

$$P_R = \frac{P}{P_{cr}}$$

Reduced
pressure

$$T_R = \frac{T}{T_{cr}}$$

Reduced
temperature

$$v_R = \frac{v_{actual}}{RT_{cr}/P_{cr}}$$

Pseudo-reduced
specific volume

$$\left. \begin{aligned} P_R &= \frac{P}{P_{cr}} \\ v_R &= \frac{v}{RT_{cr}/P_{cr}} \end{aligned} \right\} Z = \dots \quad (\text{Fig. A-15})$$

Z can also be determined from
a knowledge of P_R and v_R .

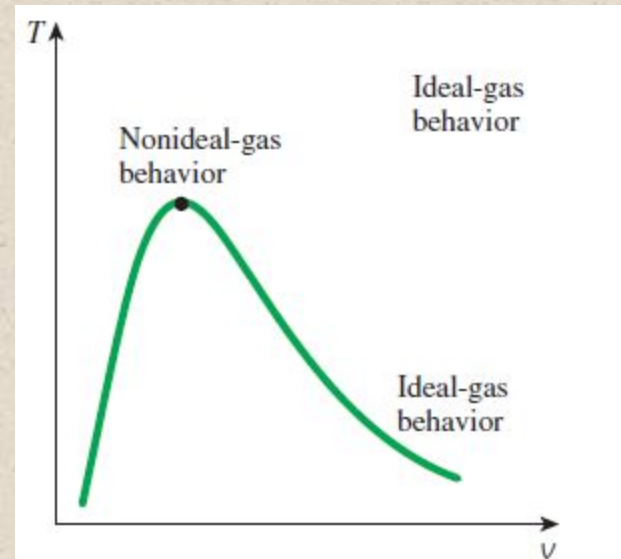
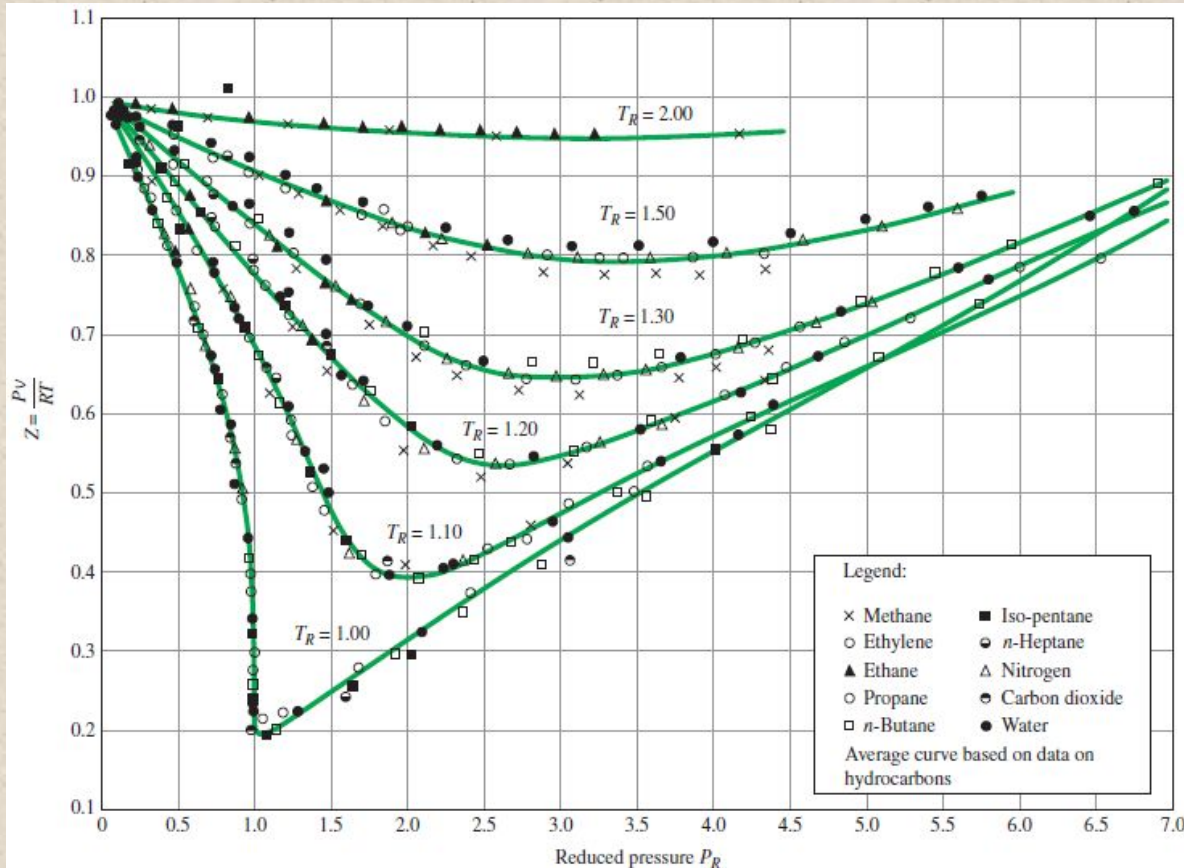
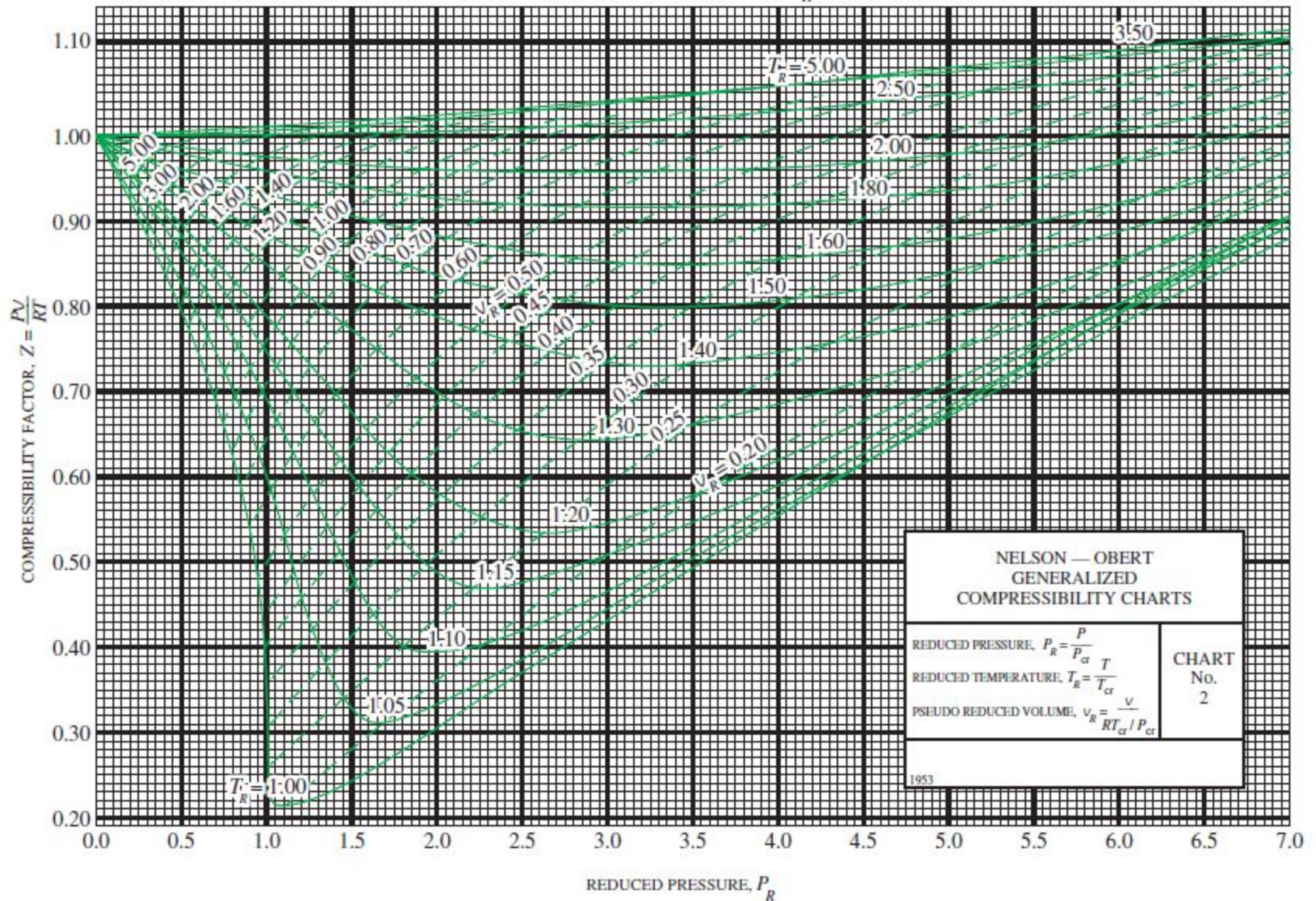


