Engineering Thermodynamics

Module -4.1

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Chapter 12: Thermodynamic Property Relations

PARTIAL DERIVATIVES AND ASSOCIATED RELATIONS

derivative of the function at that point defined as

$$\frac{df}{dx} = \lim_{\Delta x \to 0} \frac{\Delta f}{\Delta x} = \lim_{\Delta x \to 0} \frac{f(x+\Delta x) - f(x)}{\Delta x} \qquad \{12.1\}$$

Partial Differential

$$z = z(x,y)$$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \qquad 12.3$$

Now lets write Eq 12.3 as :-

$$dz = M dx + N dy$$

where,

$$M = \left(\frac{\partial z}{\partial x}\right)_y \quad \text{and} \quad N = \left(\frac{\partial z}{\partial y}\right)_x$$

Taking the partial derivative of M with respect to y and of N with respect to x yields :-

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial x \partial y} \quad \text{and} \quad \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial y \partial x}$$

The order of differentiation is immaterial for properties since they are contenuous. point function and have exact differential. Therefore, the two relations above are identical :

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

- The first relation is called the reciprocity relation

$$\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{\left(\partial z/\partial x\right)_y} \qquad (12.8)$$

- The second relation is called the cyclic relation,

$$\left(\frac{\partial x}{\partial y}\right)_z \cdot \left(\frac{\partial y}{\partial z}\right)_x \cdot \left(\frac{\partial z}{\partial x}\right)_y = -1 \qquad (12.9)$$

12-2 . THE MAXWELL RELATIONS

- Two of the Gibbs relations

$$du = T\,ds - p\,dv \qquad (12.10)$$
$$dh = T\,ds + v\,dp \qquad (12.11)$$

- the Helmholtz function a and the Gibbs function g, defined as

$$a = u - Ts \qquad (12.12)$$
$$g = h - Ts \qquad (12.13)$$

Differentiating we get :-

$$da = du - Tds - sdT$$
$$dg = dh - Tds - sdT$$

Simplifying the above relation by using eqn. 12.10 & 12.11, we get two other gibbs relation for simple compressible systems :-

$$da = -sdT - pdv \qquad -12.14$$
$$dg = -sdT + vdp \qquad -12.15$$

A careful examination of the Gibbs relation reveals that they are of the form

$$dz = M\,dx + N\,dy \quad -12.4$$

$$\text{with } \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \quad -12.5$$

Since u, h, a, g are properties, and thus have exact differential. Applying Eq. 12.5 to each of them, we obtain :-

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v \quad -12.16$$

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p \quad 12.17$$

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \quad 12.18$$

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$$

These are called the Maxwell relations ~~(Fig. 12-~~8

12-3 . THE CLAPEYRON EQUATION

During a phase-change process, the pressure is the saturation pressure, which depends on the temperature only and is independent of the specific volume. That is, Psat = f (Tsat)

- Therefore, the partial derivative $(dP/dT)_v$ can be expressed as a total derivative $(dP/dT)_{sat}$, which is the slope of the saturation curve on a P-T diagram at a specified saturation state (Fig. 12.9).
- This slope is independent of the specific volume, and thus it can be treated as a constant during the integration of Eq. 12–18 between two saturation states at the same temperature
- For an isothermal liquid–vapour ~~apor~~ phase-change process, for example, the integration yields

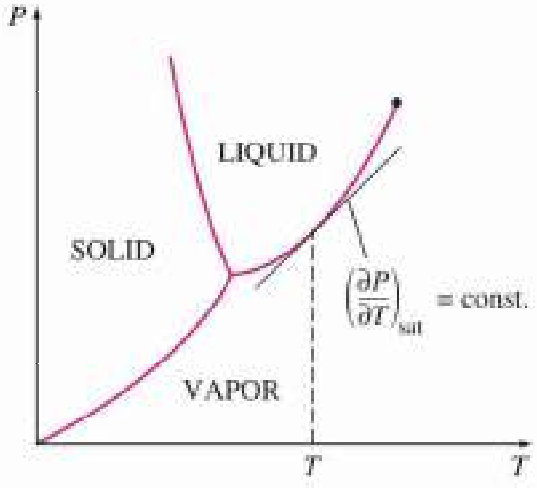


FIGURE 12–9
The slope of the saturation curve on a *P-T* diagram is constant at a constant *T* or *P*.

