

## PART III

(37)

- 1) Some thermodynamic relations:  
 $C_p - C_v$ ,  $C_p/C_v$
- 2) Math. supplement
- 3) Adiabatic process
- 4) Adiabatic process for an ideal gas.

## Calculation of $C_p - C_v$

Consider a system with equation of state  $f(p, T, V) = 0$ .

Because of the eq. only two of the variables  $p, T, V$  are independent.

One can take any pair. Let us consider  $T$  and  $V$  be independent.

Hence:  $U = U(T, V)$  - internal energy

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV$$

1st law:  $dQ = \overset{\rightarrow}{dU} + p dV =$

$$= \left( \frac{\partial U}{\partial T} \right)_V dT + \left[ \left( \frac{\partial U}{\partial V} \right)_T + p \right] dV =$$

$$= C_v dT + \left[ \left( \frac{\partial U}{\partial V} \right)_T + p \right] dV \quad (1)$$

Consider now an isobaric ( $p = \text{const}$ ) process. By definition of  $C_p$

$$dQ = C_p \cdot dT \quad (2)$$

Comparing (1) and (2)  $\Rightarrow$

$$\Rightarrow C_p - C_v = \left[ \left( \frac{\partial U}{\partial V} \right)_T + p \right] \left( \frac{\partial V}{\partial T} \right)_p$$

Example:  $C_p - C_v$  for an ideal gas

no interaction between molecules  $\Rightarrow$

$$\Rightarrow \left( \frac{\partial U}{\partial V} \right)_T = 0$$

$$pV = nRT \Rightarrow \left( \frac{\partial V}{\partial T} \right)_p = \frac{nR}{p}$$

$$C_p - C_v = p \frac{nR}{p} = nR$$

specific heat  
 $c = \frac{C}{n}$

$$C_p - C_v = R \quad - \text{ideal gas}$$

# Math supplement

(40)

$f(T, V, p) = 0$  - eq. of state

$$0 = df = \frac{\partial f}{\partial T} dT + \frac{\partial f}{\partial V} dV + \frac{\partial f}{\partial p} dp, \text{ hence}$$

$$\left(\frac{\partial T}{\partial p}\right)_V = - \frac{\left(\frac{\partial f}{\partial p}\right)_{TV}}{\left(\frac{\partial f}{\partial T}\right)_{pV}}$$

$$\left(\frac{\partial p}{\partial V}\right)_T = - \frac{\left(\frac{\partial f}{\partial V}\right)_{Tp}}{\left(\frac{\partial f}{\partial p}\right)_{TV}}$$

$$\left(\frac{\partial V}{\partial T}\right)_p = - \frac{\left(\frac{\partial f}{\partial T}\right)_{pV}}{\left(\frac{\partial f}{\partial V}\right)_{Tp}}$$

Hence

$$\boxed{\left(\frac{\partial T}{\partial p}\right)_V \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p = -1} \Rightarrow -\frac{1}{\left(\frac{\partial T}{\partial p}\right)_V} = \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

## Some other relations

(4)

consider  $p, v$  be independent:

$$(A) \quad du = \left( \frac{\partial u}{\partial p} \right)_v dp + \left( \frac{\partial u}{\partial v} \right)_p dv$$

$$(B) \quad dT = \left( \frac{\partial T}{\partial p} \right)_v dp + \left( \frac{\partial T}{\partial v} \right)_p dv$$

Now consider  $T, v$  be independent

$$(C) \quad du = \underbrace{\left( \frac{\partial u}{\partial T} \right)_v}_{C_v} dT + \left( \frac{\partial u}{\partial v} \right)_T dv \Rightarrow$$

$$\Rightarrow du = C_v \left( \frac{\partial T}{\partial p} \right)_v dp + \left[ C_v \left( \frac{\partial T}{\partial v} \right)_p + \left( \frac{\partial u}{\partial v} \right)_T \right] dv$$

