CM 3230 Thermodynamics, Fall 2016

Lecture 2

1. First law of Thermodynamics:

Total energy (E_{total}) = potential energy(E_p) + kinetic energy (E_k)
+ internal energy (U)

- **First law for closed system: (** $\Delta \equiv \Delta_{init}^{final}$)

$$\Delta E_p + \Delta E_k + \Delta U = Q_{in} - W_{by} \text{ (extensive form)}$$

$$\Delta \hat{e}_p + \Delta \hat{e}_k + \Delta \hat{u} = \hat{q}_{in} - \hat{w}_{by} \text{ (intensive form, per unit mass)}$$

$$\Delta e_p + \Delta e_k + \Delta u = q_{in} - w_{by} \text{ (intensive form, per unit mole)}$$

- $\Delta \hat{e}_p = g\Delta z$ (change in specific potential energy) and $\Delta \hat{e}_k = \frac{1}{2}\text{v}^2$ (change in specific kinetic energy). Both will be treated as negligible in a small-scale system such as gas in piston system.

- q is the heat transferred to the system from the surroundings per unit mole. (Note: sometimes, $Q = nq$ is the desired value)
    - Heat transfer is based on temperature difference: from higher temperature to lower temperature.
        - *Question: will there be heat flow for an isothermal process?*
    - However, if the boundary is next to a well insulated wall, we obtain an adiabatic process (even if the temperature outside the system is different from the system temperature)
    - Often the value is either given or determined based on heat transfer equations from surroundings. Sometimes, it is the last item to be determined via the energy balance equation.

- w_{by} is the work done by the system
  - Originally defined as $W = \int F ds$
  - For piston work by gas :
    $F = PA \rightarrow W = \int (P)(Ads) = \int PdV$
  - If external pressure changes infinitesimally from condition 1 to condition 2, then work is "reversible",

    $$W_{by,rev} = \int P_{rev,1\to 2} dV$$

    Otherwise, if external pressure undergoes sudden change, e.g. $P_{ext} = \text{constant}$, then work is irreversible,

    $$W_{by} = P_{ext} \int dV = P_{ext} \Delta V$$
  - Flow work (for open systems): work done at inlets and outlets, $\left(\frac{\dot{W}_{flow,by}}{\dot{n}}\right)_{pos1} = \pm (Pv)_{pos1}$
  - Shaft work: results from external machines with moving parts, e.g. pumps ($W_{s,by} < 0$) and turbines ($W_{s,by} > 0$)

Example: An ideal gas inside a piston cylinder expands/compressed along the path: $a \rightarrow b \rightarrow c \rightarrow d \rightarrow e \rightarrow f$, where

$a:\ P = 10\ kPa,\ V = 0.1\ m^3$
$b:\ P = 8\ kPa,\ V = 0.2\ m^3$
$c:\ P = ?,\ V = 0.1\ m^3$
$d: P = \ 36\ kPa,\ V = 0.02\ m^3$
$e: P = ?,\ V = 0.05\ m^3$
$f:\ P = 10\ kPa,\ V = 0.1\ m^3$ (same as a)

Subpaths:

$a \rightarrow b$: irreversible sudden expansion
$b \rightarrow c$: reversible polytropic compression path $PV^2 = \text{constant}$
$c \rightarrow d$: irreversible sudden compression
$d \rightarrow e$: irreversible sudden expansion
$e \rightarrow f$: reversible isothermal expansion

Find the missing pressures, sketch the path in a P vs V diagram, and calculate the net work done by the ideal gas.

Solution:

$$W_{by,a\to b} = (8kPa)([0.2-0.1]m^3) = 0.8\ kJ$$

$$P_c = P_b\left(\frac{V_b}{V_c}\right)^2 = (8kPa)\left(\frac{0.2}{0.1}\right)^2 = 32\ kPa$$

$$\begin{aligned} W_{by,b\to c} &= \int_b^c PdV = (P_bV_b^2)\int_{0.2m^3}^{0.1m^3}\frac{1}{V^2}dV \\ &= (P_bV_b^2)\left(-\frac{1}{V}\right)\Bigg|_{0.2m^3}^{0.1m^3} \\ &= (8kPa)(0.2m^3)^2\left(-\frac{1}{0.1m^3}-\left[-\frac{1}{0.2m^3}\right]\right) \\ &= -1.6\ kJ \end{aligned}$$

$$W_{by,c\to d} = (36kPa)([0.02-0.1]m^3) = -2.88kJ$$

Because path $e \to f$ is isothermal and gas is ideal, then path is also isotropic and given by $PV =$ constant. Thus,

$$P_e = P_f\left(\frac{V_f}{V_e}\right) = 10kPa\left(\frac{0.1}{0.05}\right) = 20\ kPa$$

$$W_{by,d\to e} = (20kPa)([0.05-0.02]m^3) = 0.6\ kJ$$

$$\begin{aligned} W_{by,e\to f} &= (P_eV_e)\int_{0.05m^3}^{0.1m^3}\frac{1}{V}dV = (P_eV_e)\left(\ln(V)\right)\Bigg|_{0.05m^3}^{0.1m^3} \\ &= (20kPa)(0.05m^3)\ln\left(\frac{0.1}{0.05}\right) = 0.693\ kJ \end{aligned}$$

$$\boxed{W_{by,net} = (0.8-1.6-2.88+0.6+0.693)kJ = -2.39\ kJ}$$

Note: a path that starts and ends at the same state is called a “cycle”