$$s_g - s_f = \left(\frac{\partial p}{\partial T}\right)_{sat}(v_g - v_f) \quad (12.20)$$

$$\text{or } \left(\frac{dp}{dT}\right)_{sat} = \frac{s_{fg}}{v_f} \quad — \quad (12.21)$$

During this process, the pressure also remains constant. Therefore from eqn 12.11,

$$dh = Tds + \cancel{vdp}^{\to 0}$$

$$\Rightarrow \int_f^g dh = \int_f^g Tds \rightarrow h_{fg} = T s_{fg}$$

Substituting this result in eqn 12.21, we obtain :-

$$\left(\frac{dp}{dT}\right)_{sat} = \frac{h_{fg}}{T v_{fg}} \quad (12.22)$$ ← This is known as Clapeyron eqn.

Clapeyron eqn. is applicable to any phase change process that occurs at constant Temp. and pressure. It can be expressed in general form as :-

$$\left(\frac{dp}{dT}\right)_{sat} = \frac{h_{12}}{T v_{12}}$$

where Subs 1 & 2 indicate two phases.

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$C_v = \left(\frac{\partial u}{\partial T}\right)_v$ or $C_v = \left(\frac{\delta Q}{\delta T}\right)_v$

$du = Tds - pdV$

$\delta Q = du + pdV$

At constant volume :-

$pdV = 0$

$\therefore \delta Q = du \quad \therefore C_v = \left(\frac{\partial u}{\partial T}\right)_v = \left(\frac{\delta Q}{\delta T}\right)_v$

or $\left(\frac{\delta Q}{\delta t}\right)_v = \left(\frac{du}{\delta t}\right)_v = T\left(\frac{ds}{\delta t}\right)_v = C_v$ — (1)

Maxwell Relation :-

$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$ — (2)

$C_p = \left(\frac{\partial h}{\partial T}\right)_p$

$C_p = \lim_{\delta t \to 0} \left(\frac{\delta Q}{\delta T}\right)_p$

$(\delta Q)_p = (dH)_p$

How ?

$\delta Q = du + pdV$

at const P, $dp = 0$

$\therefore \delta Q = du + pdv + vdp \Rightarrow (\delta Q)_p = (dH)_p$ (A)

$= d(u + pv) = dH$

$dH = Tds + vdp$ (Tds relation)

at const p, $dp = 0$

$\therefore (dH)_p = (Tds)_p$ — (B)

from (A) & (B) $\Rightarrow (\delta Q)_p = (dH)_p = (Tds)_p$

$C_p = \lim_{\delta t \to 0} \left(\frac{\delta Q}{\delta T}\right)_p$

$= \lim_{\delta t \to 0} \left(\frac{T ds}{\delta t}\right)_p$ — (3)

$\Rightarrow C_p = T\left(\frac{ds}{dt}\right)_p$

$-\left(\frac{\partial s}{\partial p}\right)_T = \left(\frac{\partial v}{\partial T}\right)_p$ { By Maxwell Relation } (4)

Tds Equations :-

$s = s(T, v)$

$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$

$\therefore Tds = T\left(\frac{\partial s}{\partial T}\right)_v dT + T\left(\frac{\partial s}{\partial v}\right)_T dv$ { from (1) & (2), we get $T\left(\frac{ds}{\delta T}\right)_v = C_v$, $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$

$\therefore \boxed{Tds = C_v dT + T\left(\frac{\partial p}{\partial T}\right)_v dv}$ ← 1st Tds Relation

2nd T-ds Equation :-

$s = s(T, p)$

$ds = \left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial p}\right)_T dp$