FIGURE 3-49

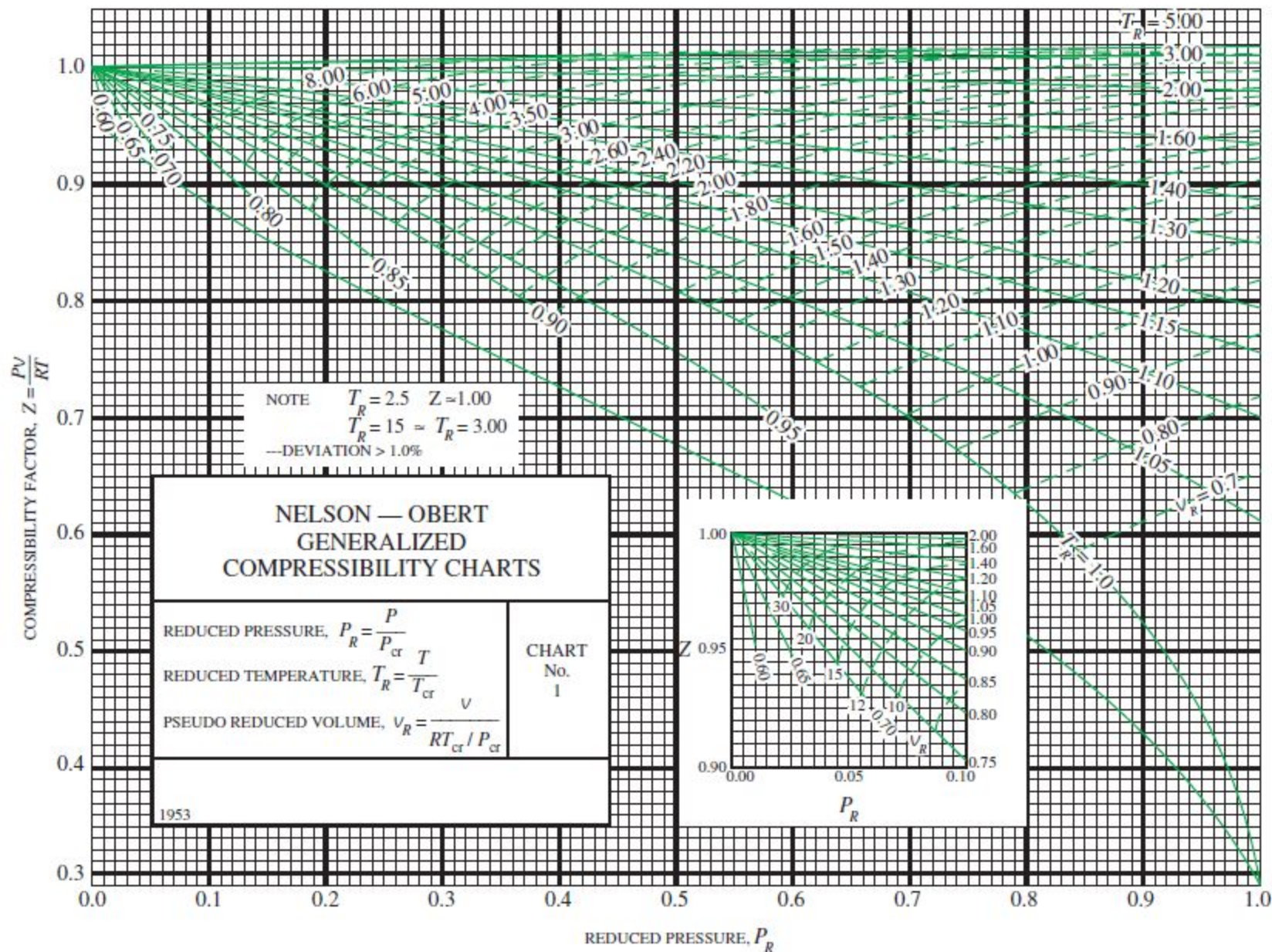
Gases deviate from the ideal-gas behavior the most in the neighborhood of the critical point.

Comparison of Z factors for various gases.

(b) Intermediate pressures, $0 < P_R < 7$



(a) Low pressures, $0 < P_R < 1.0$



OTHER EQUATIONS OF STATE

Several equations have been proposed to represent the P - v - T behavior of substances accurately over a larger region with no limitations.

