

10/4 Lecture outline

- Work done by system $\delta W = pdV$. Integrate $\Delta W = \int_{path} pdV$. The slash or bar in δW is because this is *not* an *exact differential*. What this means, is that ΔW depends on the path, not just the endpoints. Illustrations.

- So $\Delta W \neq W_f - W_i$. Doesn't make sense to discuss W_i and W_f . Work is not a *state variable*.

- Observe: for adiabatic process, then ΔW does depend just on the endpoints. (Special case of first law.)

- Heat transfer. δQ , also not exact. $\Delta Q = \int_{path} \delta Q$ also depends on path. $\Delta Q \neq Q_f - Q_i$. Doesn't make sense to discuss Q_i and Q_f , heat is not a state variable.

- Isochoric process, $dV = 0$, then $\Delta W = 0$, no work done. Observe: for isochoric process, ΔQ does depend just on endpoints. (Special case of first law.)

- First law of thermodynamics: change in internal energy of a system:

$$dU = \delta Q - \delta W,$$

where U is a **state variable**. For system in equilibrium, $U = U(T, V)$, or write as $U = U(P, V)$. Depends only on state of system (which is on the equation of state surface $f(P, V, T) = 0$ for equilibrium).

- For ideal gas, $U = U(T)$, independent of volume. Picture free expansion from V_1 to V_2 , in adiabatically isolated system. No work or heat transfer, so $U_1 = U_2$. Observe that, for dilute enough systems, $T_1 \approx T_2$. We'll later understand the connection between this and the ideal gas law (once we get to the 2nd law of thermo).

- Lots of definitions:

$$\beta \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad \text{coeff of thermal expansion}$$

$$\kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad \text{coeff of isothermal compressibility}$$

$$\kappa_{adi} \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{adi} \quad \text{coeff of adiabatic compressibility}$$

$$C_V \equiv \left(\frac{\delta Q}{dT} \right)_V \quad \text{heat capacity at constant volume}$$

$$C_P \equiv \left(\frac{\delta Q}{dT} \right)_P \quad \text{heat capacity at constant pressure}$$

$$\gamma \equiv \frac{C_P}{C_V}$$

Note that C_V and C_P are *extensive* (so depend on how much stuff there is, and thus can't be just looked up on the internet), the others are *intensive* (so can be looked up in a table or on the internet). We can form intensive (look-up-able) versions of C_P and C_V by dividing by another extensive quantity, e.g. the *specific heats*: $c_V \equiv C_V/n$ and $c_P \equiv C_P/n$.

Always the case that $\gamma \equiv C_P/C_V > 1$: more heat required, for fixed ΔT , in case of $P = \text{constant}$, because some goes into doing a positive amount of work, whereas at constant V no work is done, so all added heat goes toward increasing the internal energy, and thus the temperature.

We'll then derive some formulae, e.g.

$$dP = \frac{\beta}{\kappa_T} dT - \frac{1}{\kappa_T V} dV$$

Integrate it:

$$P_f - P_i \approx \frac{\beta}{\kappa_T} (T_f - T_i) - \frac{1}{\kappa_T V_{av}} (V_f - V_i).$$

(Give an example here.)