$\Rightarrow Tds = T\left(\frac{\partial s}{\partial T}\right)_p dT + T\left(\frac{\partial s}{\partial p}\right)_T dp$

$\Rightarrow Tds = C_p dT - T\left(\frac{\partial v}{\partial T}\right)_p dp$ { from (3) & (4) }

1st Tds Eqn :- $Tds = c_p dT - T\left(\frac{\partial v}{\partial T}\right)_p dp$

2nd Tds Eqn :- $Tds = c_v dT + T\left(\frac{\partial p}{\partial T}\right)_v dv$

Subtracting 1st Tds eqn and 2nd Tds eqn :-

$$0 = (c_p - c_v)dT - T\left(\frac{\partial v}{\partial T}\right)_p dp - T\left(\frac{\partial p}{\partial T}\right)_v dv$$

$$\Rightarrow (c_p - c_v)dT = T\left(\frac{\partial v}{\partial T}\right)_p dp + T\left(\frac{\partial p}{\partial T}\right)_v dv$$

① $$\Rightarrow dT = \frac{T}{c_p - c_v}\cdot\left(\frac{\partial v}{\partial T}\right)_p dp + \frac{T}{c_p - c_v}\cdot\left(\frac{\partial p}{\partial T}\right)_v dv$$

② $T = T(p, v)$

③ $$dT = \left(\frac{\partial T}{\partial p}\right)_v dp + \left(\frac{\partial T}{\partial v}\right)_p dv$$

Comparing ① & ③

$$\left(\frac{\partial T}{\partial p}\right)_v = \frac{T}{c_p - c_v}\cdot\left(\frac{\partial v}{\partial T}\right)_p \quad \text{and} \quad \left(\frac{\partial T}{\partial v}\right)_p = \frac{T}{c_p - c_v}\cdot\left(\frac{\partial p}{\partial T}\right)_v$$

$$\therefore c_p - c_v = T\cdot\left(\frac{\partial v}{\partial T}\right)_p\cdot\left(\frac{\partial p}{\partial T}\right)_v \quad \text{and} \quad c_p - c_v = T\cdot\left(\frac{\partial p}{\partial T}\right)_v\cdot\left(\frac{\partial v}{\partial T}\right)_p$$

From Cyclic Eqn

$$\left(\frac{\partial p}{\partial v}\right)_T\cdot\left(\frac{\partial v}{\partial T}\right)_p\cdot\left(\frac{\partial T}{\partial p}\right)_v = -1$$

$$\text{or } -\left(\frac{\partial p}{\partial v}\right)_T\cdot\left(\frac{\partial v}{\partial T}\right)_p = \left(\frac{\partial p}{\partial T}\right)_v \quad -④$$

$\therefore$ we get

$$c_p - c_v = T\left(\frac{\partial v}{\partial T}\right)_p\cdot\left(\frac{\partial p}{\partial T}\right)_v$$

$$= -T\left(\frac{\partial v}{\partial T}\right)_p\left(\frac{\partial p}{\partial v}\right)_T\left(\frac{\partial v}{\partial T}\right)_p$$

$$\boxed{c_p - c_v = -T\left(\frac{\partial v}{\partial T}\right)_p^2\cdot\left(\frac{\partial p}{\partial v}\right)_T} \quad -⑥$$

$\frac{\partial v}{\partial T} > 0$

$\frac{\partial p}{\partial v} < 0$

RHS is positive

$\therefore c_p - c_v > 0$

or $c_p > c_v$

For ideal gas :- $PV = mRT \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \frac{mR}{P}$ (A)

$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{mRT}{V^2}$ (B)

Putting these results (A & B) in (6), we get $C_P - C_V = mR$

$C_P = C_V$ when $\left(\frac{\partial V}{\partial T}\right)_P = 0$, This happens by water at 4°c.

