CH365 Chemical Engineering Thermodynamics

Lesson 11
Application of the 1st Law to Ideal Gases

Professor Andrew Biaglow

General Comments

- 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.

- 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.

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V = \frac{dU(T)}{dT} = C_V(T)$$

(3.9) & (2.15)

functions of T only

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

$$H \equiv U + PV = U + RT = H(T)$$

(3.10), from (2.10) & (3.7)

$$C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P = \frac{dH(T)}{dT} = C_P(T)$$

(3.11) & (2.19)

$$H = U + RT$$

$$\frac{dH}{dT} = \frac{d}{dT}(U + RT)$$

$$= \frac{dU}{dT} + \frac{d(RT)}{dT}$$

$$= \frac{dU}{dT} + R$$

Also function of T only

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

$$R = C_P - C_V$$

(3.12)

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

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)
$P = \dfrac{RT}{V} = P(T,V)$	$dQ = C_V dT + RT\dfrac{dV}{V}$ (3.16)	$dW = -RT\dfrac{dV}{V}$ (3.17)
$V = \dfrac{RT}{P} = V(T,P)$	$dQ = C_P dT - RT\dfrac{dP}{P}$ (3.18)	$dW = -RdT + RT\dfrac{dP}{P}$ (3.19)
$T = \dfrac{PV}{R} = T(P,V)$	$dQ = \dfrac{C_V}{R}VdP + \dfrac{C_P}{R}PdV$	$dW = -PdV$ (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 $V = \dfrac{RT}{P}$ show that $dW = -RdT + RT\dfrac{dP}{P}$ and $dQ = C_P dT - RT\dfrac{dP}{P}$

(3.19) (3.18)

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

$(3.2, L10)$

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

$dW = -PdV$ $\Rightarrow$ $dW = -P\left(-\dfrac{RT}{P^2}dP + \dfrac{R}{P}dT\right) = \dfrac{RT}{P}dP - RdT$ ✔

1.3

$dQ + dW = dU$

$dQ + dW = C_V dT$ $\Rightarrow$ $dQ + \dfrac{RT}{P}dP - RdT = C_V dT$ $C_V = C_P - R$

$dU = C_V dT$

(3.12)

$(3.13a)$

$dQ + \dfrac{RT}{P}dP - \cancel{RdT} = (C_P - R)dT = C_P dT - \cancel{RdT}$

$dQ = C_P dT - RT\dfrac{dP}{P}$ ✔

Isothermal Process

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

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

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

molar heat (energy per mole)

From 2.3 with ΔU=0

$$Q = -W$$

$$W = -RT\ln\left(\frac{V_2}{V_1}\right) = RT\ln\left(\frac{P_2}{P_1}\right) \qquad \text{(3.20), from (3.17) \& (3.19)} \qquad RdT = 0$$

molar work (energy per mole)

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

Isobaric Process

(No change in pressure)

C_P and C_V in Appendix C or assumed constant

$$\Delta U = \int C_V dT \qquad \text{and} \qquad \Delta H = \int C_P dT$$

(3.13b) (3.14b)

$$dQ = C_P dT - RT \frac{dP}{P} \quad^{dP=0} \qquad \text{and} \qquad dW = -RdT + RT \frac{dP}{P} \quad^{dP=0} \qquad \text{(3.18) and (3.19)}$$

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

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

(3.21)

Isochoric Process

(No change in volume)

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

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

$$Q = \int C_V dT$$

$$\boxed{Q = \Delta U = \int C_V dT \qquad \begin{array}{c} \text{(Constant V)} \\ \\ \text{(3.22)} \end{array}}$$

Adiabatic Process

$$dQ = 0 \qquad C_V, C_P \text{ assumed constant}$$

(any of the dQ equations from slide 4)

Mechanically reversible adiabatic expansion or compression

(3.16)

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

(3.18)

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

(un-numbered)