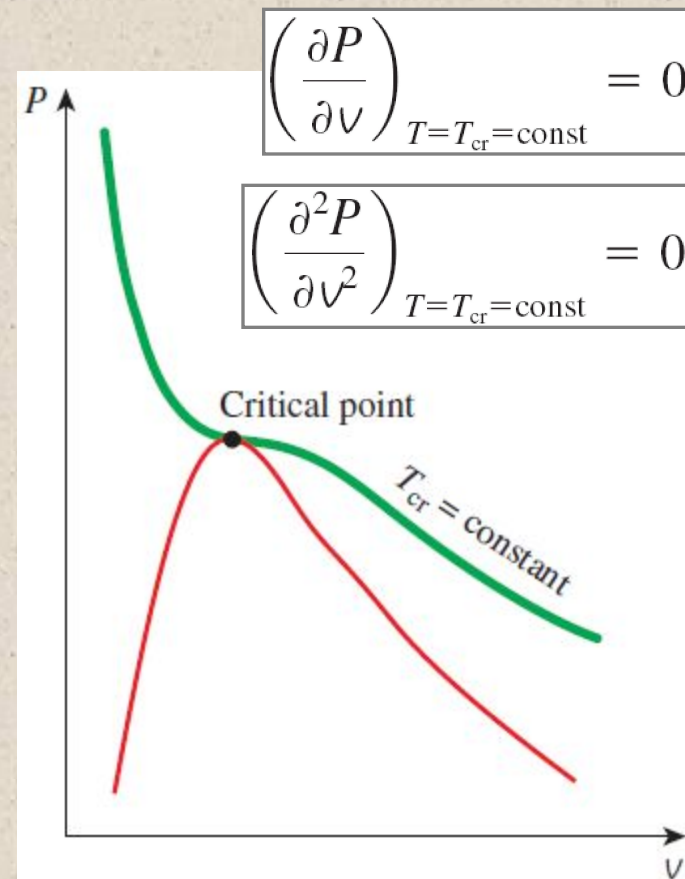
Van der Waals Equation of State

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

$$a = \frac{27R^2T_{\text{cr}}^2}{64P_{\text{cr}}} \quad b = \frac{RT_{\text{cr}}}{8P_{\text{cr}}}$$

This model includes two effects not considered in the ideal-gas model: *the intermolecular attraction forces and the volume occupied by the molecules themselves*. The accuracy of the van der Waals equation of state is often inadequate.

Critical isotherm of a pure substance has an inflection point at the critical state.



van der Waals
Berthelet
Redlich-Kwang
Beattie-Bridgeman
Benedict-Webb-Rubin
Strobridge
Virial

Beattie-Bridgeman Equation of State

$$P = \frac{R_u T}{\bar{V}^2} \left(1 - \frac{c}{\bar{V} T^3} \right) (\bar{V} + B) - \frac{A}{\bar{V}^2}$$

$$A = A_0 \left(1 - \frac{a}{\bar{V}} \right) \quad B = B_0 \left(1 - \frac{b}{\bar{V}} \right)$$

The constants are given in Table 3–4 for various substances. It is known to be reasonably accurate for densities up to about $0.8\rho_{\text{cr}}$.

Benedict-Webb-Rubin Equation of State

$$P = \frac{R_u T}{\bar{V}} + \left(B_0 R_u T - A_0 - \frac{C_0}{T^2} \right) \frac{1}{\bar{V}^2} + \frac{b R_u T - a}{\bar{V}^3} + \frac{a\alpha}{\bar{V}^6} + \frac{c}{\bar{V}^3 T^2} \left(1 + \frac{\gamma}{\bar{V}^2} \right) e^{-\gamma/\bar{V}^2}$$

The constants are given in Table 3–4. This equation can handle substances at densities up to about $2.5 \rho_{\text{cr}}$.

Virial Equation of State

$$P = \frac{RT}{V} + \frac{a(T)}{V^2} + \frac{b(T)}{V^3} + \frac{c(T)}{V^4} + \frac{d(T)}{V^5} + \dots$$

The coefficients $a(T)$, $b(T)$, $c(T)$, and so on, that are functions of temperature alone are called *virial coefficients*.

TABLE 3-4

Constants that appear in the Beattie-Bridgeman and the Benedict-Webb-Rubin equations of state

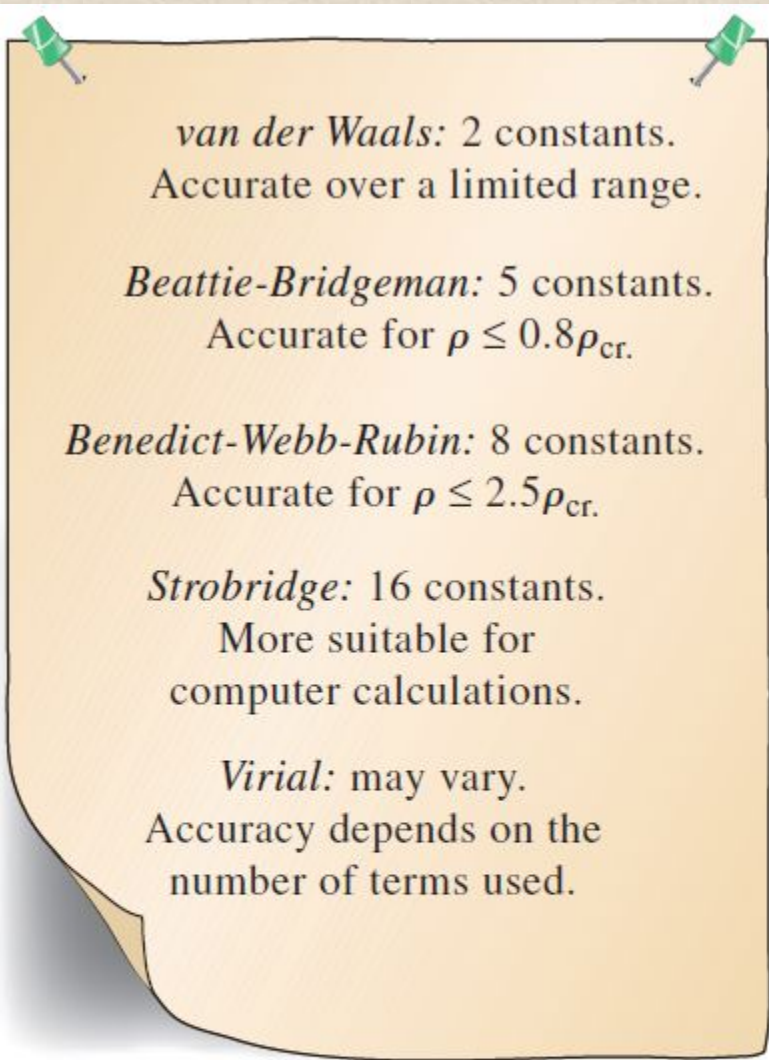
(a) When P is in kPa, \bar{v} is in m^3/kmol , T is in K, and $R_u = 8.314 \text{ kPa}\cdot\text{m}^3/\text{kmol}\cdot\text{K}$, the five constants in the Beattie-Bridgeman equation are as follows:

