

CH365 Chemical Engineering Thermodynamics

Lesson 11

Application of the 1st Law to Ideal Gases

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General Comments

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- Heat and work necessary for industrial process calculations are calculated using the equations from Chapter 2.
 - These equations require enthalpy and internal energy from volume as a function of temperature and pressure.
 - These PVT relationships are expressed mathematically as equations of state. The simplest realistic EOS is the ideal gas law, $PV = RT$.
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- First, look at phase rule. L10
 - Second, we will describe the general P-V-T behavior of pure fluids. L10
 - Third, we will discuss the ideal gas behavior in detail. L11
- Hidden Content – Take Notes
- Finally, we will discuss more realistic equations, wrapping up with generalized correlations. L12-L14

Property Relations for the Ideal Gas

Lesson 6, result of the Joule experiment.

$$C_V \equiv \left(\frac{\partial U}{\partial T} \right)_V = \frac{dU(T)}{dT} = C_V(T) \quad (3.9) \text{ \& (2.15)}$$

functions of T only

In the absence of molecular interactions, enthalpy depends on T only

$$H \equiv U + PV = U + RT = H(T) \quad (3.10), \text{ from (2.10) \& (3.7)}$$

$$C_P \equiv \left(\frac{\partial H}{\partial T} \right)_P = \frac{dH(T)}{dT} = C_P(T) \quad (3.11) \text{ \& (2.19)}$$

Also function of T only

$$\begin{aligned} H &= U + RT \\ \frac{dH}{dT} &= \frac{d}{dT}(U + RT) \\ &= \frac{dU}{dT} + \frac{d(RT)}{dT} \\ &= \frac{dU}{dT} + R \end{aligned}$$

$$C_P = \frac{dH}{dT} = \frac{dU}{dT} + R = C_V + R$$

$$R = C_P - C_V \quad (3.12)$$

$dU = C_V dT$ <p>(3.13a)</p>	$\Delta U = \int_{T_{\text{REF}}}^T C_V dT$ <p>(3.13b)</p>
$dH = C_P dT$ <p>(3.14a)</p>	$\Delta H = \int_{T_{\text{REF}}}^T C_P dT$ <p>(3.14b)</p>

Functions of T only

Q and W Equations for Process Calculations

$$dU = dQ + dW \quad \longleftrightarrow \quad dQ = dU - dW$$

$dU = C_V dT$	$dQ = C_V dT + PdV$ (3.15)	$dW = -PdV$ (1.3)
$P = \frac{RT}{V} = P(T, V)$	$dQ = C_V dT + RT \frac{dV}{V}$ (3.16)	$dW = -RT \frac{dV}{V}$ (3.17)
$V = \frac{RT}{P} = V(T, P)$	$dQ = C_P dT - RT \frac{dP}{P}$ (3.18)	$dW = -RdT + RT \frac{dP}{P}$ (3.19)
$T = \frac{PV}{R} = T(P, V)$	$dQ = \frac{C_V}{R} VdP + \frac{C_P}{R} PdV$	$dW = -PdV$ (1.3)

Derived on next slide.

Each of these can be derived as shown on next slide.

Where did Slide 4 Come From?

Example (row 3):

Using $V = \frac{RT}{P}$ show that $dW = -RdT + RT \frac{dP}{P}$ and $dQ = C_p dT - RT \frac{dP}{P}$

(3.19) (3.18)

$$dV = \left(\frac{\partial V}{\partial P} \right)_T dP + \left(\frac{\partial V}{\partial T} \right)_P dT \quad (3.2, L10)$$

$$V = \frac{RT}{P} \quad \Rightarrow \quad dV = -\frac{RT}{P^2} dP + \frac{R}{P} dT$$

$$dW = -P dV \quad \Rightarrow \quad dW = -P \left(-\frac{RT}{P^2} dP + \frac{R}{P} dT \right) = \frac{RT}{P} dP - R dT \quad \checkmark$$

$$dU = dQ + dW \quad \Rightarrow \quad dQ = dU - dW$$

$$dU = C_V dT \quad (3.13a)$$

$$C_p = C_V + R \quad (3.12)$$

$$dQ = C_V dT + R dT - \frac{RT}{P} dP$$

$$dQ = (C_V + R) dT - \frac{RT}{P} dP$$


$$dQ = C_p dT - RT \frac{dP}{P} \quad \checkmark$$

Isothermal Process

(Q, W, ΔH , and ΔU with no change in temperature)