Volume expansevity $(\beta) = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

Isothermal Compressibility $(K_T) = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

K_S (Isentropic Compressibility. $(K_S) = -\frac{1}{V}\left(\frac{\partial V}{\partial S}\right)_S$

Semester quest :- prove :- $C_P - C_V = \frac{TV\beta^2}{K_T}$

$$T.V.\frac{\beta^2}{K_T} = T.V.\frac{1}{V^2}\left(\frac{\partial V}{\partial T}\right)_P^2 \cdot \frac{1}{-\left(\frac{1}{V}\cdot\frac{\partial V}{\partial P}\right)_T} = -T.\left(\frac{\partial V}{\partial T}\right)_P^2 \cdot \left(\frac{\partial P}{\partial V}\right)_T = C_P - C_V$$

$\therefore C_P - C_V = \frac{T.V\beta^2}{K_T}$

$Tds = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$ — (i)

$Tds = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$ — (ii)

At constant S, (i) & (ii) becomes:

$C_P = T\left(\frac{\partial V}{\partial T}\right)_P \cdot \left(\frac{\partial P}{\partial T}\right)_S$

$C_V = -T\left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial V}{\partial T}\right)_S$

Cyclic eqn $\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$

$\Rightarrow \left(\frac{\partial V}{\partial T}\right)_P \cdot \left(\frac{\partial T}{\partial P}\right)_V = \frac{-1}{\left(\frac{\partial P}{\partial V}\right)_T}$

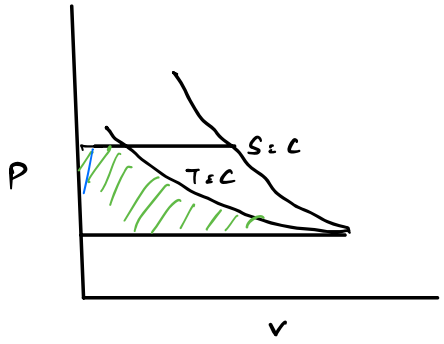
$$\frac{C_P}{C_V} = -\left(\frac{\partial V}{\partial T}\right)_P \cdot \left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial T}{\partial V}\right)_S \cdot \left(\frac{\partial T}{\partial P}\right)_V$$

$$= -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \cdot \left(\frac{\partial P}{\partial V}\right)_S$$

$$= \left(\frac{\partial P}{\partial V}\right)_S \Big/ \left(\frac{\partial P}{\partial V}\right)_T = \frac{\left(\frac{\partial V}{\partial P}\right)_T}{\left(\frac{\partial V}{\partial P}\right)_S} = \frac{K_T}{K_S}$$

$$C_p > C_v \quad \text{or} \quad \left(\frac{\partial P}{\partial v}\right)_S > \left(\frac{\partial P}{\partial v}\right)_T$$

and $\quad K_T > K_S$



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Chapter 9 GAS POWER CYCLES

Introduction

- power cycles
  - the thermodynamic cycles they operate on are called **power cycles**
- engines
  - devices or systems that are used to produce a net power output
- Thermodynamic cycles can also be categorized as **gas cycles** and **vapor cycles**
  - In gas cycles, the working fluid remains in the gaseous phase throughout the entire cycle.
  - whereas in vapor cycles the working fluid exists in the vapor phase during one part of the cycle and in the liquid phase during another part.
- Thermodynamic cycles can be categorized yet another way: **closed and open cycles**
  - closed cycles, the working fluid is returned to the initial state at the end of the cycle and is recirculated.
  - In open cycles, the working fluid is renewed at the end of each cycle instead of being recirculated
  - In automobile engines, the combustion gases are exhausted and replaced by fresh air–fuel mixture at the end of each cycle
  - Heat engines are categorized as internal combustion and external combustion engines,
  - In external combustion engines (such as steam power plants), heat is supplied to the working fluid from an external source such as a furnace
  - internal combustion engines (such as automobile engines), this is done by burning the fuel within the system boundaries

9–1· BASIC CONSIDERATIONS IN THE ANALYSIS OF POWERCYCLES

- The idealizations and simplifications commonly employed in the analysis of power cycles can be summarized as follows
  - The cycle **does not involve any friction**. Therefore, the working fluid does not experience any **pressure drop** as it flows in pipes or devices such as heat exchangers.