Gas	A_0	a	B_0	b	c
Air	131.8441	0.01931	0.04611	-0.001101	4.34×10^4
Argon, Ar	130.7802	0.02328	0.03931	0.0	5.99×10^4
Carbon dioxide, CO_2	507.2836	0.07132	0.10476	0.07235	6.60×10^5
Helium, He	2.1886	0.05984	0.01400	0.0	40
Hydrogen, H_2	20.0117	-0.00506	0.02096	-0.04359	504
Nitrogen, N_2	136.2315	0.02617	0.05046	-0.00691	4.20×10^4
Oxygen, O_2	151.0857	0.02562	0.04624	0.004208	4.80×10^4

Source: Gordon J. Van Wylen and Richard E. Sonntag, *Fundamentals of Classical Thermodynamics*, English/SI Version, 3rd ed. (New York: John Wiley & Sons, 1986), p. 46, table 3.3.

(b) When P is in kPa, \bar{v} is in m^3/kmol , T is in K, and $R_u = 8.314 \text{ kPa}\cdot\text{m}^3/\text{kmol}\cdot\text{K}$, the eight constants in the Benedict-Webb-Rubin equation are as follows:

Gas	a	A_0	b	B_0	c	C_0	α	γ
n-Butane, C_4H_{10}	190.68	1021.6	0.039998	0.12436	3.205×10^7	1.006×10^8	1.101×10^{-3}	0.0340
Carbon dioxide, CO_2	13.86	277.30	0.007210	0.04991	1.511×10^6	1.404×10^7	8.470×10^{-5}	0.00539
Carbon monoxide, CO	3.71	135.87	0.002632	0.05454	1.054×10^5	8.673×10^5	1.350×10^{-4}	0.0060
Methane, CH_4	5.00	187.91	0.003380	0.04260	2.578×10^5	2.286×10^6	1.244×10^{-4}	0.0060
Nitrogen, N_2	2.54	106.73	0.002328	0.04074	7.379×10^4	8.164×10^5	1.272×10^{-4}	0.0053



van der Waals: 2 constants.
Accurate over a limited range.

Beattie-Bridgeman: 5 constants.
Accurate for $\rho \leq 0.8\rho_{\text{cr}}$.

Benedict-Webb-Rubin: 8 constants.
Accurate for $\rho \leq 2.5\rho_{\text{cr}}$.

Strobridge: 16 constants.
More suitable for
computer calculations.

Virial: may vary.
Accuracy depends on the
number of terms used.

FIGURE 3–55

Complex equations of state represent the P - v - T behavior of gases more accurately over a wider range.

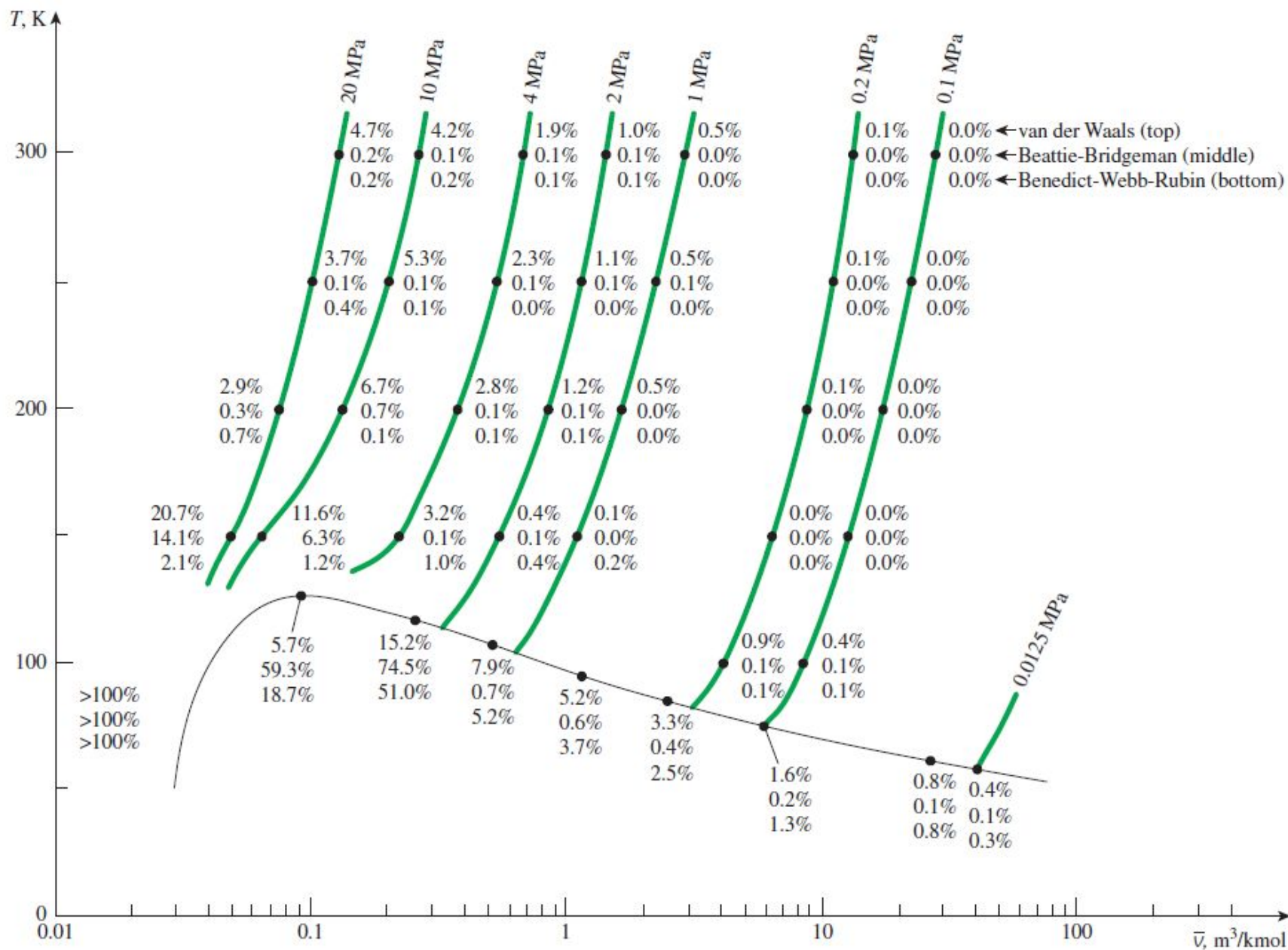


FIGURE 3-56

Percentage of error involved in various equations of state for nitrogen (% error = $[(v_{\text{table}} - v_{\text{equation}})/v_{\text{table}}] \times 100$).

