

# CH365 Chemical Engineering Thermodynamics

## Lesson 11

### Application of the 1<sup>st</sup> 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, we will describe the general P-V-T behavior of pure fluids.
  - Second, we will discuss the ideal gas behavior in detail.

Hidden Content – Take Notes

- Third, we will discuss more realistic equations, wrapping up with generalized correlations.

# Property Relations for the Ideal Gas

Lesson 6, result of the Joule experiment.

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

Also functions of T only

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

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

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

Also function of T only

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

$$C_P = \frac{dH}{dT} = \frac{dU}{dT} + R = C_V + R \quad R = C_P - C_V \quad (3.12)$$

$dU = C_V dT$ <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

# 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)

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

(3.2, L10)

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

$$dW = -P dV \quad \xrightarrow{1.3} \quad dW = -P \left( -\frac{RT}{P^2} dP + \frac{R}{P} dT \right) = \frac{RT}{P} dP - R dT \quad \checkmark$$

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$$dQ + dW = dU$$

$$dU = C_V dT$$

(3.13a)

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

$C_V = C_P - R$ 

(3.12)

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


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

# Isothermal Process

(Q, W,  $\Delta H$ , and  $\Delta U$  with no change in temperature)

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


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

 molar heat (energy per mole)

From 2.3 with  $\Delta U=0$

$$Q = -W$$

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

 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

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

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

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

(3.21)

# Isochoric Process

(No change in volume)

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

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

$$Q = \int C_V dT$$

$$Q = \Delta U = \int C_V dT \quad (\text{Constant } V) \quad (3.22)$$



# 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”

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

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

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

$\delta$  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  $\gamma$  replaced by  $\delta$ )