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

$TV^{\gamma-1} = \text{constant}$	$TP^{(1-\gamma)/\gamma} = \text{constant}$	$PV^{\gamma} = \text{constant}$
(3.23a)	(3.23b)	(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

$$dW = dU = C_V dT$$

(3.25)

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

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

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

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

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

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

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

Polytropic Process

"many ways" or "many paths"

δ is the "polytropic constant"

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

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

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

(3.23c and integral of -PdV)

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

(same as 3.34 with γ replaced by δ)

$$Q = \frac{(\delta - \gamma)RT_1}{(\delta - 1)(\gamma - 1)}\left[\left(\frac{P_2}{P_1}\right)^{(\delta-1)/\delta} - 1\right] \qquad \text{(3.37)}$$
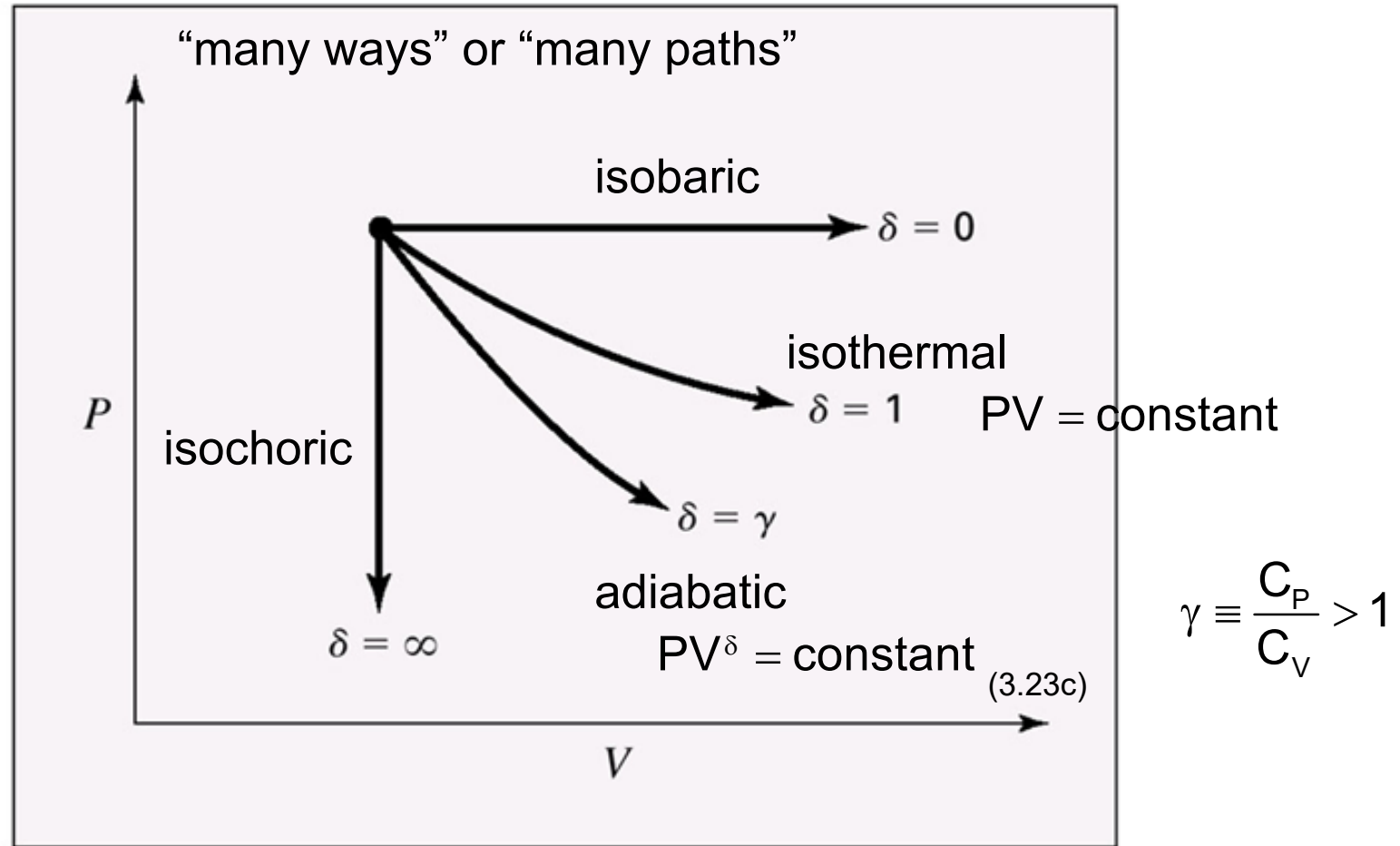
$$K \equiv \frac{dQ}{dW}$$