$$\Delta U = \Delta H = 0 \quad (3.13b) \text{ \& } (3.14b)$$


$$Q = RT \ln \left(\frac{V_2}{V_1} \right) = -RT \ln \left(\frac{P_2}{P_1} \right) \quad \begin{array}{l} (3.20), \text{ from } (3.16) \text{ \& } (3.18) \\ \text{(rows 2 and 3)} \end{array} \quad \begin{array}{l} C_V dT = 0 \\ C_P dT = 0 \end{array}$$

 molar heat (energy per mole)

From 2.3 with $\Delta U=0$

$$Q = -W$$

$$W = -RT \ln \left(\frac{V_2}{V_1} \right) = RT \ln \left(\frac{P_2}{P_1} \right) \quad \begin{array}{l} (3.20), \text{ from } (3.17) \text{ \& } (3.19) \\ \text{(rows 2 and 3)} \end{array} \quad R dT = 0$$

 molar work (energy per mole)

$$Q = -W = RT \ln \left(\frac{V_2}{V_1} \right) = -RT \ln \left(\frac{P_2}{P_1} \right) \quad \begin{array}{l} \text{(Constant T)} \\ (3.20) \end{array}$$

Isobaric Process

(No change in pressure)

$$\Delta U = \int C_V dT \quad (3.13b)$$

and

$$\Delta H = \int C_P dT \quad (3.14b)$$

C_P and C_V in
Appendix C or
assumed constant

$$dQ = C_P dT - RT \frac{dP}{P} \quad \text{and} \quad dW = -RdT + RT \frac{dP}{P} \quad (3.18) \text{ and } (3.19)$$

(rows 2 and 3)

$$Q = \int C_P dT \quad \text{and} \quad W = -R(T_2 - T_1)$$

$$Q = \Delta H = \int C_P dT \quad (\text{Constant } P)$$

(3.21)

Isochoric Process

(No change in volume)

$$\Delta U = \int C_V dT \quad \text{and} \quad \Delta H = \int C_P dT \quad (3.13b) \text{ and } (3.14b)$$

$$dQ = C_V dT + RT \frac{dV}{V} \quad \text{and} \quad W = - \int P dV = 0 \quad (3.16) \text{ and } (1.2)$$

(Note: In the original image, blue diagonal lines are drawn through the $\frac{dV}{V}$ term in the first equation and the dV term in the second equation, with $dV=0$ written above each line.)

$$Q = \int C_V dT$$

$$Q = \Delta U = \int C_V dT \quad \text{(Constant V)}$$

(3.22)

Adiabatic Process

$$dQ = 0$$

C_V, C_P assumed constant

(any of the dQ equations from slide 4)

Mechanically reversible adiabatic expansion or compression

$$(3.16) \quad 0 = C_V dT + RT \frac{dV}{V} \quad \Rightarrow \quad \frac{dT}{T} = -\frac{R}{C_V} \frac{dV}{V} \quad \Rightarrow \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{R/C_V}$$

$$(3.18) \quad 0 = C_P dT - RT \frac{dP}{P} \quad \Rightarrow \quad \frac{dT}{T} = \frac{R}{C_P} \frac{dP}{P} \quad \Rightarrow \quad \frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{R/C_P}$$

$$\text{(un-numbered)} \quad 0 = \frac{C_V}{R} V dP + \frac{C_P}{R} P dV \quad \Rightarrow \quad \frac{dP}{P} = -\frac{C_P}{C_V} \frac{dV}{V} \quad \Rightarrow \quad \frac{P_2}{P_1} = \left(\frac{V_1}{V_2} \right)^{C_P/C_V}$$

$$TV^{\gamma-1} = \text{constant}$$

(3.23a)

$$TP^{(1-\gamma)/\gamma} = \text{constant}$$

(3.23b)

$$PV^{\gamma} = \text{constant}$$

(3.23c)

$$\gamma \equiv \frac{C_P}{C_V}$$

$$P_2 = P_1 \cdot \left(\frac{V_1}{V_2} \right)^{\gamma}$$

Adiabatic Process - Work

$$dW = dU = C_V dT \quad (3.25)$$

$$W = \Delta U = C_V \Delta T$$

$$\gamma \equiv \frac{C_P}{C_V} = \frac{C_V + R}{C_V} = 1 + \frac{R}{C_V} \quad \text{or} \quad C_V = \frac{R}{\gamma - 1}$$

$$W = C_V \Delta T = \frac{R \Delta T}{\gamma - 1}$$

For ideal gas with constant heat capacities in a closed, adiabatic system:

$$W = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1} \quad (\text{or}) \quad W = \frac{R(T_2 - T_1)}{\gamma - 1} \quad (3.26, \text{ both equations})$$