- All expansion and compression processes take place in a **quasi-equilibrium manner**.
- The pipes connecting the various components of a system are **well insulated**, and **heat transfer through them is negligible**

- On both the P-v and T-s diagrams, the area enclosed by the process curves of a cycle represents the net work produced during the cycle
  - The **area under the heat addition process** on a T-s diagram is a geometric measure of the total heat supplied during the cycle qin,
  - and the **area under the heat rejection** process is a measure of the total heat rejected qout.
  - The d**ifference between these two** (the area enclosed by the cyclic curve) is the net heat transfer, which is also the net work produced during the cycle
  - Therefore, on a T-s diagram, the ratio of the area enclosed by the cyclic curve to the area under the heat-addition process curve represents the thermal efficiency of the cycle.

9–2 THE CARNOT CYCLE AND TTS VALUE IN ENGINEERING

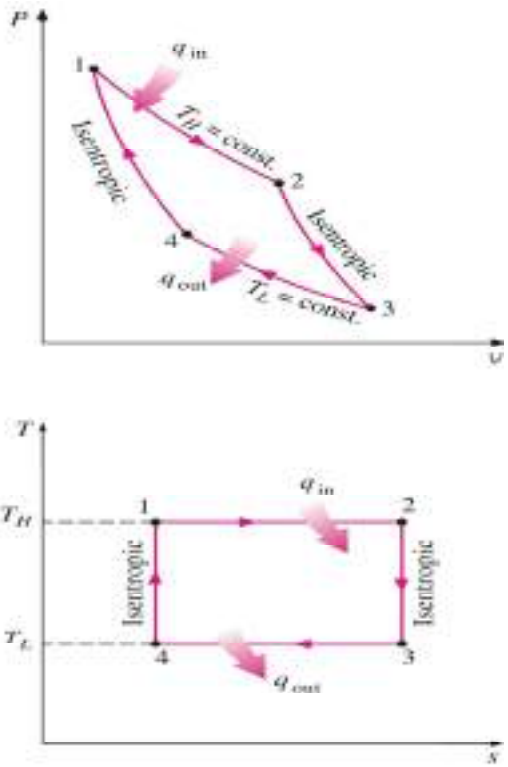


FIGURE 9–6
P-v and *T-s* diagrams of a Carnot cycle.

- **Reversible isothermal heat transfer is very difficult** to achieve in reality because it would require very large heat exchangers and it would take a very long time

$$\eta_{Carnot} = 1 - \frac{T_L}{T_H} \quad \{\text{Ref to fig. 9.6}\} - \underline{\text{Eq. 9.2}}$$

- Thermal efficiency increases with an **increase in the average temperature** at which heat is supplied to the system or with a **decrease in the average temperature at which heat is rejected** from the system.

9–3 AIR–STANDARD ASSUMPTIONS

- In gas
- Spark-ignition engines, diesel engines, and conventional
    - energy is provided by burning a fuel
    - composition of the working fluid changes from air and fuel to combustion products during the course of the cycle
    - Working on an open cycle is the characteristic of all internal combustion engines.
    - Fuel is thrown out of the engine at some point in the cycle (as exhaust gasses
- we utilize the following approximations, commonly known as the air-standard assumptions
    - The **working fluid is air**, which continuously circulates in a closed loop and always behaves as an ideal gas
    - All the processes that make up the cycle are **internally reversible**
    - The combustion process is replaced by a **heat-addition process from an external source** (Fig. 9–9)
    - The e**xhaust process is replaced by a heat-rejection process** that restores the working fluid to its initial state
    - **air has constant specific heats** whose values are determined at room temperature (25°C, or 77°F).
        - When this assumption is utilized, the air-standard assumptions are called the **cold-air-standard assumptions**
    - A cycle for which the air-standard assumptions are applicable is frequently referred to as an air-standard cycle.

