: $\Delta U = 0$. $\Delta Q = -\Delta W = Nk_BT\ln(V_f/V_i) = Nk_BT\ln(P_i/P_f)$. Isochoric $\Delta W = 0$. $\Delta Q = \Delta U = C_V\Delta T$. Isobaric: $\Delta W = -P\Delta V = -Nk_B\Delta T$. $\Delta Q = C_P\Delta T = (C_V + Nk_B)\Delta T$. Adiabatic: $\Delta Q = 0$. $\Delta W = \Delta U = C_V\Delta T = \frac{1}{\gamma-1}\Delta(PV)$.

Engine efficiency $\eta \equiv |W|/|Q_H|$. E.g. isothermal expansion of ideal gas: $|W| = |Q| = nRT\ln(P_i/P_f)$ has $\eta = 1$, but this is a one-shot process. Final state differs from initial. For an engine, want cyclic process, coming back to starting state, i.e. closed loop in P/V diagram. For complete cycle, $\Delta U = 0$ (state variable). Total work of process = $|W|$ = area enclosed by cycle in P/V diagram. In process, some heat $|Q_H|$ is taken out of some hot working substance (e.g. boiler), and then some heat is ejected into cold area (e.g. the smoke going out into the atmosphere). $|W| = |Q_H| - |Q_C|$, so $\eta = 1 - |Q_C|/|Q_H| \leq 1$. Perfect engine would have $\eta = 1$, but this is impossible.

• Refrigerator performance: $\omega = |Q_C|/|W| = 1/(1 - |Q_C|/|Q_H|)$. Perfect refrigerator would have $\omega = \infty$, but this is impossible.

• Early version of the 2nd law: (Clauius 1850) *no device can be made that operates in a cycle and whose* **SOLE** *effect is to transfer heat from cooler to hotter body.* In other words, no perfect refrigerators. Equivalent to Kelvin-Planck statement *It is impossible to construct a device that operates in a cycle and produces no other effect than the performance of work and the exchange of heat with a single reservoir.* In other words, no perfect engines. Carnot (1824): there is an upper limit to the efficiency of a cyclic engine.

• Show that two statements are equivalent: with a perfect engine, could make a perfect refrigerator; and given a perfect refrigerator could make a perfect engine.

• Nothing beats a reversible engine! Because otherwise, in combination with the reversed engine (acting as a refrigerator) would violate Clauius' statement. All reversible engines have the same efficiency. $\eta \leq \eta_{max} = \eta_{rev}$. We'll compute it for the Carnot engine.

• Mention non-cyclic process, $A \to B$. Recall $\Delta U = \Delta Q - \Delta W = \Delta Q_R - \Delta W_R$. General result: $\Delta W \leq \Delta W_R$ and $\Delta Q \leq \Delta Q_R$. Illustrate with ideal gas for 2 cases: reversible isotherm and reversible adiabat, vs. irreversible counterparts.

• Stirling engine (2 isotherms, 2 isochorics). Non-zero Q_H on two sides and non-zero Q_C on two sides of the PV diagram.

• Work through examples of a Carnot engine (2 isotherms, 2 adiabats). Obtain $\eta = 1 - T_C/T_H$. Fill in the details: let the T_H isotherm connect points (p_1, V_1) to points (p_2, V_2)

so $p_1V_1 = p_2V_2$. Let the adiabat from T_H to T_C connect (p_2, V_2) to (p_3, V_3) so $p_2V_2^\gamma = p_3V_3^\gamma$. Let the isotherm at T_C connect (p_3, V_3) to (p_4, V_4) so $p_3V_3 = p_4V_4$. Finally, the adiabat from T_C to T_H has $p_4V_4^\gamma = p_1V_1^\gamma$. Compute $Q_H = Nk_BT_H \ln(V_2/V_1)$ and $Q_C = Nk_BT_C \ln(V_4/V_3)$. Let us show that $V_2/V_1 = V_3/V_4$. Note that the adiabatic equation $pV^\gamma = const$ can be written, using $p = Nk_BT/V$, as $TV^{\gamma-1}$ =const. So $T_HV_2^{\gamma-1} = T_CV_3^{\gamma-1}$ and $T_HV_1^{\gamma-1} = T_CV_4^{\gamma-1}$. Dividing these equations gives $V_2/V_1 = V_3/V_4$. So $W = Q_H + Q_C = |Q_H| - |Q_C| = Nk_B(T_H - T_C)\ln(V_2/V_1)$ and $\eta = W/Q_H = (T_H - T_C)/T_H = (1 - \frac{T_C}{T_H})$. Note that we can write this as

$$\text{Carnot reversible engine} : \eta = \frac{|W|}{|Q_H|} = 1 - \frac{T_C}{T_H} \leftrightarrow \qquad \frac{|Q_H|}{T_H} = \frac{|Q_C|}{T_C}.$$

We will see next time that, when we put in the correct signs, this is the statement that the entropy change of the two reservoirs sums to zero for a reversible engine (and that of the cyclic engine is also zero, since entropy is a state variable).