For ideal gas with constant heat capacities in a closed, adiabatic, reversible system:

$$W = \frac{P_1 V_1}{\gamma - 1} \left[\left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} - 1 \right] = \frac{RT_1}{\gamma - 1} \left[\left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} - 1 \right] \quad (3.27)$$

Polytropic Process

“many ways” or “many paths”

$$PV^\delta = \text{constant} \quad (3.23c)$$

$$TV^{\delta-1} = \text{constant} \quad (3.23a)$$

$$TP^{(1-\delta)/\delta} = \text{constant} \quad (3.23b)$$

δ is the “polytropic constant”

(3.23c and integral of $-PdV$)

$$W = \frac{RT_1}{\delta - 1} \left[\left(\frac{P_2}{P_1} \right)^{(\delta-1)/\delta} - 1 \right] \quad (3.27)$$

(same as 3.34 with γ replaced by δ)

$$Q = \frac{(\delta - \gamma)RT_1}{(\delta - 1)(\gamma - 1)} \left[\left(\frac{P_2}{P_1} \right)^{(\delta-1)/\delta} - 1 \right] \quad (3.37)$$

$$K \equiv \frac{dQ}{dW}$$

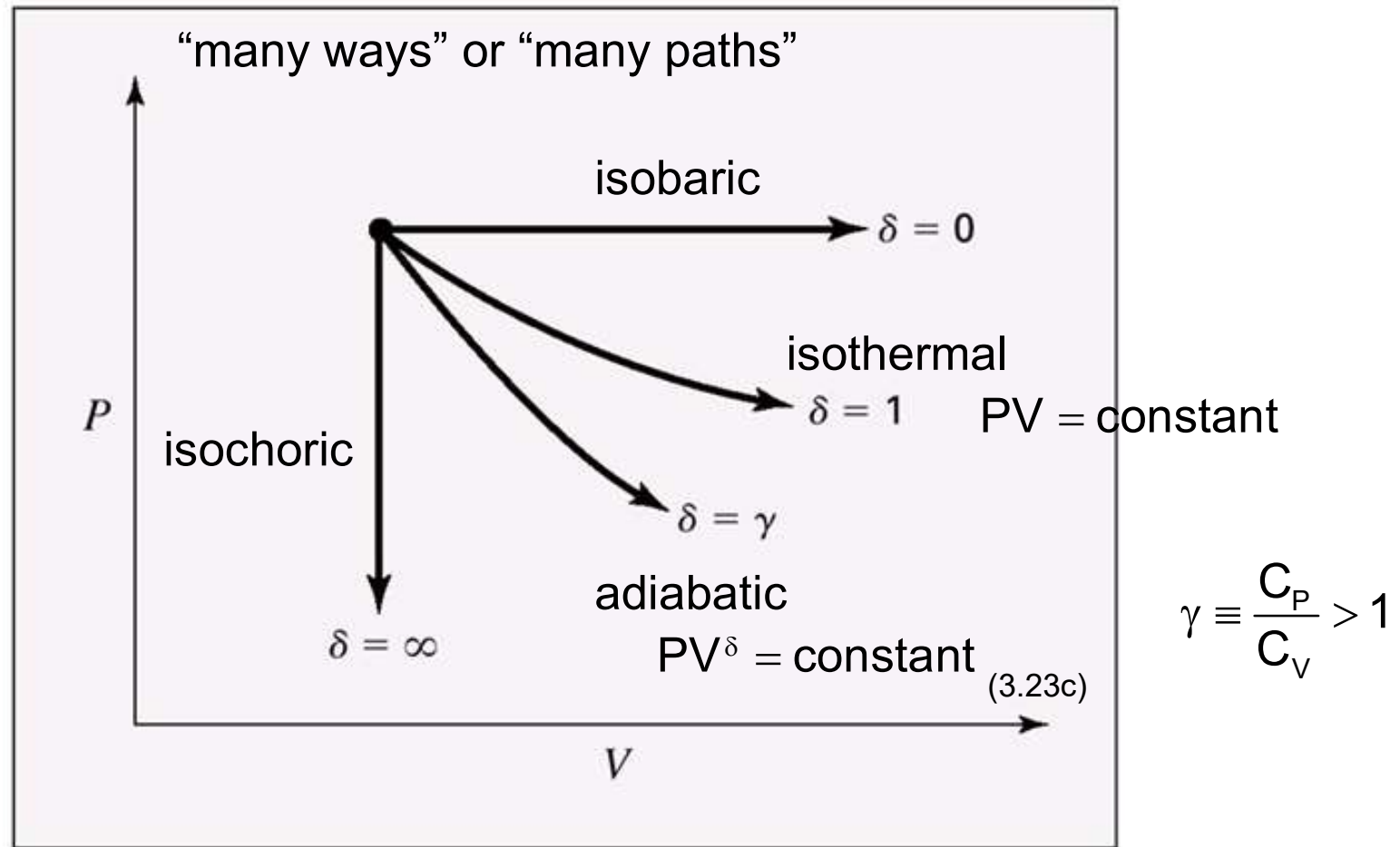
$$\delta = (1 - \gamma)K + \gamma$$

(derivation not shown)

- Write 1st Law with definition of K
- Use differential form of ideal gas law

This graph is very important!

Polytropic Process



Paths of polytropic processes characterized by specific values of δ .

The importance of the polytropic constant δ is that it shows the general shape of the PV curve under different conditions

Irreversible Processes

For an ideal gas

Any equation for dU , ΔU , dH , or ΔH is valid regardless of the process

Q and W are subject to the conditions of the derivations.

Work of an irreversible process:

- Step 1: Determine reversible work
- Step 2: Multiply or divide by an efficiency that gives the irreversible work

Example 3.3

Air is compressed from an initial state of 1 bar and 25 °C to a final state of 3 bar and 25 °C by three different mechanically reversible processes in a closed system:

- (a) Heating at constant volume followed by cooling at constant pressure
- (b) Isothermal compression
- (c) Adiabatic compression followed by cooling at constant volume.

Assume air to be an ideal gas with constant heat capacities, $C_V = (5/2)R$ and $C_P = (7/2)R$. Calculate the work required, heat transferred, and the changes in internal energy and enthalpy of the air for each process.

Solution: The system is one mole of air.

Additional givens:

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$V_1 = 0.02479 \text{ m}^3$$

$$\text{In all cases: } \Delta H = \Delta U = 0$$

$$C_V = 20.785 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$V_2 = 0.004948 \text{ m}^3$$

$$C_P = 29.100 \text{ J mol}^{-1} \text{ K}^{-1}$$

Example 3.2, part (a)