comparing this with (A) we conclude

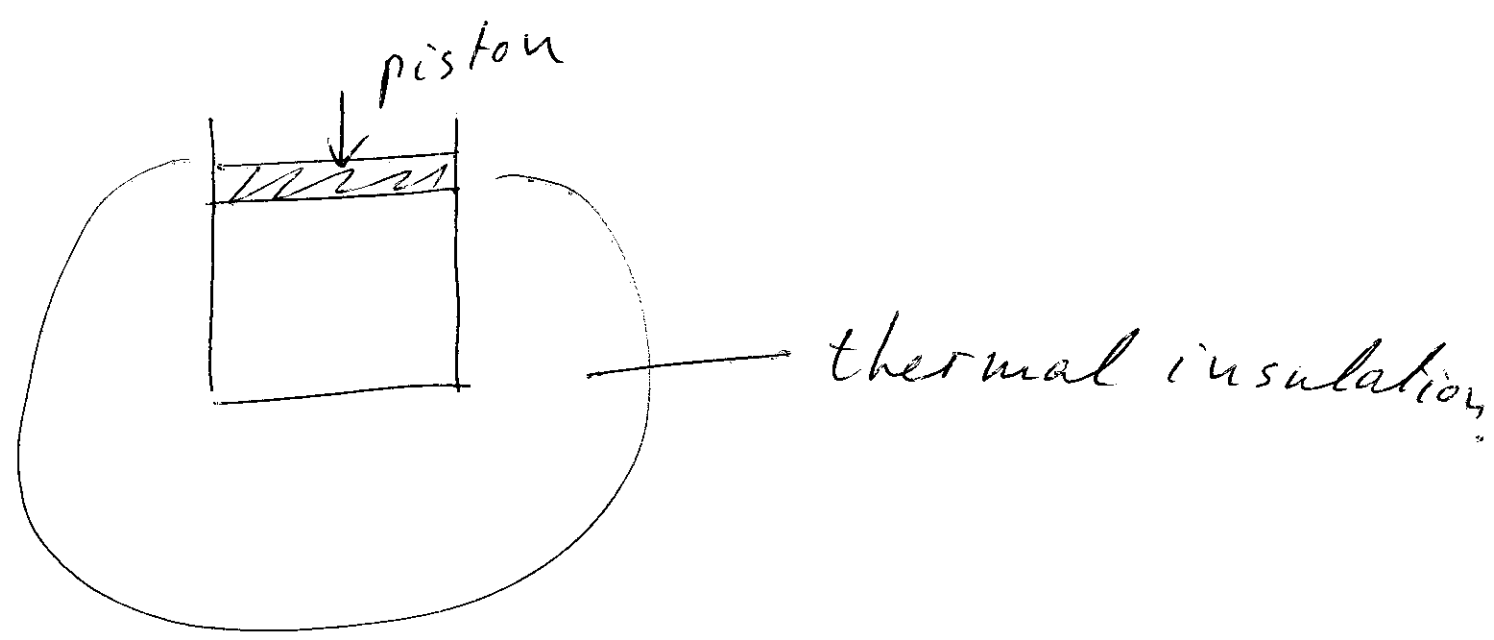
$$\boxed{\left( \frac{\partial u}{\partial p} \right)_v = C_v \left( \frac{\partial T}{\partial p} \right)_v} \quad \text{— identity (I)}$$

$$\boxed{\left( \frac{\partial u}{\partial v} \right)_p = C_v \left( \frac{\partial T}{\partial v} \right)_p + \left( \frac{\partial u}{\partial v} \right)_T}$$

# Adiabatic process

It means a process with  $dq = 0$

$\Leftrightarrow$  perfect thermal insulation.



Notation:  $S = \text{const.}$   $S$  is entropy

Meaning will become clear later.

At this stage it means only

that  $dq = 0$

# Calculation of $C_p/C_v$

$P, V$  - independent variables

$$dQ = du + p dv = \left(\frac{\partial u}{\partial p}\right)_v dp + \left[\left(\frac{\partial u}{\partial v}\right)_p + p\right] dv$$

consider now an adiabatic process:  $dQ=0$ ,

$dp_s$  is variation of the pressure in the process

$dv_s$  is variation of the volume in the process

$$\Rightarrow 0 = \left(\frac{\partial u}{\partial p}\right)_v dp_s + \left[\left(\frac{\partial u}{\partial v}\right)_p + p\right] dv_s \Rightarrow$$

$$\Rightarrow \left(\frac{\partial p}{\partial v}\right)_s = - \frac{1}{\left(\frac{\partial u}{\partial p}\right)_v} \left[\left(\frac{\partial u}{\partial v}\right)_p + p\right]$$

using also the identity (I) from p 41 we get

$$C_v \left(\frac{\partial p}{\partial v}\right)_s = - \frac{1}{\left(\frac{\partial T}{\partial p}\right)_v} \left[\left(\frac{\partial u}{\partial v}\right)_p + p\right]$$

Let us also use identity derived <sup>(44)</sup>  
on page 40. This gives

$$c_v \left( \frac{\partial p}{\partial v} \right)_s = \left( \frac{\partial p}{\partial v} \right)_T \left( \frac{\partial v}{\partial T} \right)_p \left[ \left( \frac{\partial u}{\partial v} \right)_p + p \right] =$$
$$= \left( \frac{\partial p}{\partial v} \right)_T \underbrace{\left[ \left( \frac{\partial u}{\partial T} \right)_p + p \left( \frac{\partial v}{\partial T} \right)_p \right]}_{c_p}$$

$$\frac{c_p}{c_v} = \frac{\left( \frac{\partial p}{\partial v} \right)_s}{\left( \frac{\partial p}{\partial v} \right)_T}$$

# Adiabatic process for an ideal gas

$$\gamma = \frac{C_p}{C_v}$$

- $\gamma = \frac{5}{3} = 1.666$       monoatomic gas
- $\gamma = \frac{7}{5} = 1.4$       gas of diatomic molecules.
- .....