Summary

- Pure substance
- Phases of a pure substance
- Phase-change processes of pure substances
 - ✓ Compressed liquid, Saturated liquid, Saturated vapor, Superheated vapor
 - ✓ Saturation temperature and Saturation pressure
- Property diagrams for phase change processes
 - ✓ The T - v diagram, The P - v diagram, The P - T diagram, The P - v - T surface
- Property tables
 - ✓ Enthalpy
 - ✓ Saturated liquid, saturated vapor, Saturated liquid vapor mixture, Superheated vapor, compressed liquid
 - ✓ Reference state and reference values
- The ideal gas equation of state
 - ✓ Is water vapor an ideal gas?
- Compressibility factor
- Other equations of state
 - ✓ van der Waals Equation of State, Beattie-Bridgeman Equation of State
 - ✓ Benedict-Webb-Rubin Equation of State, Virial Equation of State

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CHAPTER 4

ENERGY ANALYSIS OF CLOSED SYSTEMS

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Objectives

- Examine the moving boundary work or $P dV$ work commonly encountered in reciprocating devices such as automotive engines and compressors.
- Identify the first law of thermodynamics as simply a statement of the conservation of energy principle for closed (fixed mass) systems.
- Develop the general energy balance applied to closed systems.
- Define the specific heat at constant volume and the specific heat at constant pressure.
- Relate the specific heats to the calculation of the changes in internal energy and enthalpy of ideal gases.
- Describe incompressible substances and determine the changes in their internal energy and enthalpy.
- Solve energy balance problems for closed (fixed mass) systems that involve heat and work interactions for general pure substances, ideal gases, and incompressible substances.

BOUNDARY WORK

Moving boundary work ($P dV$ work):

The expansion and compression work in a piston-cylinder device.

$$\delta W_b = F ds = PA ds = P dV$$

$$W_b = \int_1^2 P dV \quad (\text{kJ})$$

Quasi-equilibrium process:

A process during which the system remains nearly in equilibrium at all times.

W_b is positive \rightarrow for expansion

W_b is negative \rightarrow for compression

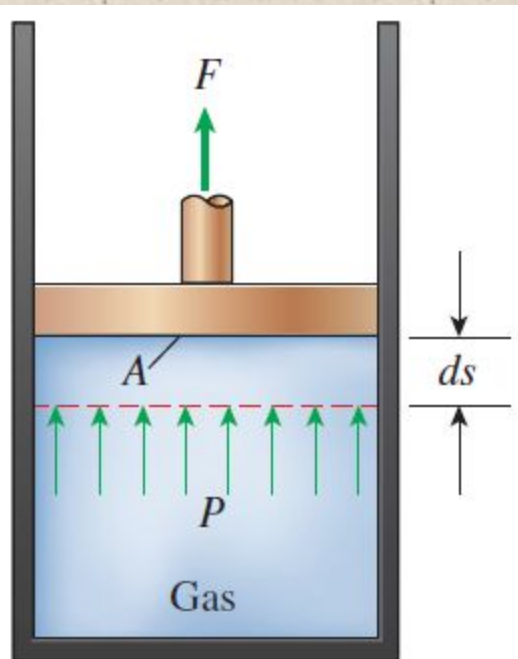
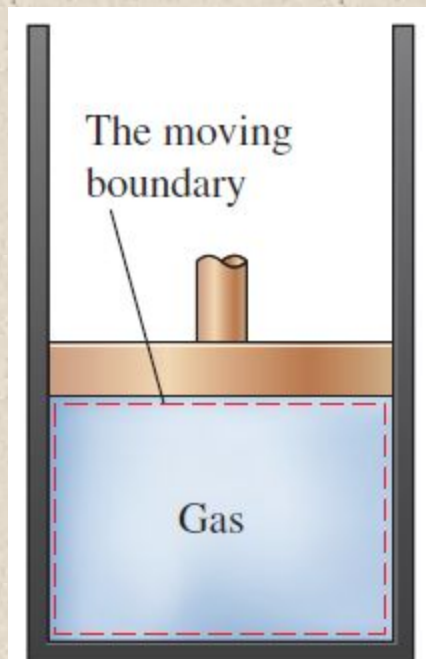


FIGURE 4-1

The work associated with a moving boundary is called *boundary work*.

FIGURE 4-2

A gas does a differential amount of work δW_b as it forces the piston to move by a differential amount ds .



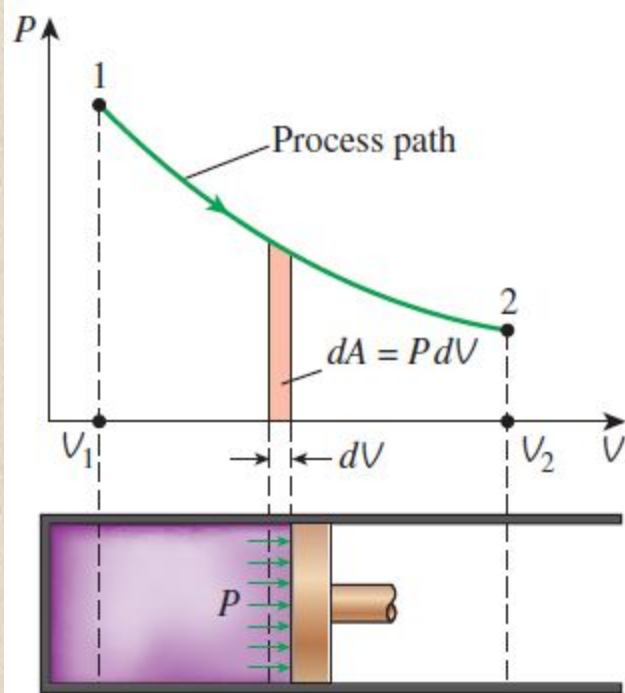


FIGURE 4-3

The area under the process curve on a P - V diagram represents the boundary work.

$$\text{Area} = A = \int_1^2 dA = \int_1^2 P dV$$

The area under the process curve on a P - V diagram is equal, in magnitude, to the work done during a quasi-equilibrium expansion or compression process of a closed system.

The boundary work done during a process depends on the path followed as well as the end states.

