Applications of the First Law

(Lecture 4)

1st semester, 2021

Advanced Thermodynamics (M2794.007900)

Song, Han Ho

(*) Some materials in this lecture note are borrowed from the textbook of Ashley H. Carter.

서울대학교
기계항공공학부

Heat Capacity

- Definition: the limiting ratio of the heat absorbed divided by the temperature increase

$$C = \lim_{\Delta T \to 0}\left(\frac{Q}{\Delta T}\right) = \frac{\delta Q}{dT} \rightarrow \text{not truly derivative}$$

- *Specific heat capacity* (or *specific heat*)

$$c = \frac{1}{m}\left(\frac{\delta Q}{dT}\right) = \frac{\delta q}{dT} \quad (\text{J/kg}\cdot\text{K})$$

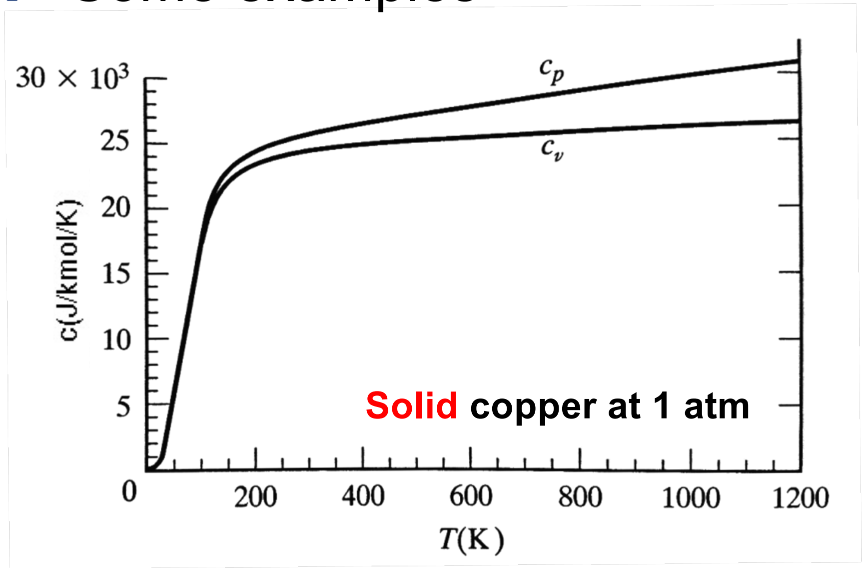
$$\bar{c} = \frac{1}{n}\left(\frac{\delta Q}{dT}\right) = \frac{\delta \bar{q}}{dT} \quad (\text{J/kmol}\cdot\text{K})$$

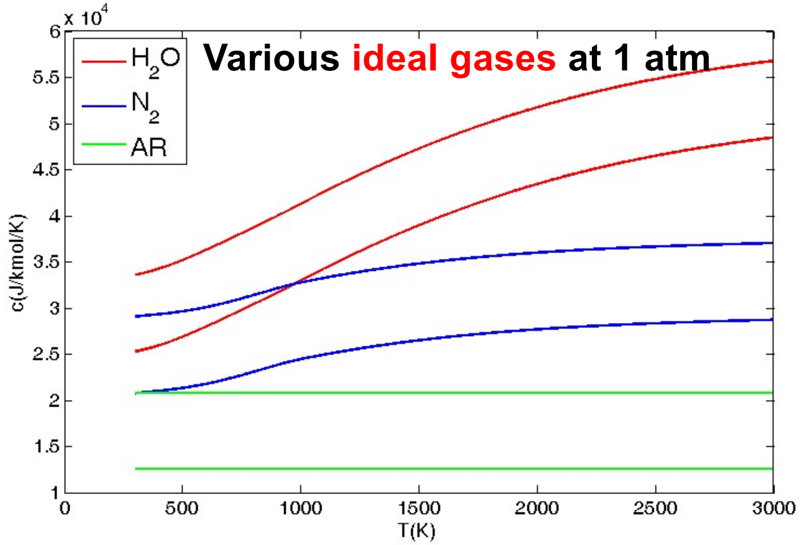
- *Specific heat at constant volume and at constant pressure*

$$c_v = \left(\frac{\delta q}{dT}\right)_v \quad \text{and} \quad c_P = \left(\frac{\delta q}{dT}\right)_P \quad (\text{J/kg}\cdot\text{K})$$

