1.6 Implied Property Relations for an Ideal Gas

The definition of heat capacity at constant volume, Eq. (2.16), leads for an ideal gas to the conclusion that Cv is a function of temperature only:

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V = \frac{dU}{dT} = C_V(T) \qquad (3.15)$$

The defining equation for enthalpy, Eq. (2.1 I), applied to an ideal gas, leads to the conclusion that H also is a function of temperature only:

$$H \equiv U + PV = U(T) + RT = H(T) \qquad (3.16)$$

The heat capacity at constant pressure Cp, defined by Eq. (2.20), like Cv, is a function of temperature only:

$$C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P = \frac{dH}{dT} = C_P(T) \qquad (3.17)$$

A useful relation between Cp and Cv for an ideal gas comes from differentiation of Eq. (3.16):

$$C_P = \frac{dH}{dT} = \frac{dU}{dT} + R = C_V + R \qquad (3.18)$$

This equation does not imply that Cp and CV are themselves constant for an ideal gas, but only that they vary with temperature in such a way that their difference is equal to R.

For any change of state of an ideal gas Eq. (3.15) may be written:

$$dU = C_V\,dT \qquad (3.19a)$$

Whence,

$$\Delta U = \int C_V\,dT \qquad (3.19b)$$

By Eq. (3.17),

$$dH = C_P\,dT \qquad (3.20a)$$

Whence,

$$\Delta H = \int C_P\,dT \qquad (3.20b)$$

Equations for Process Calculations: Ideal Gases

For an ideal gas in any mechanically reversible closed-system process, Eq. (2.6), written for a unit mass or a mole may be combined with Eq. (3.19a):

$$dQ + dW = C_V\,dT$$

The work for a mechanically reversible closed-system process is given by Eq. (1.2), also written for one mole or a unit mass:

$$dW = -P\,dV$$

Whence,

$$dQ = C_V\,dT + P\,dV$$

The two preceding equations for an ideal gas undergoing a reversible process in a closed system take several forms through elimination of one of the variables P, V, or T by Eq. (3.13). Thus, with P = RT/V they become:

$$\boxed{PV = RT} \quad \textbf{(ideal gas)} \qquad (3.13)$$

$$dQ = C_V\,dT + RT\frac{dV}{V} \qquad (3.21)$$

$$dW = -RT\frac{dV}{V} \qquad (3.22)$$

Alternatively, let V = RT/ P:

$$dQ = C_V\,dT + P\left(\frac{R}{P}dT - \frac{RT}{P^2}dP\right)$$

With Eq. (3.18) this reduces to:

$$dQ = C_P\,dT - RT\frac{dP}{P} \qquad (3.23)$$

Also,

$$dW = -R\,dT + RT\frac{dP}{P} \qquad (3.24)$$

Finally, let T = PV/R:

$$dQ = C_V\left(\frac{V}{R}dP + \frac{P}{R}dV\right) + P\,dV$$

Again with Eq. (3.18) this becomes:

$$dQ = \frac{C_V}{R} V\,dP + \frac{C_P}{R} P\,dV \qquad (3.25)$$

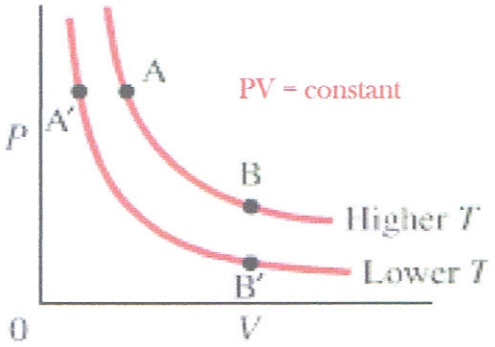
The work is simply: dW = -PdV

These equations may be applied to various processes, as described in what follows. The general restrictions implicit in their derivation are:

- **The equations are valid for ideal gases.**
- **The process is mechanically reversible.**
- **The system is closed.**

1. Isothermal Process (constant Temperature):

By Eqs. (3.19b) and (3.20b), **ΔU=ΔH=0**



By Eqs. (3.21) and (3.23)

$$Q = RT\ln\frac{V_2}{V_1} = -RT\ln\frac{P_2}{P_1}$$

By Eqs. (3.22) and (3.24),

$$W = -RT\ln\frac{V_2}{V_1} = RT\ln\frac{P_2}{P_1}$$

Note that Q = - W, a result that also follows from Eq. (2.3). Therefore,

$$Q = -W = RT\ln\frac{V_2}{V_1} = -RT\ln\frac{P_2}{P_1} \qquad (\text{const } T) \qquad (3.26)$$