9–4 AN OVERVIEW OF RECIPROCATING ENGINES

- The piston reciprocates in the cylinder between two fixed positions called the top dead center (TDC) and the bottom dead center (BDC)
- distance between the TDC (is called the **stroke of the engine**
- The diameter of the piston is called the **bore**
- Working:
  - air or air–fuel mixture is drawn into the cylinder through the intake valve
  - the combustion products are expelled from the cylinder through the exhaust valve
- **clearance volume**
  - The minimum volume formed in the cylinder when the piston is at TDC is called the clearance volume (Fig. 9–11
- displacement volume
  - The volume displaced by the piston as it moves between TDC and BDC is called the **displacement volume**.
- compression ratio r
  - The ratio of the maximum volume formed in the cylinder to the minimum (clearance) volume is called the **compression ratio r** of the engine

$$r = \frac{V_{max}}{V_{min}} = \frac{V_{BDC}}{V_{TDC}} \quad (9.3)$$

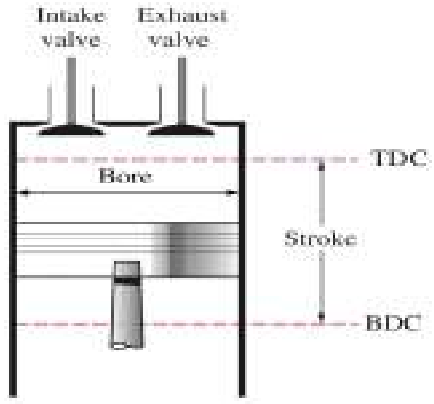


FIGURE 9–10
Nomenclature for reciprocating engines.

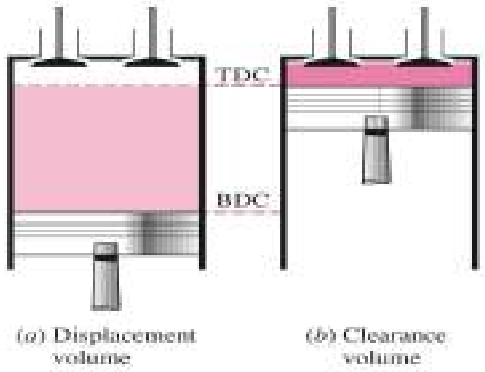


FIGURE 9–11
Displacement and clearance volumes of a reciprocating engine.

- **mean effective pressure** (MEP)
  - It is a fictitious pressure that, if it acted on the piston during the entire power stroke, would produce the same amount of net work as that produced during the actual cycle

$$W_{net} = MEP \times \text{piston area} \times \text{stroke} = MEP \times \text{Displacement Volume}$$

or

$$MEP = \frac{W_{net}}{V_{max} - V_{min}} = \frac{W_{net}}{V_{max} - V_{min}} \quad \{kPa\} \quad (9.4)$$

- Reciprocating engines are classified as spark-ignition (SI) engines or compression-ignition (CI) engines
  - In SI engines, the combustion of the air–fuel mixture is initiated by a spark plug
  - CI engines, the air–fuel mixture is self-ignited as a result of compressing the mixture above its self ignition temperature.

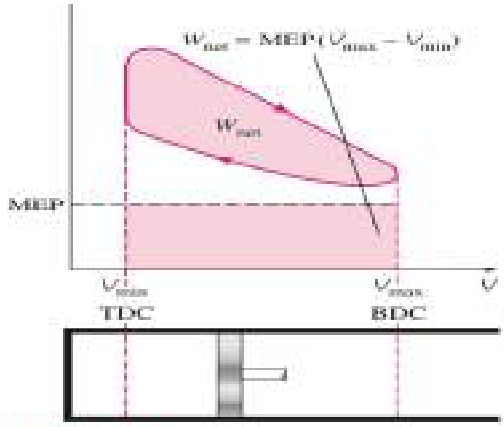


FIGURE 9–12
The net work output of a cycle is equivalent to the product of the mean effective pressure and the displacement volume.