Heat Capacity

➔ Some examples





1. At high temperatures, c_v is almost constant. (Law of Dulong and Petit ~ $3\bar{R}$ from 6 d.o.f.)
2. At low temperatures, c_P is almost same with c_V. At high temperatures, they deviate due to thermal expansion.
3. Specific heats tend toward zero as T→0K. (→ Einstein's or Debye's theory)

1. Various ideal gases show different limit behaviors.
2. Argon has constant specific heats.
3. There is almost constant difference between c_P and c_V. (→ Mayer's equation)

Mayer's Equation

➔ Let's find the relationship between c_v and c_P for an ideal gas.

For a simple compressible substance, the first law is

$$du = \delta q - \delta w = \delta q - Pdv$$

In general, $u = u(v,T) \rightarrow du = \left(\frac{\partial u}{\partial v}\right)_T dv + \left(\frac{\partial u}{\partial T}\right)_v dT$

Then, $\delta q = du + Pdv = \left(\frac{\partial u}{\partial T}\right)_v dT + \left\{\left(\frac{\partial u}{\partial v}\right)_T + P\right\} dv$

$$\rightarrow \delta q = c_v dT + \left\{\left(\frac{\partial u}{\partial v}\right)_T + P\right\} dv \quad \left(\because c_v = \left(\frac{\delta q}{\partial T}\right)_v = \left(\frac{\partial u}{\partial T}\right)_v\right)$$

But for an ideal gas, $u = u(T)\ \text{only} \rightarrow \left(\frac{\partial u}{\partial v}\right)_T = 0$ (Gay-Lussac-Joule exp.)

Then, $c_v = \left(\frac{\partial u}{\partial T}\right)_v = \frac{du}{dT}$ or $du = c_v dT$ or $u - u_0 = \int_{T_0}^{T} c_v dT$

Mayer's Equation

- Continue on.

  Using ideal gas EOS, $Pv = RT \rightarrow Pdv + vdP = RdT$

  Substituting this equation,

$$\delta q = c_v dT + Pdv \rightarrow \delta q = (c_v + R)dT - vdP$$

  Then,

$$c_P \equiv \left(\frac{\delta q}{\partial T}\right)_P = c_v + R$$

  Mayer's equation

  "Over the range of variables for which the ideal gas law holds, the two specific heat capacities differ by the constant *R*."

- *The ratio of specific heat capacities* (or *specific heat ratio*) $\gamma \equiv \frac{c_P}{c_v}$

Enthalpy and Heats of Transformation

➔ The heat of transformation

- Heat transfer accompanying a phase change
- Phase change is an isothermal and isobaric process with changing volume.
- Applying the first law for a phase change, from phase 1 to phase 2,