A microscopic explanation will be given later.

$$\gamma = \frac{i+2}{i}$$

$$PV = nRT \Rightarrow \left(\frac{\partial P}{\partial V}\right)_T = -\frac{nRT}{V^2} = -\frac{P}{V}$$

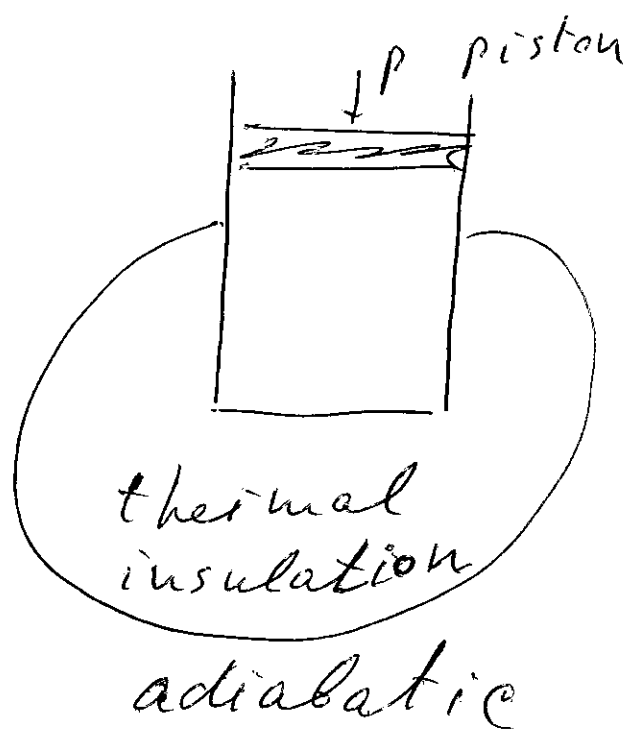
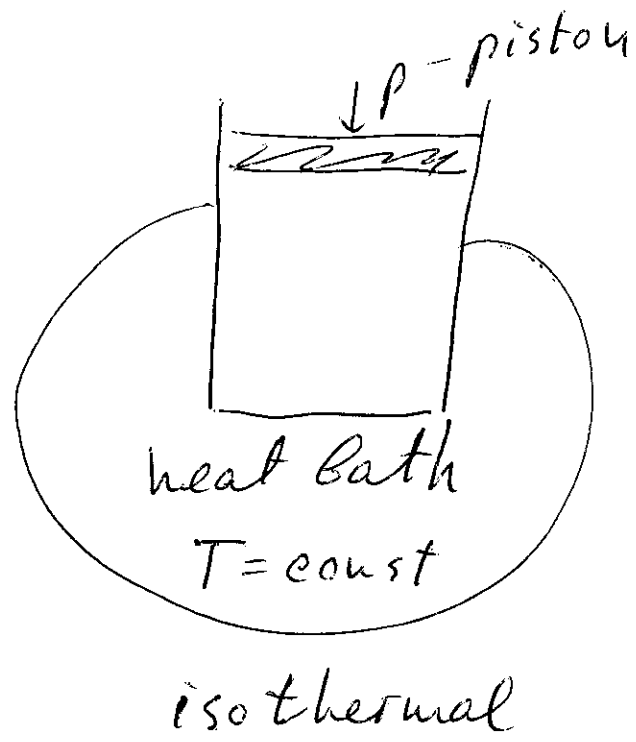
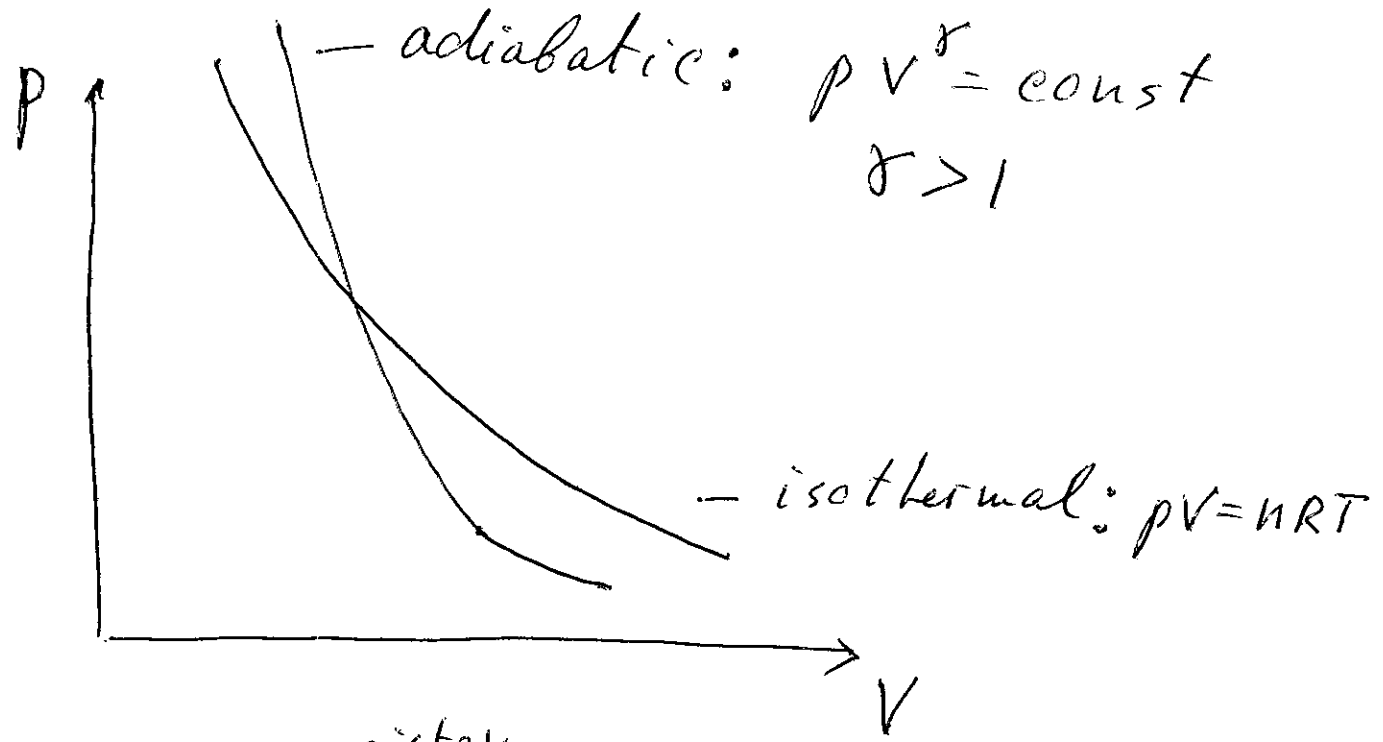
$$\gamma = \frac{C_p}{C_v} = \frac{\left(\frac{\partial P}{\partial V}\right)_s}{\left(\frac{\partial P}{\partial V}\right)_T} = -\frac{V}{P} \left(\frac{\partial P}{\partial V}\right)_s$$