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

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

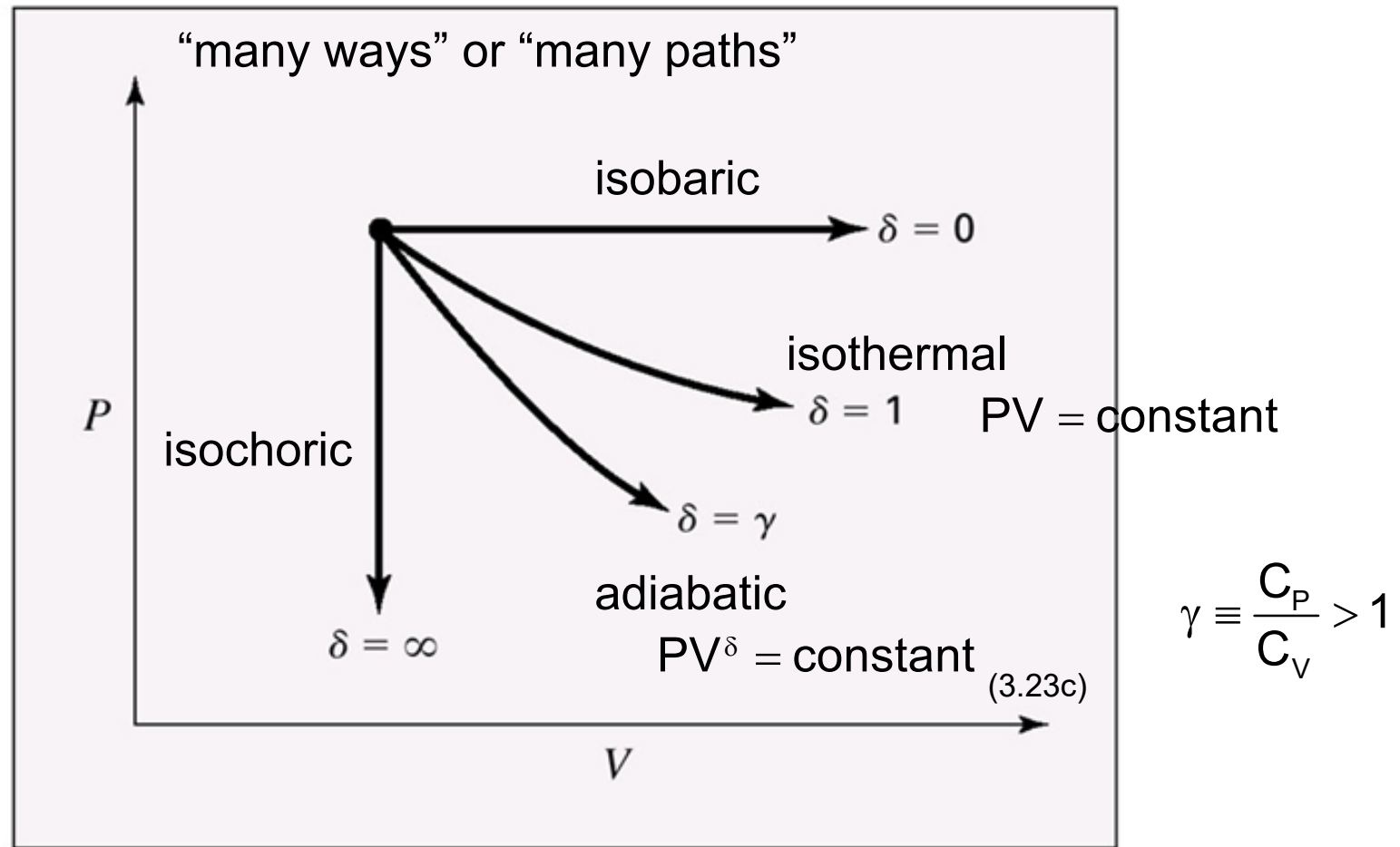
$$\delta = (1 - \gamma)K + \gamma$$

(derivation not shown)

- Write 1<sup>st</sup> 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  $\delta$ .

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

# Irreversible Processes

For an ideal gas

Any equation for  $dU$ ,  $\Delta U$ ,  $dH$ , or  $\Delta H$  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.

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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)