$$du = \delta q - Pdv$$

$$u_2 - u_1 = l - P(v_2 - v_1) \rightarrow l = (u_2 + Pv_2) - (u_1 + Pv_1)$$

where l : latent heat of phase change

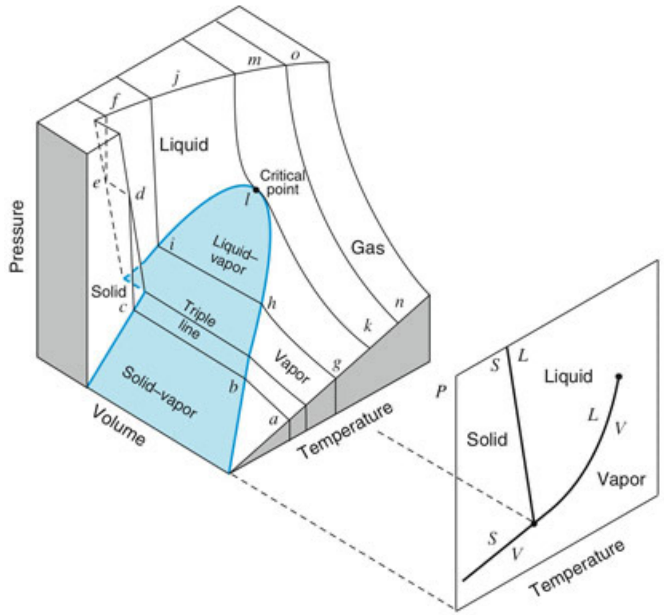
(i.e. vaporization, fusion, sublimation)

Here, we define *enthalpy(h)*, a state variable.

$$h \equiv u + Pv$$

Then,

$$l = h_2 - h_1$$



P-v-T Surface for Water

Latent Heat of Vaporization at Steam Point, 1 atm		Latent Heat of Fusion at Melting Point, 1 atm	
Water	538 kcal/kg	Water	80 kcal/kg
Mercury	63	Mercury	3
Alcohol	207	Lead	5
Gasoline	95	Aluminum	77

Latent Heat of Phase Change

Relationships involving Enthalpy

➔ Let's find some useful relationship using enthalpy for an ideal gas.

For S.C.S., the first law is $du = \delta q - Pdv \rightarrow du + Pdv = \delta q$

From the definition of enthalpy,

$$dh = d(u + Pv) = du + Pdv + vdP \rightarrow du + Pdv = dh - vdP$$

Then,

$$\delta q = dh - vdP$$

In general, $h = h(P,T) \rightarrow dh = \left(\frac{\partial h}{\partial P}\right)_T dP + \left(\frac{\partial h}{\partial T}\right)_P dT$

$$c_P = \left(\frac{\delta q}{\partial T}\right)_P = \left(\frac{\partial h}{\partial T}\right)_P$$

$$\delta q = \left(\frac{\partial h}{\partial T}\right)_P dT + \left\{\left(\frac{\partial h}{\partial P}\right)_T - v\right\} dP \rightarrow \delta q = c_P dT + \left\{\left(\frac{\partial h}{\partial P}\right)_T - v\right\} dP$$

But for an ideal gas, $h = h(T)\text{ only} \rightarrow \left(\frac{\partial h}{\partial P}\right)_T = 0$ (Joule-Thomson exp.)

Then, $c_P = \left(\frac{\partial h}{\partial T}\right)_P = \frac{dh}{dT}$ or $dh = c_P dT$ or $h - h_0 = \int_{T_0}^{T} c_P dT$

Work done in an Adiabatic Process

- Let's calculate work done in an adiabatic process for an ideal gas.

For a simple compressible substance of an ideal gas, the first law is

$$\delta q = c_v dT + P dv \rightarrow P dv = -c_v dT$$
$$\delta q = c_P dT - v dP \rightarrow v dP = c_P dT$$
$$\rightarrow \frac{v dP}{P dv} = -\frac{c_P}{c_v} = -\gamma$$

Then,

$$\frac{dP}{P} = -\gamma \frac{dv}{v} \quad \text{or} \quad P v^{\gamma} = const = K \ \text{(when } \gamma \text{ constant)}$$

Work is given by the following expression for a constant specific heats,

$$w = \int P dv = K \int_{v_1}^{v_2} v^{-\gamma} dv = \frac{1}{1-\gamma} \left(K v^{1-\gamma} \right) \Big|_{v_1}^{v_2} = \frac{1}{1-\gamma} \left[K v_2^{1-\gamma} - K v_1^{1-\gamma} \right] = \frac{1}{1-\gamma} \left[P_2 v_2 - P_1 v_1 \right]$$

$$K = P_1 v_1^{\gamma} = P_2 v_2^{\gamma}$$