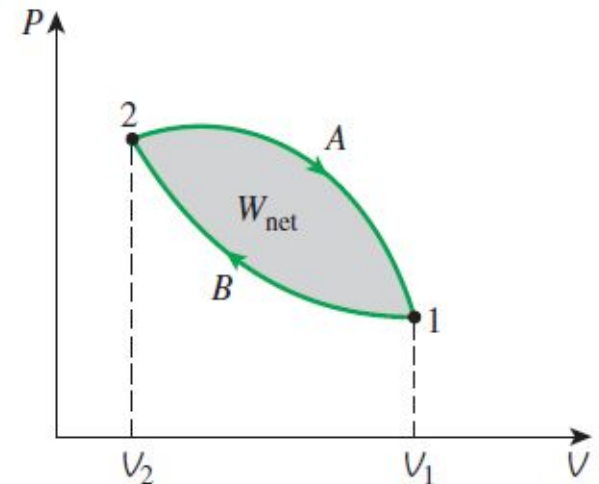
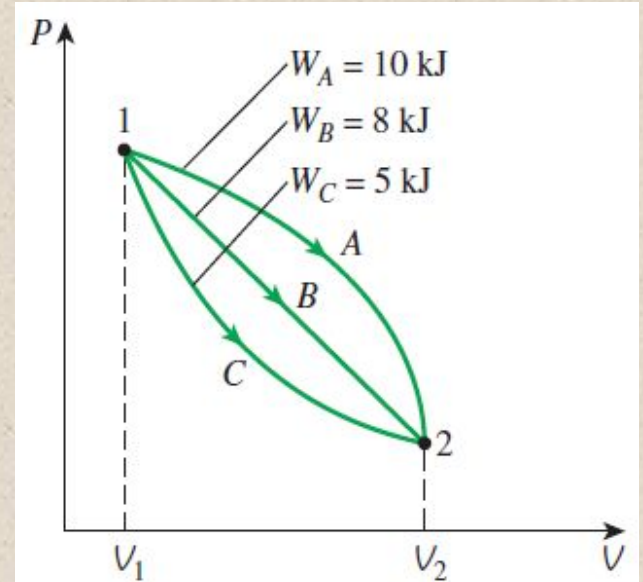
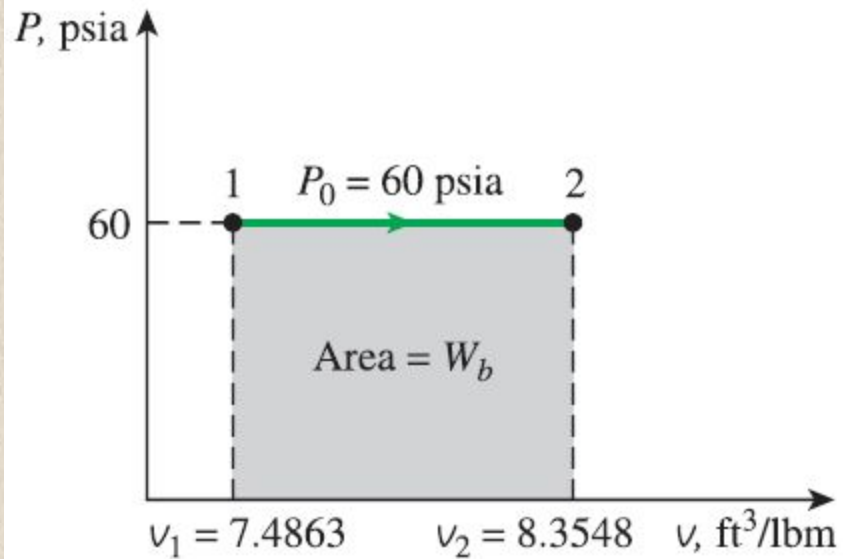
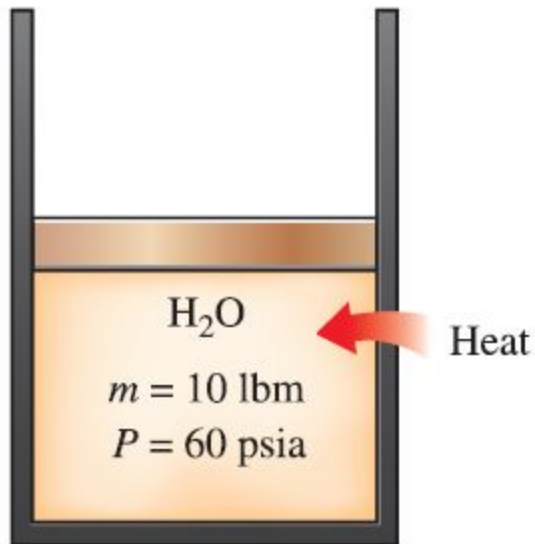


FIGURE 4-5

The net work done during a cycle is the difference between the work done by the system and the work done on the system.

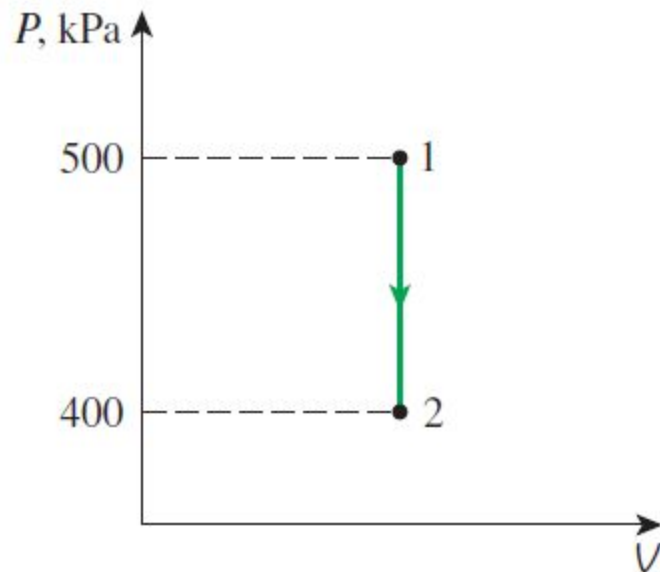
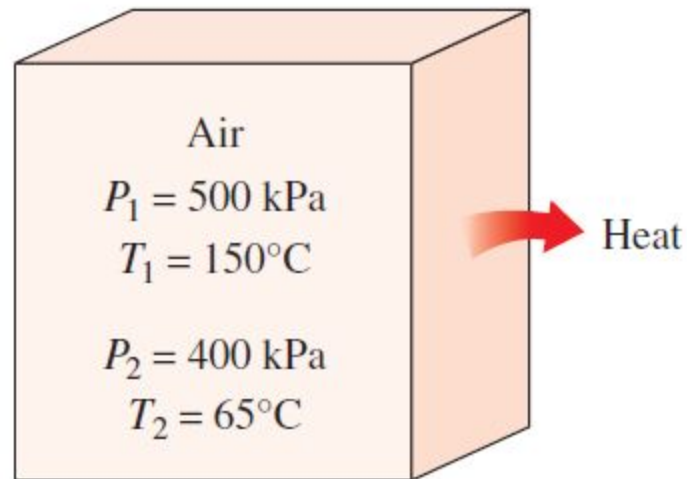
Boundary Work for a Constant-Pressure Process