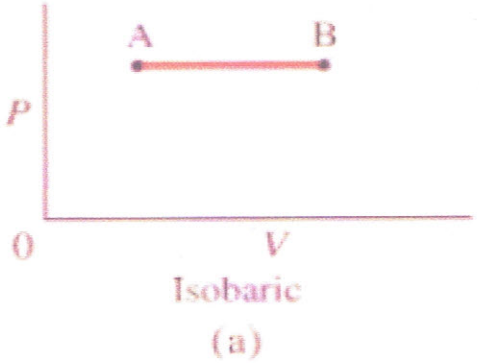
2. Isobaric Process (constant pressure)

By Eqs. (3.19b) and (3.20b),

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

and by Eqs. (3.23) and (3.24),

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



Note that Q = ΔH, a result also given by Eq. (2.13). Therefore,

$$Q = \Delta H = \int C_P \, dT \qquad (\text{const } P) \qquad (3.27)$$

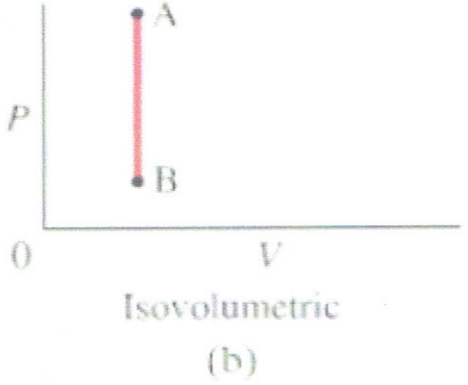
3. Isochoric (Constant- V) Process

Equations (3.19b) and (3.20b) again apply:

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

By Eqs. (3.21) and (1.3),

$$Q = \int C_V \, dT \qquad \text{and} \qquad W = 0$$



Note that Q = ΔU, a result also given by Eq. (2.10). Therefore,

$$Q = \Delta U = \int C_V \, dT \qquad (\text{const } V) \qquad (3.28)$$

4. Adiabatic Process: Constant Heat Capacities

An adiabatic process is one for which there is no heat transfer between the system and its surroundings; that is, dQ = 0.

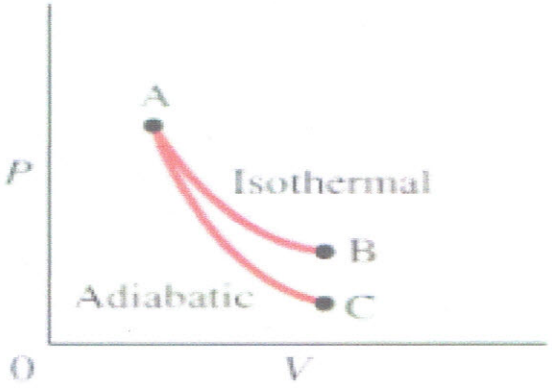
Integration with Cv and Cp constant then yields simple relations among the variables T, P, and V. For example, Eq. (3.21) becomes:

$$\frac{dT}{T} = -\frac{R}{C_V}\frac{dV}{V}$$

Integration with Cv constant then gives:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{R/C_V}$$

Similarly, Eqs. (3.23) and (3.25) lead to:



$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{R/C_P} \qquad \text{and} \qquad \frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{C_P/C_V}$$

These equations may also be expressed as:

$$\boxed{\gamma \equiv \frac{C_P}{C_V}} \tag{3.30}$$

Cp = Cv+R from Eq. 3.18

(Cp = Cv + R) ÷Cv

$\gamma = 1+R/Cv$, $R/Cv = \gamma-1$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \qquad \frac{T_2}{T_1} = \left(\frac{P_1}{P_2}\right)^{\gamma-1/\gamma}$$

From $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$\left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left(\frac{P_1}{P_2}\right)^{\gamma-1/\gamma}$$

$$\boxed{\begin{aligned} TV^{\gamma-1} &= \text{constant} \\ TP^{(1-\gamma)/\gamma} &= \text{constant} \\ PV^{\gamma} &= \text{constant} \end{aligned}} \qquad \begin{aligned} &(3.29a) \\ &(3.29b) \\ &(3.29c) \end{aligned}$$

Equations (3.29) apply to an ideal gas with constant heat capacities undergoing a mechanically reversible adiabatic process.

