Equations of State

Reading	**Problems**
3-6, 3-7, 4-3 → 4-5	3-54, 3-64, 3-80, 4-25, 4-39, 4-42
6-6	
7-3, 7-4, 7-7 → 7-10	7-43, 7-116, 7-166, 7-193

Ideal Gas

- When is the ideal gas assumption viable?
  - for a low density gas where:
    - the gas particles take up negligible volume
    - the intermolecular potential energy between particles is small
    - particles act independent of one another
  - Under what conditions can it be used?
    - low density
    - high temperatures - considerably in excess of the saturation region
    - at very low pressures

- for any gas whose equation of state is exactly

$$Pv = RT$$

  the specific internal energy depends only on temperature

$$u = u(T)$$

- the specific enthalpy is given by

$$h = u + Pv$$

  where

$$h(T) = u(T) + RT$$

  Note: Since $u = u(T)$, and R is a constant, enthalpy is only a function of temperature.

- for a ideal gas

$$c_v = \frac{du}{dT} \quad \Rightarrow \quad c_v = c_v(T) \ \ only$$

$$c_p = \frac{dh}{dT} \quad \Rightarrow \quad c_p = c_p(T) \ \ only$$

From the equation for enthalpy,

$$RT = h(T) - u(T)$$

If we differentiate with respect to T

$$R = \frac{dh}{dT} - \frac{du}{dT}$$

$$\boxed{R = c_p - c_v}$$

Is Water Vapor an Ideal Gas?

- Figure 3-49 can be used to determine the regions where water vapor behaves as an ideal gas
  - YES - at pressures below $10\ kPa$ regardless of temperature
  - NO - at high pressure
  - what about at atmospheric pressure and temperature ($P_{atm} \approx 100\ kPa$ and $T_{atm} < 50\ °C$)? Figure 3-49 would indicate YES
    - look at the $T - s$ diagram for water: $h \approx$ constant for atmospheric conditions
    - for an ideal gas: $h = h(T)$ - since h only varies with respect to T, it must behave like an ideal gas

In Summary

For an ideal gas with constant c_p and c_v

$$\begin{aligned} Pv &= RT \\ u_2 - u_1 &= c_v(T_2 - T_1) \\ h_2 - h_1 &= c_p(T_2 - T_1) \end{aligned}$$

There are 3 forms of a change in entropy as a function of T & v, T & P, and P & v.

$$\begin{aligned} s_2 - s_1 &= c_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1} \\ &= c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \\ &= c_p \ln \frac{v_2}{v_1} + c_v \ln \frac{P_2}{P_1} \end{aligned}$$

$$R = c_p - c_v$$

Isentropic and Polytropic Processes for Ideal Gases

Gibb's equation can be written as

$$T ds = du + P dv = c_v dT + P dv = 0 \qquad (1)$$

The definition of enthalpy is

$$h = u + Pv$$

Taking the derivative yields

$$dh = \underbrace{du + P dv}_{\equiv T ds} + v dP$$

$$dh = T ds + v dP \;\; \Rightarrow \;\; T ds = 0 = dh - v dP$$

$$\boxed{c_p dT - v dP = 0} \qquad (2)$$

Equating Eqs. (1) and (2) through the dT term gives

$$\frac{dP}{P} = -\frac{c_p}{c_v} \frac{dv}{v} \qquad (3)$$

Integrating (3) from its initial state to a final state

$$
\begin{aligned}
\ln P\big|_1^2 &= -k \, \ln v\big|_1^2 \\
\ln P_1 - \ln P_2 &= k[\ln v_2 - \ln v_1] \\
\ln\left(\frac{P_1}{P_2}\right) &= \ln\left(\frac{v_2}{v_1}\right)^k \\
&\quad \text{take exp of each side} \\
P_2 v_2^k &= P_1 v_1^k
\end{aligned}
$$

where $k = \dfrac{c_p}{c_v}$

The product of $P \cdot v^k$ remains constant for an ideal gas when:

- specific heats are constant
- the gas undergoes an isentropic process ⟶ reversible + adiabatic

Combining this result with the ideal gas equation of state

$$\boxed{\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{k-1} = \left(\frac{P_2}{P_1}\right)^{(k-1)/k}}$$

Relative Pressure and Relative Specific Volume

- typically we assume specific heat to be constant with respect to temperature
- *but* when temperature swings are significant, this assumption can lead to inaccuracies, i.e.