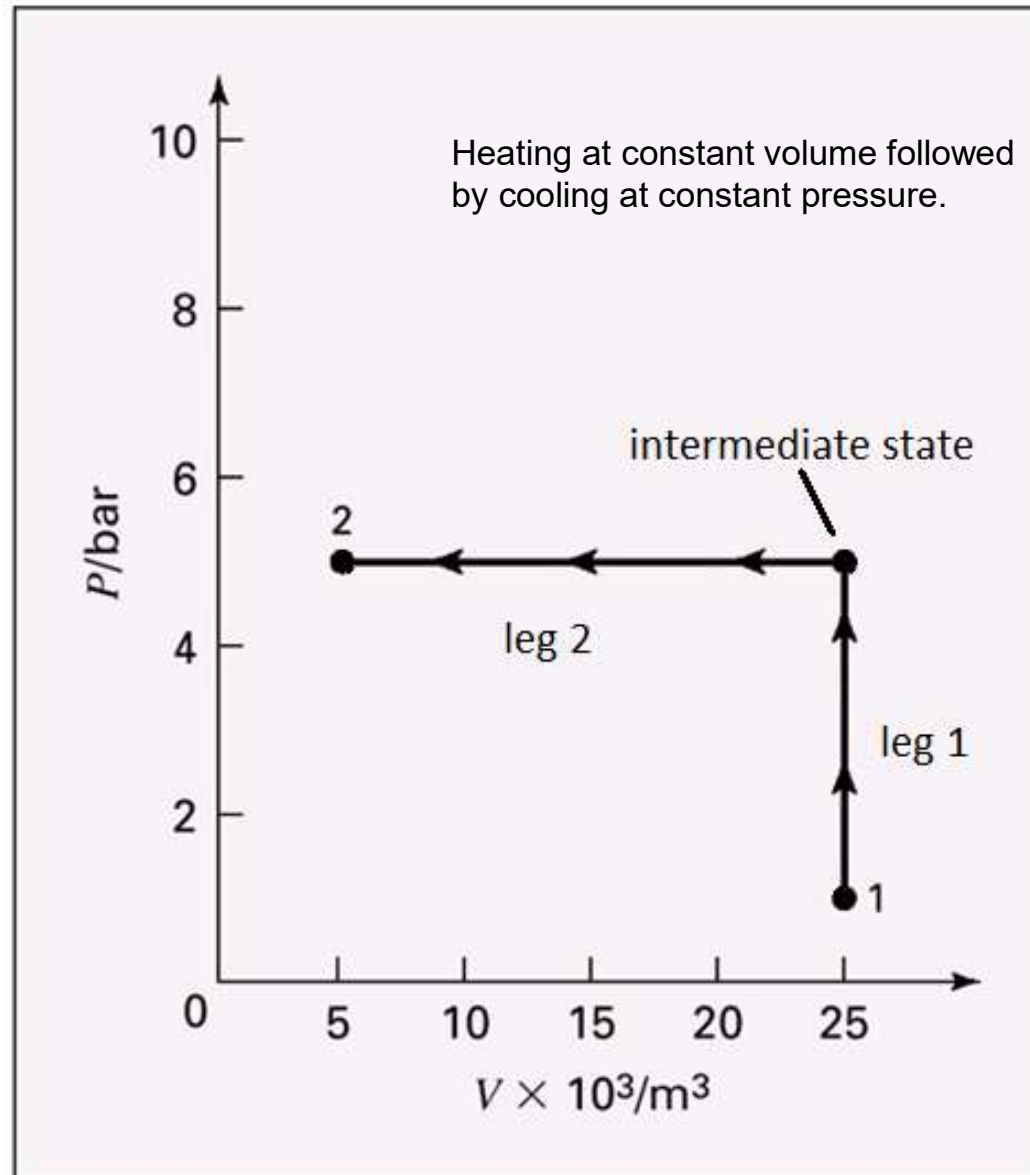


Diagram for Ex. 3.3.a

Example 3.3, part (a), cont.

Air is compressed from an initial state of 1 bar and 25 °C to a final state of 5 bar and 25 °C by three different mechanically reversible processes in a closed system:

(a) Heating at constant volume followed by cooling at constant pressure

$$\Delta H_{\text{overall}} = \Delta U_{\text{overall}} = 0 \quad T \text{ is constant (25 °C)}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_{\text{int}} V_{\text{int}}}{T_{\text{int}}} = \frac{P_2 V_1}{T_{\text{int}}} \quad T_{\text{intermediate}} = T_1 \frac{P_2}{P_1} = 298.15 \cdot \left(\frac{5}{1} \right) = 894.45 \text{ K}$$

$$Q_{\text{leg1}} = \Delta U = C_V \Delta T = (20.785)(894.45 - 298.15) = 12,394 \text{ J}$$

$$Q_{\text{leg2}} = \Delta H = C_P \Delta T = (29.10)(298.15 - 894.45) = -17,352 \text{ J}$$

Ex. 2.7a

$$Q_{\text{overall}} = 12,391 - 17,352 = -4,958 \text{ J}$$

$$\Delta U_{\text{overall}} = 0 = Q_{\text{overall}} + W_{\text{overall}} \Rightarrow W_{\text{overall}} = -Q_{\text{overall}} = 4,958 \text{ J}$$

Example 3.3, part (b)

Air is compressed from an initial state of 1 bar and 25 °C to a final state of 3 bar and 25 °C by three different mechanically reversible processes in a closed system:

(b) Isothermal compression

$$\Delta H_{\text{overall}} = \Delta U_{\text{overall}} = 0$$

T is constant (25 °C)