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

(derivation not shown)
- Write 1st Law with definition of K
- Use differential form of ideal gas law

This graph is very important!

Polytropic Process

"many ways" or "many paths"

isobaric
$\delta = 0$

isothermal
$\delta = 1$ $\quad$ PV = constant

P

isochoric

$\delta = \gamma$

adiabatic

$\delta = \infty$ $\quad$ PV$^\delta$ = constant

(3.23c)

$\gamma \equiv \dfrac{C_P}{C_V} > 1$

V

Paths of polytropic processes characterized by specific values of δ.

The importance of the polytropic constant δ is that is 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 <u>system</u> is one mole of air.

Additional givens:

  $R = 8.314$ J mol^{-1} K^{-1} $V_1 = 0.02479$ m^3 In all cases: $\Delta H = \Delta U = 0$

  $C_V = 20.785$ J mol^{-1} K^{-1} $V_2 = 0.004948$ m^3

  $C_P = 29.100$ J mol^{-1} K^{-1}
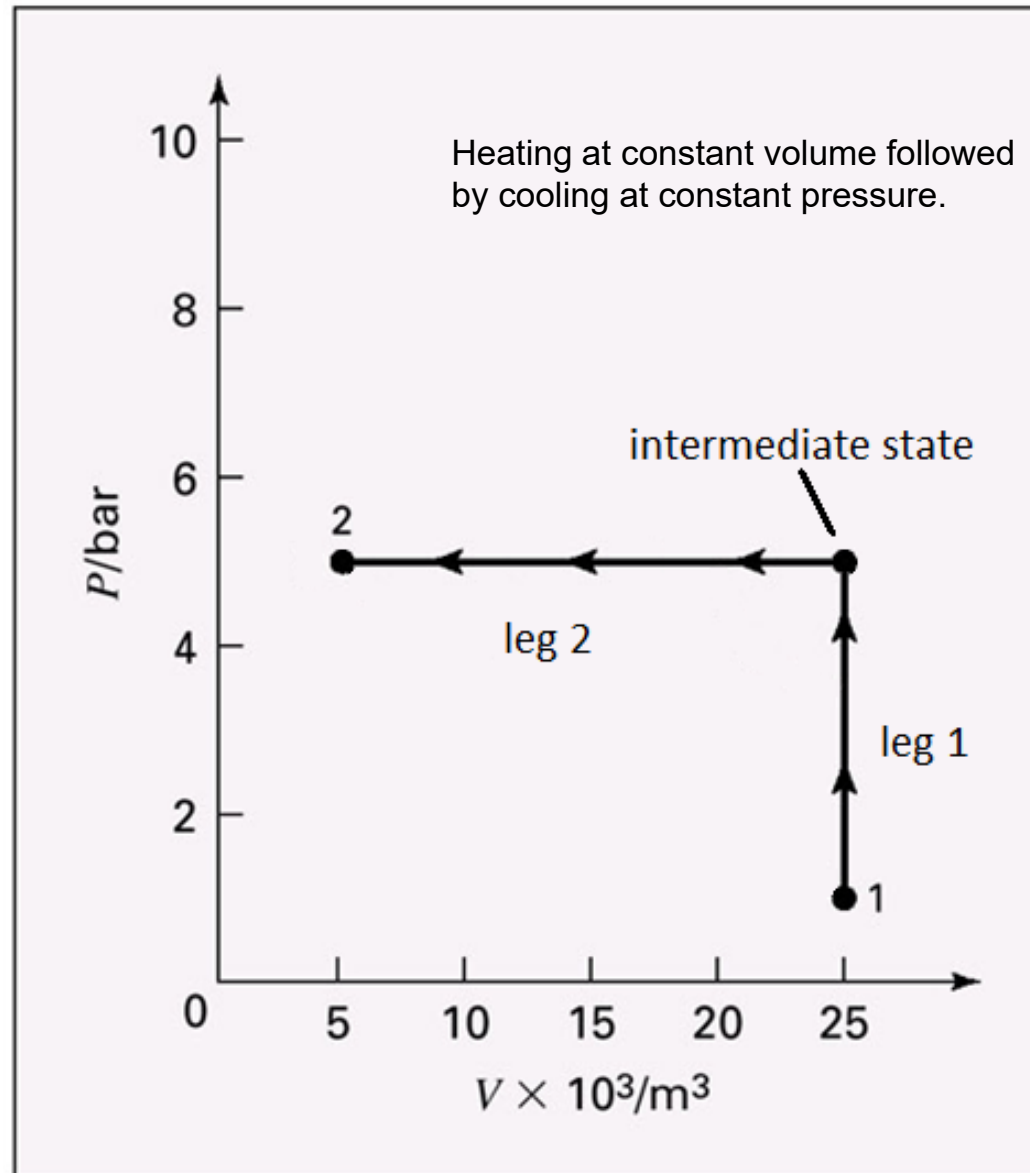
Example 3.2, part (a)