$T\ (K)$	$c_p\ (kJ/kg \cdot K)$	**% difference**
300	1.0057	
1000	1.1417	13.5
2500	1.688	67.8

- the relative pressure and relative volume tables (C&B Table A-17), provide an accurate way of including the temperature effects on specific heat for ideal gases during isentropic processes
- note: the specific heat ratio term given by $k = c_p/c_v$ will also be influenced by temperature
- **Procedure:**
  - given T_1, P_1 and P_2 for an isentropic process
  - determine P_{r1} at T_1 from Table A-17
  - calculate P_{r2}, where

$$\left(\frac{P_2}{P_1}\right)_{s=const} = \frac{P_{r2}}{P_{r1}}$$

  - read T_2 from Table A-17 for the calculated value of P_{r2}
- use a similar procedure if volume is known instead of pressure, where

$$\left(\frac{v_2}{v_1}\right)_{s=const} = \frac{v_{r2}}{v_{r1}}$$

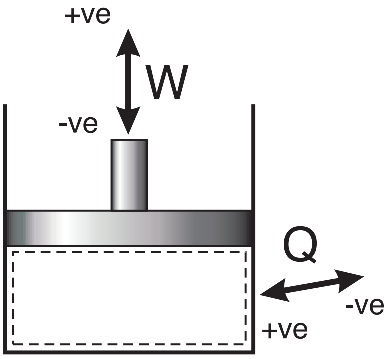
Sign Convention

There are many potential sign conventions that can be used.

Cengel Approach

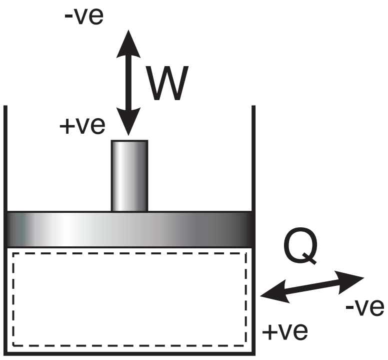
Heat Transfer: heat transfer to a system is positive and heat transfer from a system is negative.

Work Transfer: work done by a system is positive and work done on a system is negative.



Culham Approach

Anything directed into the system is positive, anything directed out of the system is negative.



Incompressible Liquids

- a substance whose volume cannot be changed
- no substance is truly incompressible, but this model is good for most liquids and solids

State Postulate

- the number of independent intensive thermodynamic properties is equal to the number of relevant <u>reversible</u> work modes <u>plus one</u>.
- the "plus one" is for the independent control on energy through heat transfer
- we know that for a *simple* (has only one work mode), *compressible* (the work mode is Pdv work) substance
  - 2 thermodynamic properties will fix the rest
    - list of intensive properties includes, T, u, P, v, s
    - state postulate says two will fix the rest, i.e. if u and v are known, the equations of state are

$$\begin{aligned} T &= T(u, v) \\ P &= P(u, v) \\ s &= s(u, v) \end{aligned}$$

Hence, if the substance is assumed to be incompressible, then its internal energy, for example, cannot be varied independently by work transfer $\longrightarrow$ but it can be varied by heat transfer at constant volume, i.e. $Pdv = 0$ since $dv = constant$. There are no reversible work modes.

In summary

$$\begin{aligned} u_2 - u_1 &= \bar{c}\,(T_2 - T_1) \\ h_2 - h_1 &= (u_2 - u_1) + v(P_2 - P_1) \\ s_2 - s_1 &= \bar{c}\ \ln(T_2/T_1) \end{aligned}$$

$$c_p = c_v = \bar{c}$$