10/11 Lecture outline

• Last time: Ideal gas has $U = U(T)$, so $\text{đ}Q = C_V dT + pdV$. Using ideal gas law, get $\text{đ}Q = (C_V + nR)dT - VdP$. Conclude $C_P = C_V + nR$ for ideal gas. Thus $C_V = nR/(\gamma - 1)$, $C_P = \gamma nR/(\gamma - 1)$. Can integrate $C_V = dU/dT$ to find $U(T)$ in terms of $\gamma$. Note: in general $\gamma = \gamma(T)$. We will not assume it is $T$ independent. Its $T$ dependence depends on gas type. Write $\gamma - 1 = 2/f$. If it is monatomic, find $f = 3$, independent of $T$. If diatomic, find $f \approx 3$ for $T < \theta_{rot}$, and $f \approx 5$ for $\theta_{rot} < T < \theta_{vib}$, and $f \approx 7$ for $T > \theta_{vib}$, so $C_V$ is nearly constant, but with occasional jumps. Approximating $C_V$ as contant, get $U(T) = C_V T = fnRT$. But, in what follows here, we'll write general formulae.

• $P, V$ diagrams and ideal gas. Picture of $\beta = (\partial \ln V/\partial T)_P = 1/T$, and $\kappa_T = -(\partial \ln V/\partial P)_T = 1/P$.

• Now picture $\text{đ}Q = C_V dT + PdV = C_P dT - VdP$. Comparing, see that $dT = (\text{đ}Q + VdP)/C_P = (\text{đ}Q - PdV)/C_V$, and thus $nR\text{đ}Q = C_V VdP + C_P PdV$. For a quasistatic and adiabatic process, have $dT = -PdV/C_V = VdP/C_P$, which integrates to $PV^\gamma =$ constant.

So get $\left(\frac{\partial P}{\partial V}\right)_{adi} = -\gamma P/V = \gamma \left(\frac{\partial P}{\partial V}\right)_T > \left(\frac{\partial P}{\partial V}\right)_T$. So adiabatic curve has steeper slope than isothermal curve in $P/V$ diagram. See here $\kappa_T = \gamma \kappa_{adi}$ (and more generally too).

• Examples of $\Delta W$ for various processes. E.g. for solid with $\kappa_T \approx$ constant, get $\Delta W \approx -\frac{1}{2}\kappa_T V_{av}(P_f^2 - P_i^2)$, e.g. $10g$ Copper, from $P_i = 1atm$ to $P_f = 10^3 atm$.

Examples of $\Delta W$ for ideal gas

1. isothermal: $\Delta U = 0$. $\Delta Q = \Delta W = nRT \ln(V_f/V_i) = nRT \ln(P_i/P_f)$.
2. isochoric: $\Delta W = 0$. $\Delta Q = \Delta U = C_V \Delta T$
3. isobaric: $\Delta W = P\Delta V = nR\Delta T$. $\Delta Q = C_P \Delta T = (C_V + nR)\Delta T$
4. adiabatic: $\Delta Q = 0$. $\Delta W = -\Delta U = -C_V \Delta T$.

• Engines. 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 $\eta = 1 - |Q_C|/|Q_H| \le 1$. 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.

• Preview of 2nd law: (Clauius) *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 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.

• 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. $\eta \leq \eta_{max} = \eta_{rev}$.