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

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

$$\frac{P_1 \cancel{V_1}}{T_1} = \frac{P_{int} V_{int}}{T_{int}} = \frac{P_2 \cancel{V_1}}{T_{int}} \qquad T_{int\,ermediate} = T_1 \frac{P_2}{P_1} = 298.15 \cdot \left(\frac{3}{1}\right) = 894.45 \text{K}$$

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

$$Q_{leg2} = \Delta H = C_P \Delta T = (29.10)(298.15 - 894.45) = -17,352 \, J \qquad \text{Ex. 2.7a}$$

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

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

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

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

T is constant (25 °C)

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

$Q = -W = RT\ln\left(\dfrac{P_1}{P_2}\right)$

$= (8.314)(298.15)\ln\left(\dfrac{1}{3}\right)$

$= -2,723.26\,J$
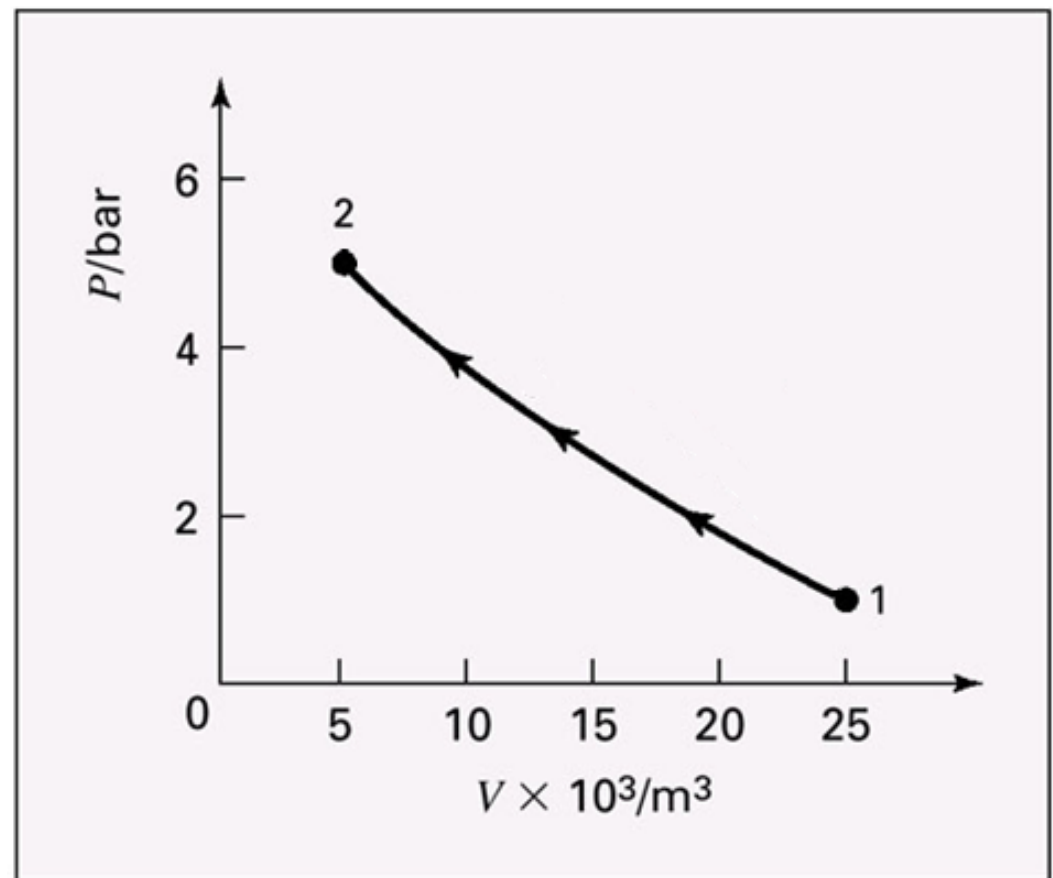
Diagram for Ex. 3.3.b

Example 3.3, part (c)

intermediate state

Adiabatic compression followed by cooling at constant volume.