$$W_b = \int_1^2 P dV = P_0 \int_1^2 dV = P_0(V_2 - V_1)$$

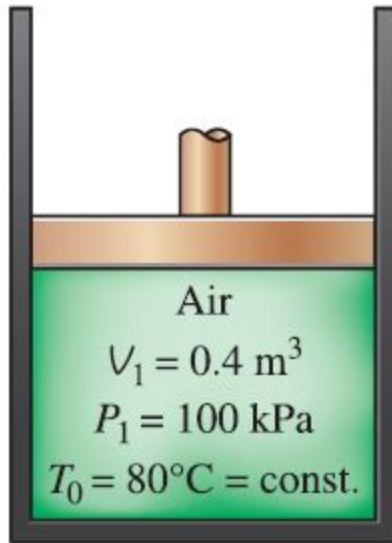
$$W_b = mP_0(v_2 - v_1)$$

Boundary Work for a Constant-Volume Process



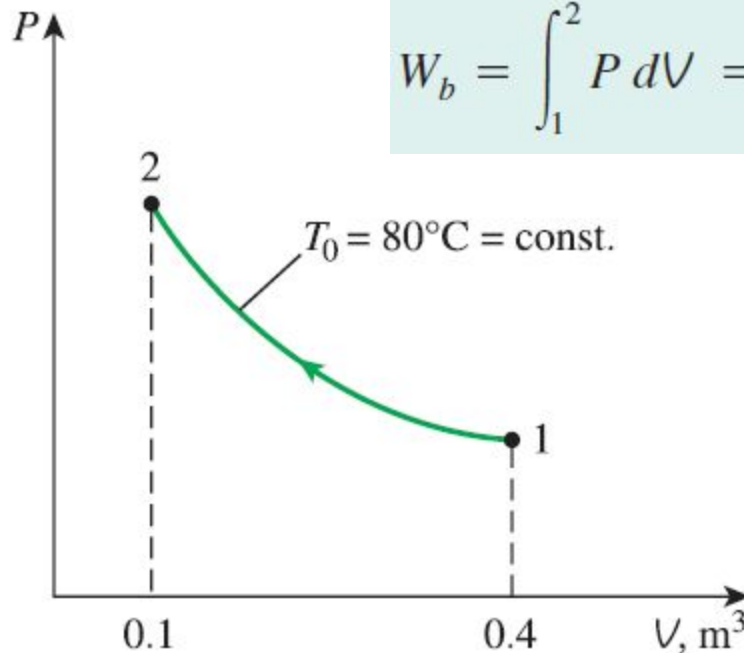
What is the boundary work for a constant-volume process?

Boundary Work for an Isothermal Compression Process



$$W_b = \int_1^2 P dV = \int_1^2 C V^{-1} dV = P V \ln\left(\frac{V_2}{V_1}\right)$$

$$P V = m R T_0 = C \quad \text{or} \quad P = \frac{C}{V}$$



$$W_b = \int_1^2 P dV = \int_1^2 \frac{C}{V} dV = C \int_1^2 \frac{dV}{V} = C \ln \frac{V_2}{V_1} = P_1 V_1 \ln \frac{V_2}{V_1}$$

Boundary Work for a Polytropic Process

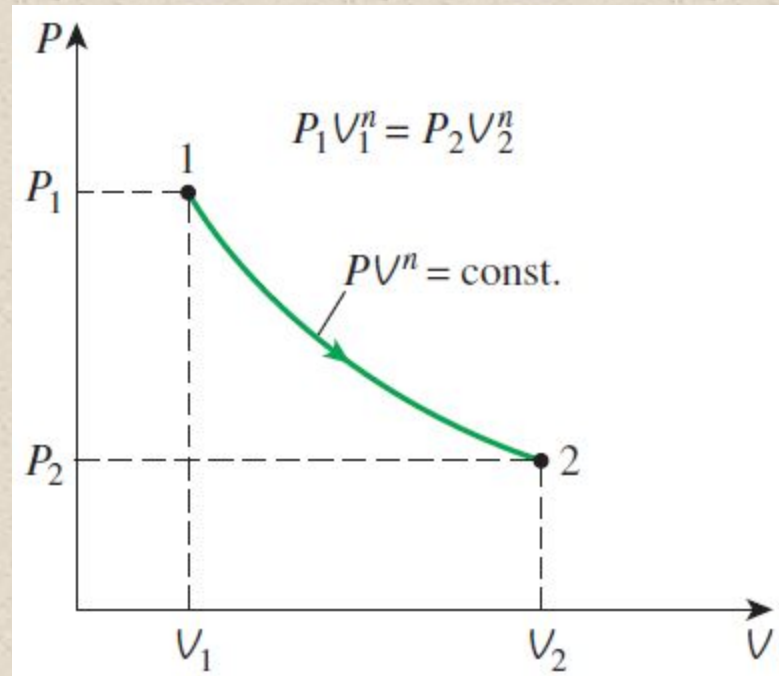
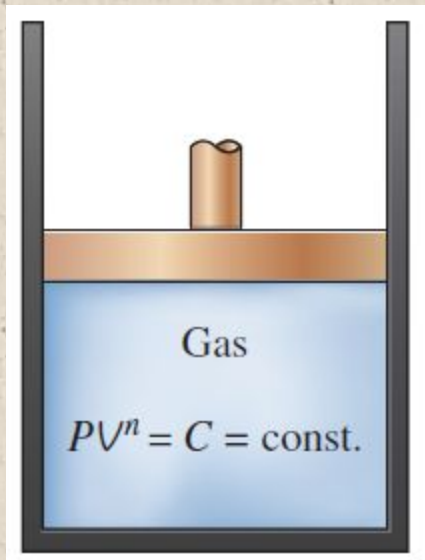
$$PV^n = C$$