$$\left[ \gamma = -\frac{V}{P} \left(\frac{\partial P}{\partial V}\right)_s \right] \Rightarrow \left[ \frac{dP_s}{P} + \gamma \frac{dV_s}{V} = 0 \right]$$

Perform integration

$$\ln p + \gamma \ln V = \text{const} \implies$$

$$\implies \boxed{pV^\gamma = \text{const}} \quad \text{eq. of the adiabatic curve}$$



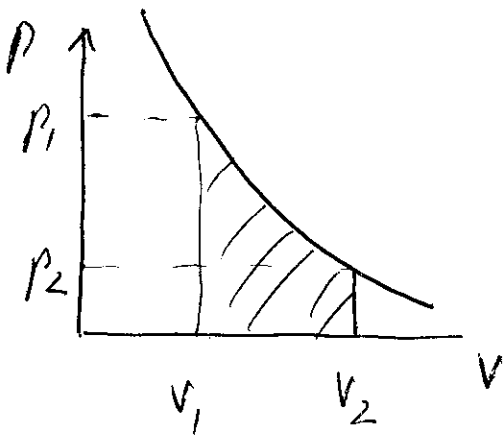
$PV = nRT$ , hence one can rewrite 47  
eq of adiabatic process

a) in terms of  $T$  and  $p$ :  $TP^{\frac{1-\gamma}{\gamma}} = \text{const}$

b) in terms of  $T$  and  $V$ :  $TV^{\gamma-1} = \text{const}$

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Work in adiabatic process



$$PV^{\gamma} = c$$

$$c = P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

$$W = \int_{V_1}^{V_2} P dV = c \int_{V_1}^{V_2} \frac{dV}{V^{\gamma}} = \frac{c}{1-\gamma} (V_2^{1-\gamma} - V_1^{1-\gamma}) =$$

$$= \frac{1}{1-\gamma} (P_2 V_2 - P_1 V_1) = \frac{1}{1-\gamma} (nRT_2 - nRT_1)$$

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In adiabatic process  $dQ = 0 \Rightarrow W = u_1 - u_2$

$$\Rightarrow \boxed{u = \frac{nRT}{\gamma-1}} \Rightarrow \boxed{C_V = \frac{nR}{\gamma-1}}$$