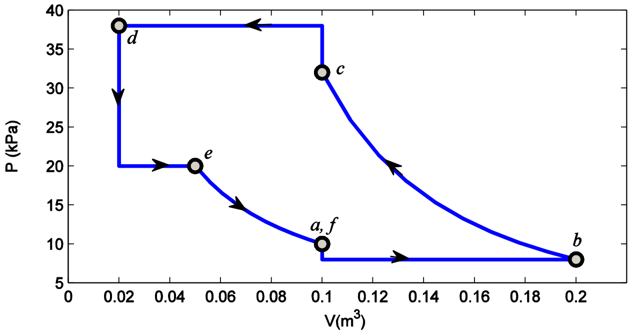


Figure 1. Sketch of path/cycle.

- **First law for open system at steady state: ($\Delta \equiv \Delta_{\sum in}^{\sum out}$)**

$$\Delta\hat{e}_p + \Delta\hat{e}_k + \Delta\hat{u} = \hat{q}_{in} - \hat{w}_{by} \text{ (intensive form, per unit mass)}$$

$$\Delta e_p + \Delta e_k + \Delta u = q_{in} - w_{by} \text{ (intensive form, per unit mole)}$$

$$w_{by} = w_{by,shaft} + w_{by,flow} = w_{by,shaft} + \sum(Pv)_{out} - \sum(Pv)_{in}$$

Thus,

$$\Delta e_p + \Delta e_k + (\Delta u + \Delta Pv) = q_{in} - w_{by,shaft}$$

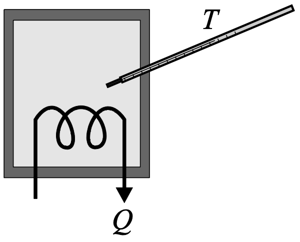
Define “enthalpy” as: $H = U + PV$

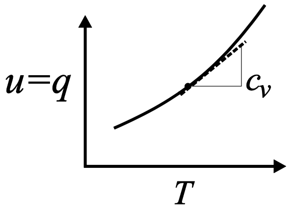
and molar enthalpy as $h = u + Pv$, then

$$\Delta e_p + \Delta e_k + \Delta h = q_{in} - w_{by,shaft}$$

2. Heat Capacities (used to calculate “sensible heat”)

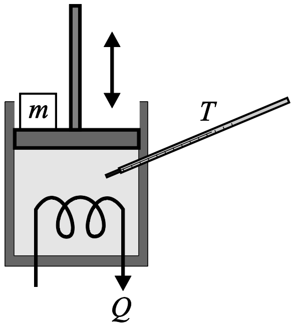
- 2 types of experiments (both under closed system)
  - Expt. Type 1: Heat the system (of known amount) under rigid boundaries (constant volume), and monitor temperature changes.

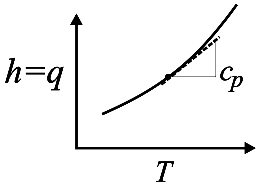




$$c_v = \left(\frac{\partial u}{\partial T}\right)_v = \text{constant volume heat capacity}$$

- Expt. Type 2. Heat the system (of known amount) under constant pressure (isobaric), and monitor temperature changes.





$$c_p = \left(\frac{\partial h}{\partial T}\right)_p = \text{constant pressure heat capacity}$$

Question: Why is $\Delta h = q$ for this experiment?

Thus, $\Delta u = q = \int c_v \ dT$ (under constant volume process)

$$\Delta h = q = \int c_p \ dT \text{ (under constant pressure)}$$

Remarks:

1. Appendix A.2.1 and A.2.2 are $\frac{c_p}{R}$ (no units) as function of temperature (in K) (for gases under ideal behavior, i.e. low pressure). For higher pressures, real gas correction is needed.
2. For liquids and solids, we will generally consider both c_p and c_v to be about the same (not so for gases).
3. **Fact:** for ideal gases, both u and h are functions only of temperature. (this fact will be used in solving several problems later! – e.g., isothermal paths for <u>ideal gases</u> should be taken as $\Delta u = 0$ and $\Delta h = 0$)
4. For steam, one should use the steam tables for calculating Δu and Δh rather than using heat capacity formulas (unless assumed or specified in the problem/analysis).