The work of an adiabatic process may be obtained from the relation:

$$dW=dU=CvdT$$

If Cv is constant, integration gives:

$$W = \Delta U = C_V \Delta T \qquad (3.31)$$

Alternative forms of Eq. (3.31) are obtained when Cv is eliminated in favour of the heat-capacity ratio γ:

$$\gamma = \frac{C_P}{C_V} = \frac{C_V + R}{C_V} = 1 + \frac{R}{C_V}$$

whence $$C_V = \frac{R}{\gamma - 1}$$

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

Since $RT_1 = P_1 V_1$ and $RT_2 = P_2V_2$, this expression may be written:

$$W = \frac{RT_2 - RT_1}{\gamma - 1} = \frac{P_2V_2 - P_1V_1}{\gamma - 1} \qquad (3.32)$$

Equations (3.31) and (3.32) are general for an adiabatic process, whether reversible or not. However, V_2 is usually not known, and is eliminated from Eq. (3.32) by Eq. (3.29c), valid only for mechanically reversible processes. This leads to the expression:

$$W = \frac{P_1V_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma} - 1\right] = \frac{RT_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma} - 1\right] \qquad (3.33)$$

- For monatomic gases, γ = 1.67;
- Approximate values of γ are 1.4 for diatomic gases (H_2, O_2 and N_2)
- and 1.3 for simple polyatomic gases such as CO_2, SO_2, NH_3, and CH_4.

5. Polytropic Process

Since polytropic means "turning many ways:' polytropic process suggests a model of some versatility. With δ a constant, it is defined as a process represented by empirical equation

$$PV^{\delta} = \text{constant} \qquad (3.34a)$$

For an ideal gas equations analogous to Eqs. (3.29a) and (3.29b) are readily derived:

$$TV^{\delta-1} = \text{constant} \qquad (3.34b)$$

$$TP^{(1-\delta)/\delta} = \text{constant} \qquad (3.34c)$$

When the relation between P and V is given by Eq. (3.34a), evaluation of PV yields

Eq. (3.33) with γ replaced by δ

:

$$W = \frac{RT_1}{\delta - 1}\left[\left(\frac{P_2}{P_1}\right)^{(\delta-1)/\delta} - 1\right] \qquad (3.35$$

Moreover, for constant heat capacities, the first law solved for Q yields:

$$Q = \frac{(\delta - \gamma)RT_1}{(\delta - 1)(\gamma - 1)}\left[\left(\frac{P_2}{P_1}\right)^{(\delta-1)/\delta} - 1\right] \qquad (3.36)$$

The processes described in this section correspond to the four paths shown in Fiq. 3.6 for specific values of δ

Isobaric process: By Eq. (3.34a), δ = 0.

Isothermal process: By Eq. (3.34b), δ= 1.

Adiabatic process: δ = γ.

Isochoric process: By Eq. (3.34a), dV/dP = V/Pδ; for constant V, δ = ± ∞

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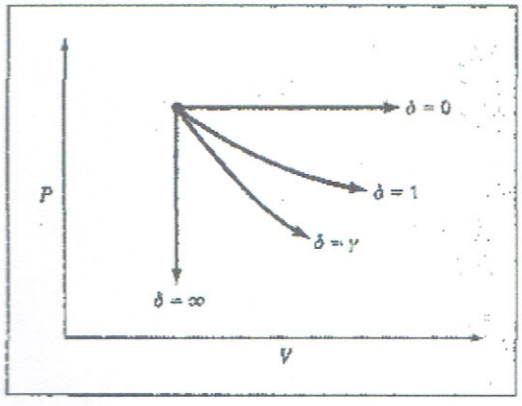


Figure 3.6 Paths of polytropic processes characterized by specific values of δ

Examples 3.2-.37

Example 3.2

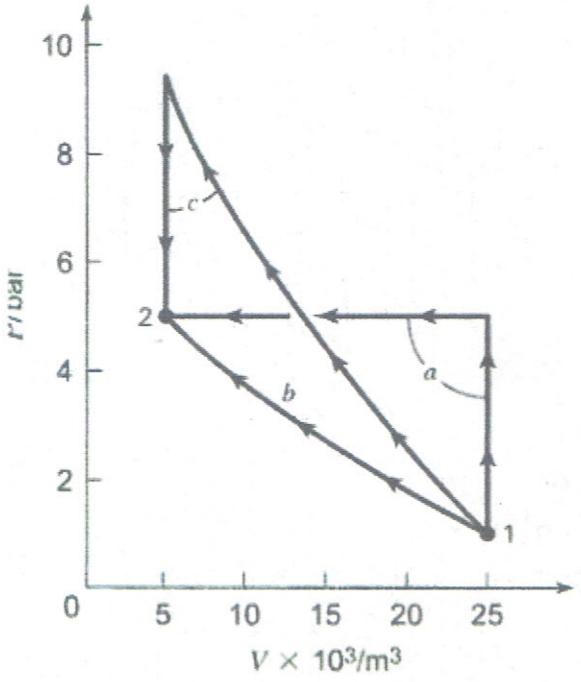
Air is compressed from an initial state of 1 bar and 25°C to a final state of 5 bar and 25°C by three different mechanically reversible processes in a closed system:

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

(*b*) Isothermal compression.

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

Assume air to be an ideal gas with the 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 3.2

Choose the system as 1 mol of air. For $R = 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}$,

$$C_V = 20.785 \qquad C_P = 29.099\ \text{J mol}^{-1}\ \text{K}^{-1}$$

The initial and final states of the air are identical with those of Ex. 2.9, where:

$$V_1 = 0.02479 \qquad V_2 = 0.004958\ \text{m}^3$$

Because T is the same at the beginning and end of the process, in all cases,

$$\Delta U = \Delta H = 0$$

(*a*) The process here is exactly that of Ex. 2.9(*b*), for which:

$$Q = -9{,}915\ \text{J} \qquad \text{and} \qquad W = 9{,}915\ \text{J}$$

(*b*) Equation (3.27) for the isothermal compression of an ideal gas applies:

$$Q = -W = RT \ln \frac{P_1}{P_2} = (8.314)(298.15) \ln \frac{1}{5} = -3{,}990\ \text{J}$$

(*c*) The initial step of adiabatic compression takes the air it to its final volume of $0.004958\ \text{m}^3$. By Eq. (3.30a), the temperature at this point is:

$$T' = T_1 \left(\frac{V_1}{V_2}\right)^{\gamma - 1} = (298.15) \left(\frac{0.02479}{0.004958}\right)^{0.4} = 567.57\ \text{K}$$

For this step, $Q = 0$, and by Eq. (3.32), the work of compression is:

$$W = C_V\, \Delta T = (20.785)(567.57 - 298.15) = 5{,}600\ \text{J}$$

For the constant-volume step, no work is done; the heat transfer is:

$$Q = \Delta U = C_V (T_2 - T') = -5{,}600\ \text{J}$$

Thus for process (*c*),

$$W = 5{,}600\ \text{J} \qquad \text{and} \qquad Q = -5{,}600\ \text{J}$$

Although the property changes ΔU and ΔH are zero for each process, Q and W are path-dependent, but here $Q = -W$. Figure 3.7 shows each process on a PV diagram. Because the work for each of these mechanically reversible processes is given by $W = -\int P\, dV$, the work for each process is proportional to the total area below the paths on the PV diagram from 1 to 2. The relative sizes of these areas correspond to the numerical values of W.

Example 3.3

An ideal gas undergoes the following sequence of mechanically reversible processes in a closed system:

(*a*) From an initial state of 70°C and 1 bar, it is compressed adiabatically to 150°C.

(*b*) It is then cooled from 150 to 70°C at constant pressure.

(*c*) Finally, it is expanded isothermally to its original state.

Calculate W, Q, ΔU, and ΔH for each of the three processes and for the entire cycle. Take $C_V = (3/2)R$ and $C_P = (5/2)R$.

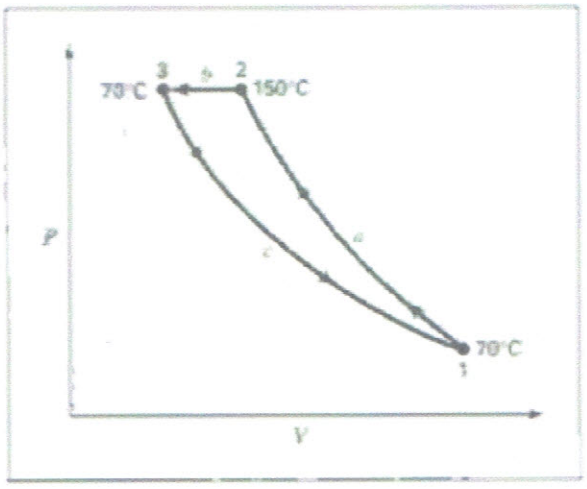


Figure 3.8: Diagram for Ex. 3.3.