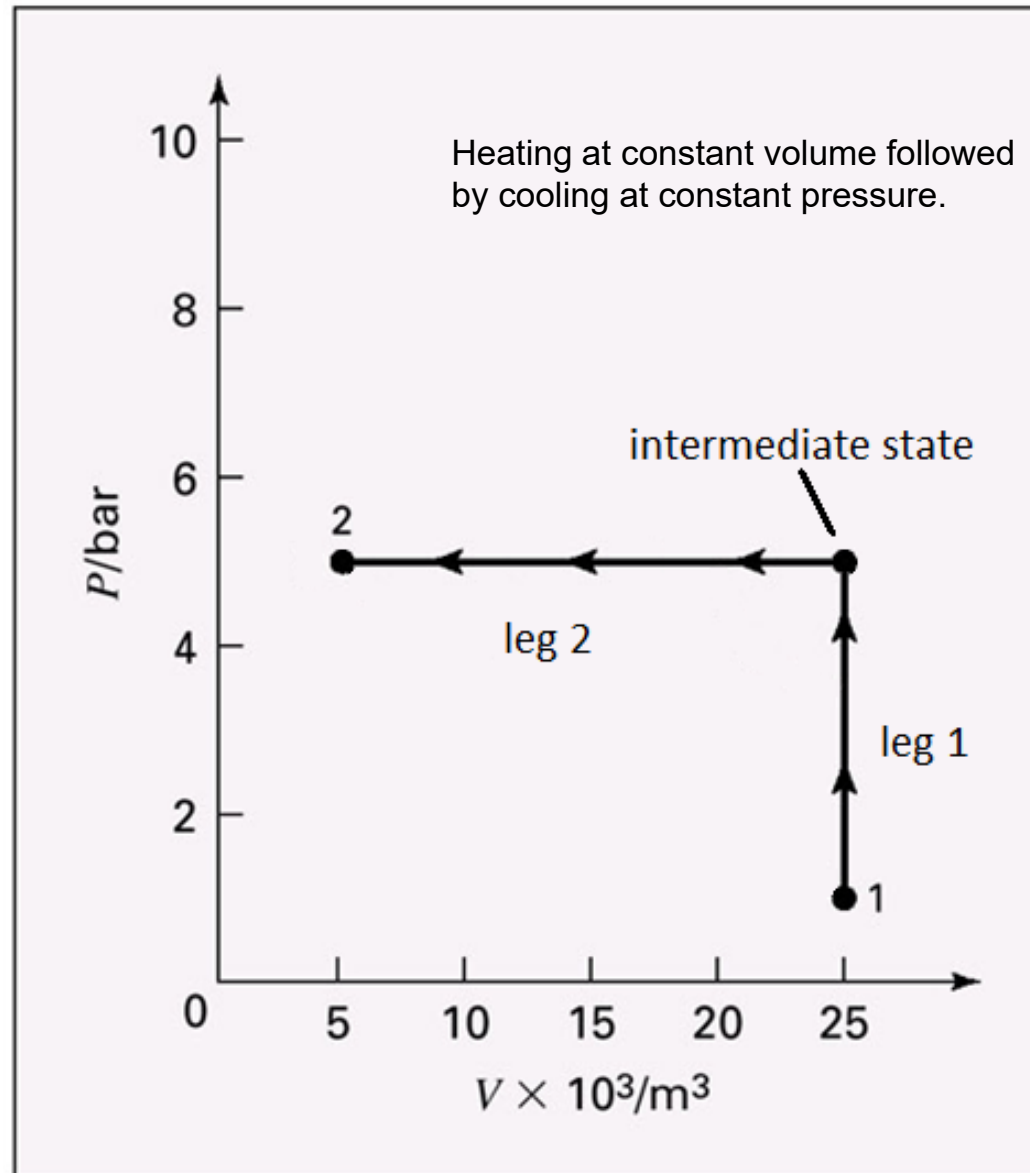


Diagram for Ex. 3.3.a

## 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

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

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

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

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

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):