Use equation 3.2 for Q and W
(slide 7):

$$\begin{aligned} Q = -W &= RT \ln \left(\frac{P_1}{P_2} \right) \\ &= (8.314)(298.15) \ln \left(\frac{1}{3} \right) \\ &= -2,723.26 \text{ J} \end{aligned}$$

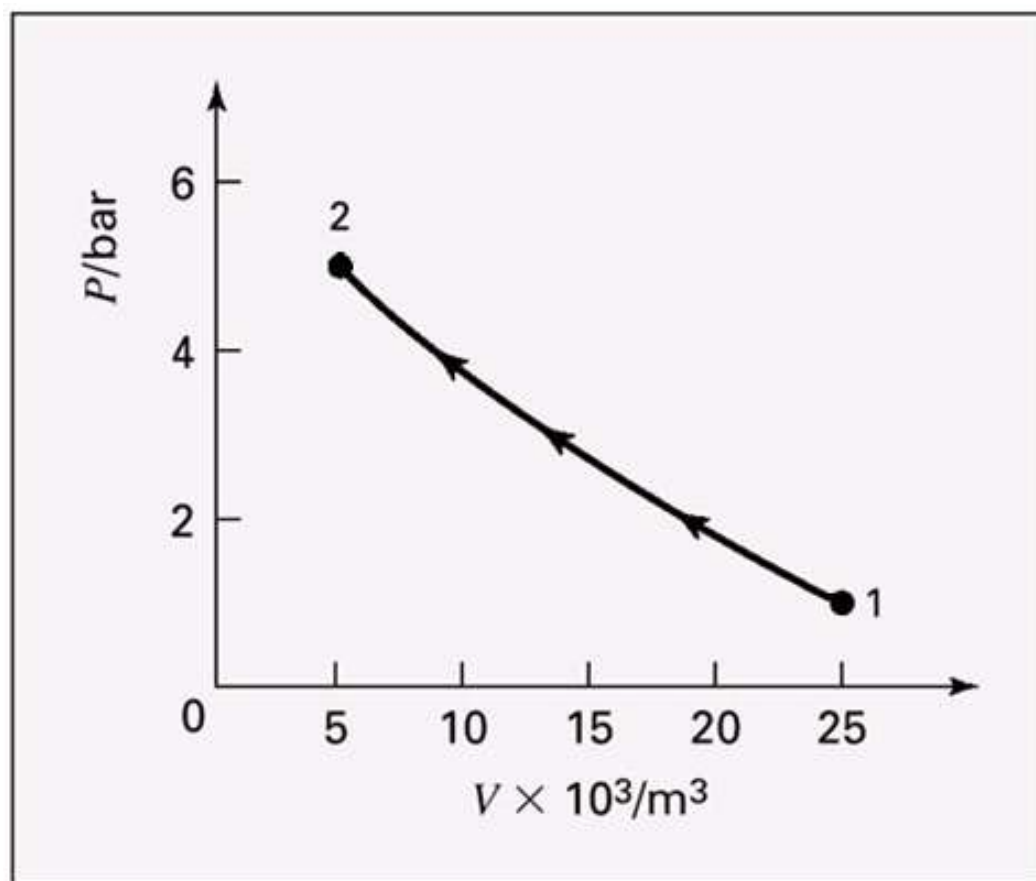


Diagram for Ex. 3.3.b

Example 3.3, part (c)