$$P = CV^{-n}$$

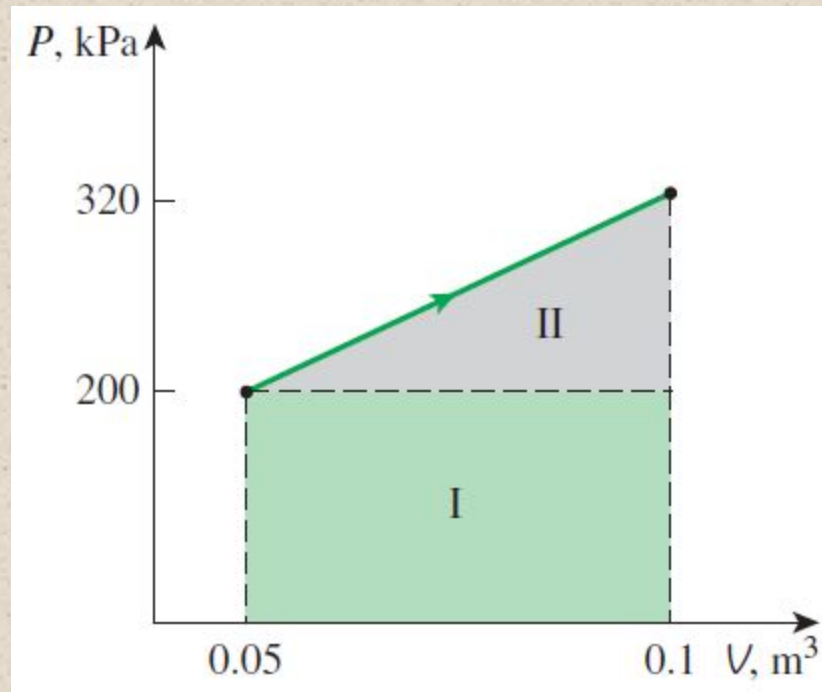
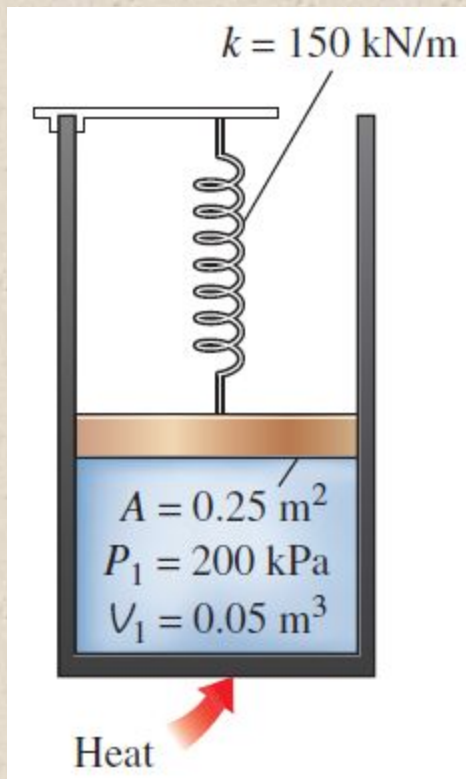
$$W_b = \int_1^2 P dV = \int_1^2 CV^{-n} dV = C \frac{V_2^{-n+1} - V_1^{-n+1}}{-n + 1} = \frac{P_2 V_2 - P_1 V_1}{1 - n}$$

$$W_b = \frac{mR(T_2 - T_1)}{1 - n}$$

For ideal gas



Expansion of a Gas against a Spring



ENERGY BALANCE FOR CLOSED SYSTEMS

$$\underbrace{E_{\text{in}} - E_{\text{out}}}_{\text{Net energy transfer by heat, work, and mass}} = \underbrace{\Delta E_{\text{system}}}_{\text{Change in internal, kinetic, potential, etc., energies}} \quad (\text{kJ})$$

Energy balance for any system undergoing any process

$$\underbrace{\dot{E}_{\text{in}} - \dot{E}_{\text{out}}}_{\text{Rate of net energy transfer by heat, work, and mass}} = \underbrace{dE_{\text{system}}/dt}_{\text{Rate of change in internal, kinetic, potential, etc., energies}} \quad (\text{kW})$$

Energy balance in the rate form

The total quantities are related to the quantities per unit time is

$$Q = \dot{Q} \Delta t, \quad W = \dot{W} \Delta t, \quad \text{and} \quad \Delta E = (dE/dt) \Delta t \quad (\text{kJ})$$

$$e_{\text{in}} - e_{\text{out}} = \Delta e_{\text{system}} \quad (\text{kJ/kg})$$

Energy balance per unit mass basis

$$\delta E_{\text{in}} - \delta E_{\text{out}} = dE_{\text{system}} \quad \text{or} \quad \delta e_{\text{in}} - \delta e_{\text{out}} = de_{\text{system}}$$

Energy balance in differential form

$$W_{\text{net,out}} = Q_{\text{net,in}} \quad \text{or} \quad \dot{W}_{\text{net,out}} = \dot{Q}_{\text{net,in}}$$

Energy balance for a cycle

$$Q_{\text{net,in}} - W_{\text{net,out}} = \Delta E_{\text{system}} \quad \text{or} \quad Q - W = \Delta E$$

$$Q = Q_{\text{net,in}} = Q_{\text{in}} - Q_{\text{out}}$$

$$W = W_{\text{net,out}} = W_{\text{out}} - W_{\text{in}}$$

Energy balance when sign convention is used: (i.e., heat input and work output are positive; heat output and work input are negative).

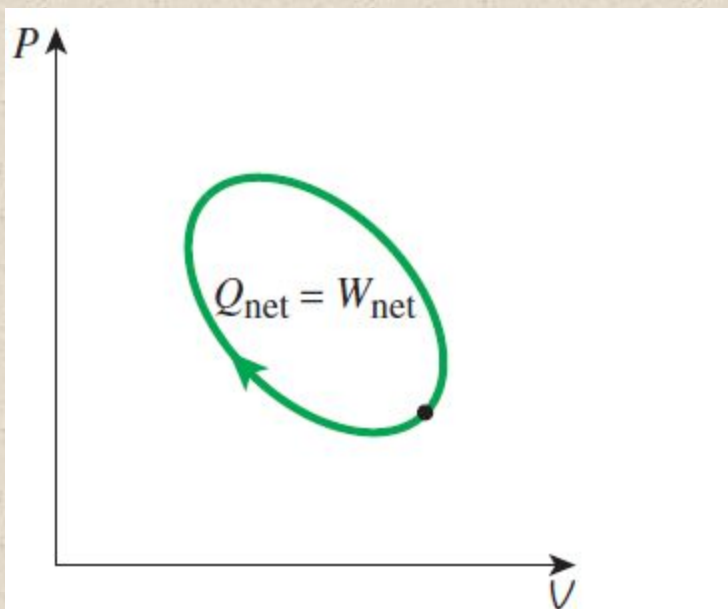


FIGURE 4-11

For a cycle $\Delta E = 0$, thus $Q = W$.

General $Q - W = \Delta E$

Stationary systems $Q - W = \Delta U$

Per unit mass $q - w = \Delta e$

Differential form $\delta q - \delta w = de$

Various forms of the first-law relation for closed systems when sign convention is used.

The first law cannot be proven mathematically, but no process in nature is known to have violated the first law, and this should be taken as sufficient proof.