Solution 3.3

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

$$C_V = 12.471 \qquad C_P = 20.785\ \text{J mol}^{-1}\ \text{K}^{-1}$$

The cycle is shown on a PV diagram in Fig. 3.8. Take as a basis 1 mol of gas.

(a) For an ideal gas undergoing adiabatic compression, $Q = 0$; whence

$$\Delta U = W = C_V\,\Delta T = (12.471)(150 - 70) = 998\ \text{J}$$

$$\Delta H = C_P\,\Delta T = (20.785)(150 - 70) = 1{,}663\ \text{J}$$

Pressure P_2 is found from Eq. (3.30b):

$$P_2 = P_1\left(\frac{T_2}{T_1}\right)^{\gamma/(\gamma-1)} = (1)\left(\frac{150 + 273.15}{70 + 273.15}\right)^{2.5} = 1.689\ \text{bar}$$

(b) For this constant-pressure process,

$$Q = \Delta H = C_P\,\Delta T = (20.785)(70 - 150) = -1{,}663\ \text{J}$$

$$\Delta U = C_V\,\Delta T = (12.471)(70 - 150) = -998\ \text{J}$$

$$W = \Delta U - Q = -998 - (-1{,}663) = 665\ \text{J}$$

(c) For ideal gases undergoing an isothermal process, ΔU and ΔH are zero; Eq. (3.27) yields:

$$Q = -W = RT\ln\frac{P_3}{P_1} = RT\ln\frac{P_2}{P_1} = (8.314)(343.15)\ln\frac{1.689}{1} = 1{,}495\ \text{J}$$

For the entire cycle,

$$\begin{aligned} Q &= 0 - 1{,}663 + 1{,}495 = -168\ \text{J} \\ W &= 998 + 665 - 1{,}495 = 168\ \text{J} \\ \Delta U &= 998 - 998 + 0 = 0 \\ \Delta H &= 1{,}663 - 1{,}663 + 0 = 0 \end{aligned}$$

The property changes ΔU and ΔH both are zero for the entire cycle, because the initial and final states are identical. Note also that $Q = -W$ for the cycle. This follows from the first law with $\Delta U = 0$.

Example 3.4

If the processes of Ex. 3.3 are carried out *irreversibly* but so as to accomplish exactly the same *changes of state*— the same changes in P, T, U, and H— then different values of Q and W result. Calculate Q and W if each step is carried out with an efficiency of 80%.

Solution 3.4

If the same changes of state as in Ex. 3.3 are carried out by irreversible processes, the property changes for the steps are identical with those of Ex. 3.3. However, the values of Q and W change.

(*a*) For mechanically reversible, adiabatic compression, $W = 998$ J. If the process is 80% efficient compared with this, $W = 998/0.80 = 1{,}248$ J. This step cannot here be adiabatic. By the first law,

$$Q = \Delta U - W = 998 - 1{,}248 = -250 \text{ J}$$

(*b*) The work for the mechanically reversible cooling process is 665 J. For the irreversible process, $W = 665/0.80 = 831$ J, and

$$Q = \Delta U - W = -998 - 831 = -1{,}829 \text{ J}$$

(*c*) As work is done *by* the system in this step, the irreversible work in absolute value is less than the reversible work of $-1{,}495$ J:

$$W = (0.80)(-1{,}495) = -1{,}196 \text{ J}$$

$$Q = \Delta U - W = 0 + 1{,}196 = 1{,}196 \text{ J}$$

For the entire cycle, ΔU and ΔH are zero, with

$$Q = -250 - 1{,}829 + 1{,}196 = -883 \text{ J}$$

$$W = 1{,}248 + 831 - 1{,}196 = 883 \text{ J}$$

A summary of these results and those for Ex. 3.3 is given in the following table; values are in joules.

	Mechanically reversible, Ex. 3.3				Irreversible, Ex. 3.4			
	ΔU	ΔH	Q	W	ΔU	ΔH	Q	W
(*a*)	998	1,663	0	998	998	1,663	−250	1,248
(*b*)	−998	−1,663	−1,663	665	−998	−1,663	−1,829	831
(*c*)	0	0	1,495	−1,495	0	0	1,196	−1,196
Sum	0	0	−168	168	0	0	−883	883

The cycle is one which requires work and produces an equal amount of heat. The striking feature of the comparison shown in the table is that the total work required when the cycle consists of three irreversible steps is more than five times the total work required when the steps are mechanically reversible, even though each irreversible step is assumed 80% efficient.