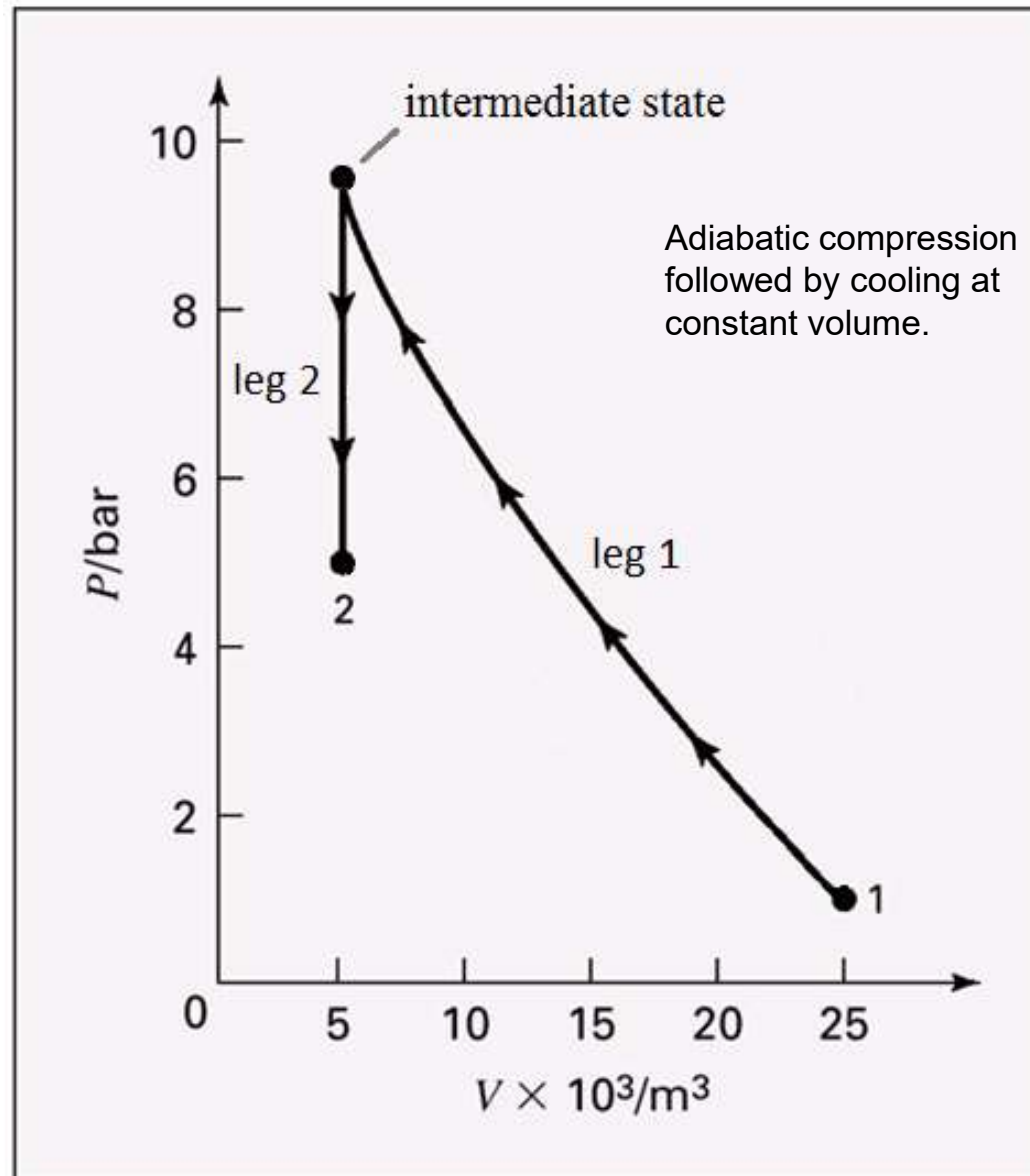


Diagram for Ex. 3. 3c

Example 3.3, part (c), cont.

Air is compressed from an initial state of 1 bar and 25 °C to a final state of 3 bar and 25 °C by three different mechanically reversible processes in a closed system:

(c) Adiabatic compression followed by cooling at constant volume.

Adiabatic compression step (leg 1):

$$\gamma - 1 = \frac{C_P}{C_V} - 1 = \frac{7}{2} - 1 = 0.4$$

Use equation 3.30a:

$$T_{\text{intermediate}} = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1} = (298.15) \cdot \left(\frac{0.02479}{0.004958} \right)^{0.4} = 462.69\text{K}$$

Then use equation 3.32 (Recall first Law: $Q + W = \Delta U$, $Q = 0$, and $\Delta U = C_V \Delta T$):

$$W_{\text{leg1}} = C_V \Delta T = (20.785)(462.69 - 298.15) = 3,419\text{ J} \quad \text{and} \quad Q_{\text{leg1}} = 0$$

Constant volume step (leg 2):

$$Q_{\text{leg2}} = \Delta U = C_V \Delta T = (20.785)(298.15 - 462.69) = -3,419\text{ J} \quad \text{and} \quad W_{\text{leg2}} = 0$$

$$\text{Overall:} \quad W_{\text{overall}} = 3,419 + 0 = 3,419\text{ J} \quad \text{and} \quad Q_{\text{overall}} = 0 - 3,419 = -3,419\text{ J}$$

Questions?