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

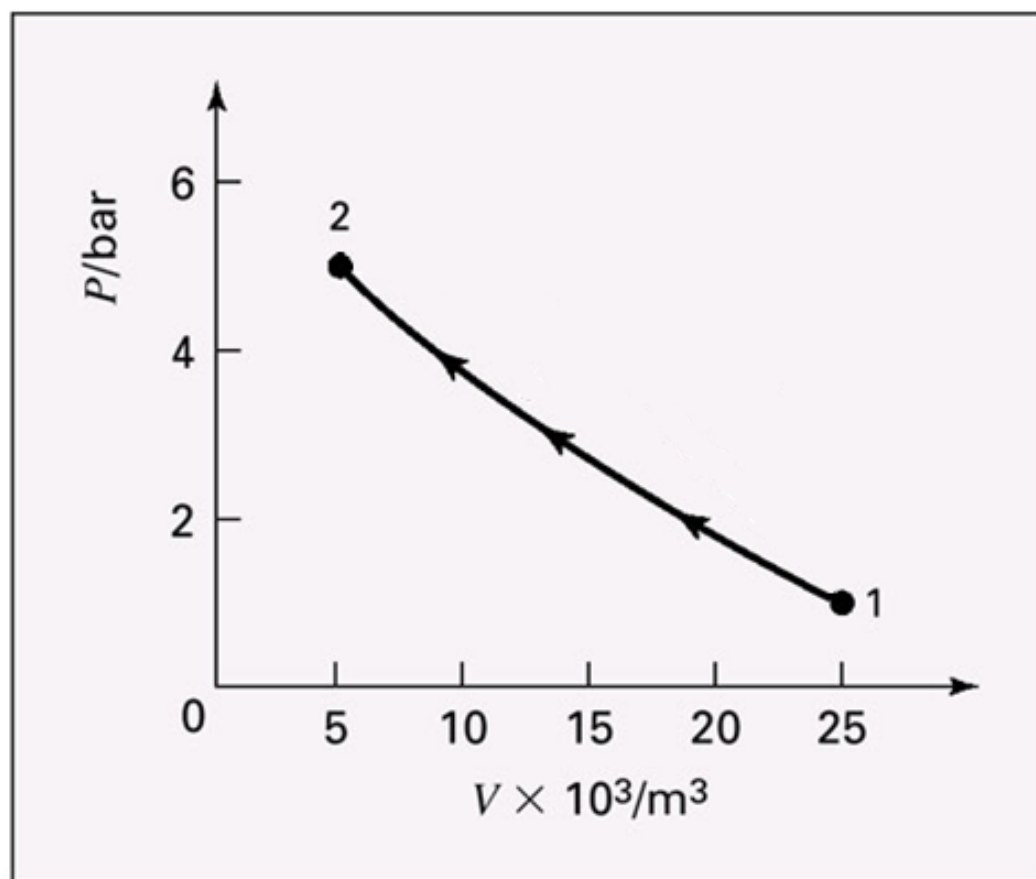


Diagram for Ex. 3.3.b

# Example 3.3, part (c)

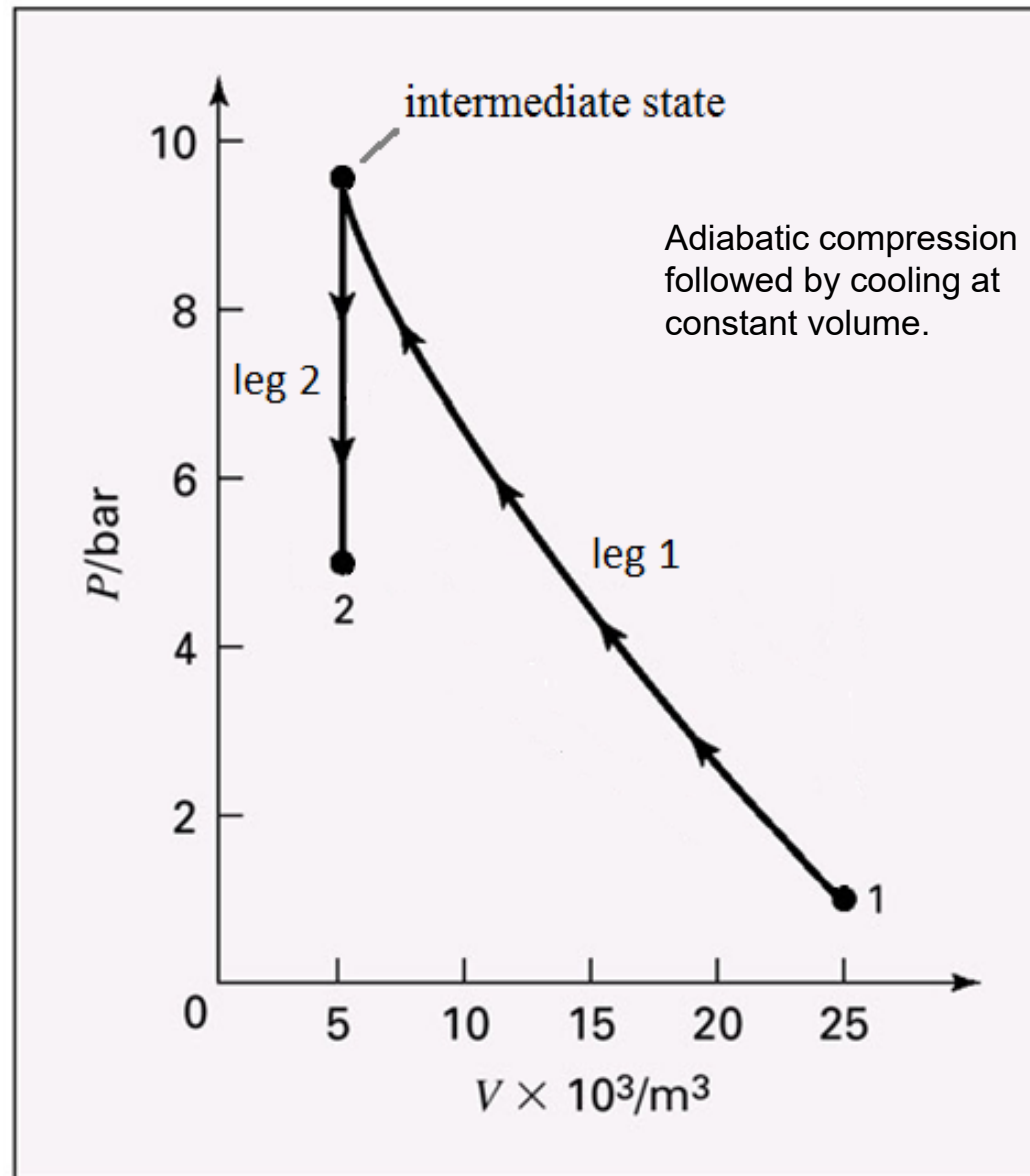


Diagram for Ex. 3. 3c

# 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):

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

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

# 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  $W$ ,  $Q$ ,  $\Delta U$ , and  $\Delta H$  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  $V_1^t = 12 \text{ m}^3$  to  $P_2 = 12$  bar and  $V_2^t = 1 \text{ m}^3$  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  $Q$ ,  $W$ ,  $\Delta U^t$ , and  $\Delta H^t$  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.