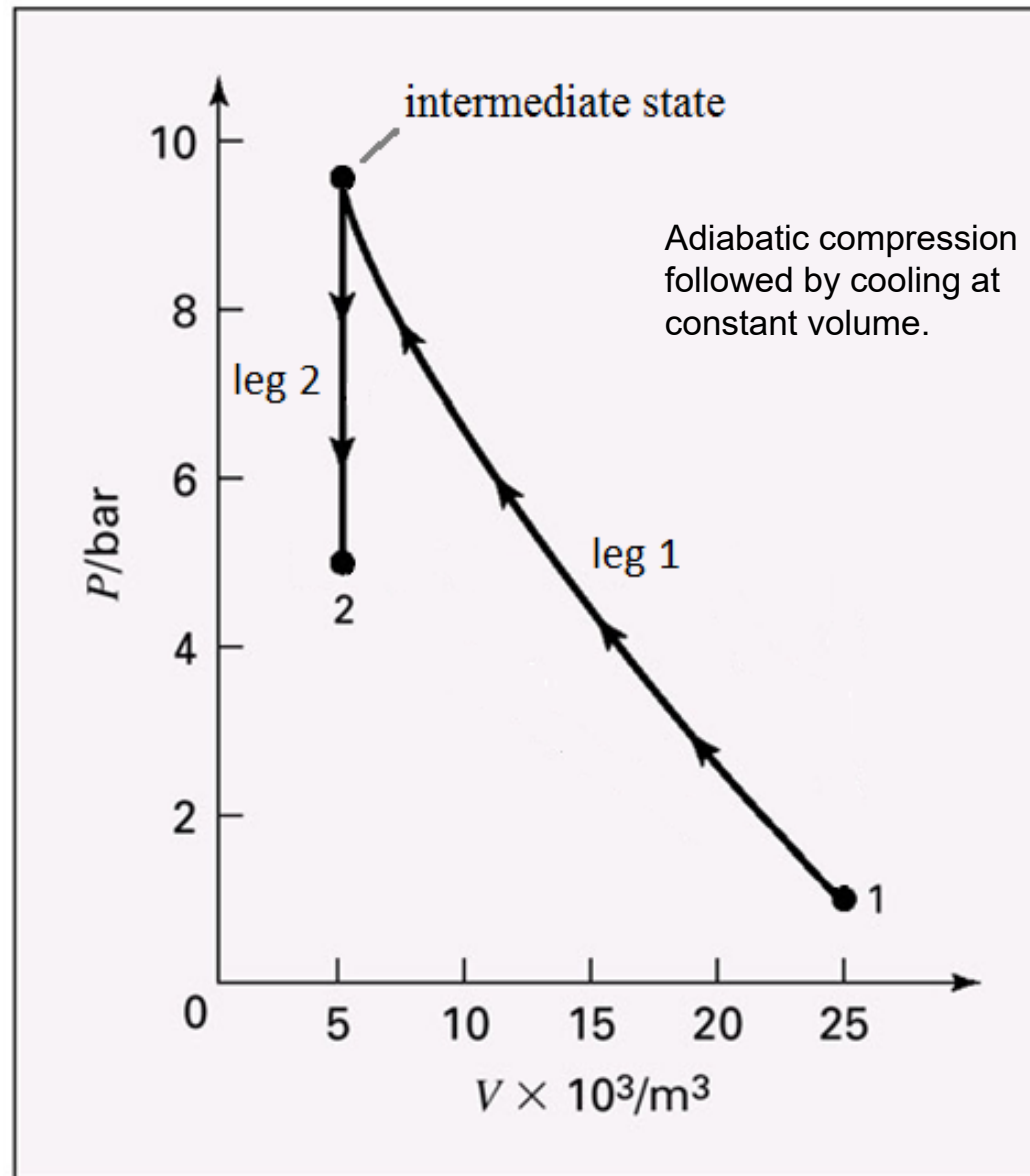Diagram for Ex. 3. 3c

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:

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

Then use equation 3.32 (Recall first Law: Q + W = ΔU, Q = 0, and ΔU=C_VΔT):

$$W_{leg1} = C_V \Delta T = (20.785)(462.69 - 298.15) = 3,419\,J \qquad \text{and} \qquad Q_{leq1} = 0$$

Constant volume step (leg 2):

$$Q_{leg2} = \Delta U = C_V \Delta T = (20.785)(298.15 - 462.69) = -3,419\,J \qquad \text{and} \qquad W_{leg\,2} = 0$$

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

Homework Problems

Problem 3.17

One mole of an ideal gas with $C_P = (7/2) R$ and $C_V = (5/2) R$ expands from $P_1 = 8$ bar and $T_1 = 600\,K$ to $P_2 = 1$ bar by each of the following paths:

(a) Constant volume,
(b) Constant temperature,
(c) Adiabatically

Assuming mechanical reversibility, calculate W, Q, ΔU, and ΔH for each process. Sketch each path on a single PV diagram.

Problem 3.21

An ideal gas, $C_P = (5/2)\,R$ and $C_V = (3/2)\,R$, is changed from $P_1 = 1\,bar$ and $V_1^t = 12\,m^3$ to $P_2 = 12\,bar$ and $V_2^t = 1\,m^3$ by the following mechanically reversible processes:

(a) Isothermal compression
(b) Adiabatic compression followed by cooling at constant pressure
(c) Adiabatic compression followed by cooling at constant volume.
(d) Heating at constant volume followed by cooling at constant pressure.
(e) Cooling at constant pressure followed by heating at constant volume.

Calculate Q, W, ΔU^t, and ΔH^t for each of these processes, and sketch the path of each process on a single PV diagram.

Sketches for (a) through (e) on common set of axes.

Sketches are neat and easy to read – show care.