UNIT V

GAS MIXTURES AND THERMODYNAMIC RELATIONS

5.1 IDEAL GAS

An **ideal gas** is a theoretical gas composed of a set of randomly-moving point particles that interact only through elastic collisions. The ideal gas concept is useful because it obeys the ideal gas law, a simplified equation of state, and is amenable to analysis under statistical mechanics.

At normal ambient conditions such as standard temperature and pressure, most real gases behave qualitatively like an ideal gas. Generally, deviation from an ideal gas tends to decrease with higher temperature and lower density, as the work performed by intermolecular forces becomes less significant compared with the particles' kinetic energy, and the size of the molecules becomes less significant compared to the empty space between them.

EQUATION TABLE FOR AN IDEAL GAS

Quantity	General Equation	Isobaric $\Delta p = 0$	Isochoric $\Delta V = 0$	Isothermal $\Delta T = 0$	Adiabatic $Q = 0$
Work W	$\delta W = p dV$	$p\Delta V$	0	$nRT \ln \dfrac{V_2}{V_1}$	$C_V (T_1 - T_2)$
Heat Capacity C	(as for real gas)	$C_p = \dfrac{5}{2} nR$	$C_V = \dfrac{3}{2} nR$		
Internal Energy ΔU	$\Delta U = \dfrac{3}{2} nR\Delta T$	$Q - W$ $Q_p - p\Delta V$	Q $C_V (T_2 - T_1)$	0 $Q = W$	$-W$ $C_V (T_2 - T_1)$
Enthalpy ΔH	$H = U + pV$	$C_p (T_2 - T_1)$	$Q_V + V\Delta p$	0	$C_p (T_2 - T_1)$
Entropy ΔS	$ds = c_p \dfrac{dT}{T} - R \dfrac{dp}{p}$ [2]	$C_p \ln \dfrac{T_2}{T_1}$	$C_V \ln \dfrac{T_2}{T_1}$	$\dfrac{nR \ln \dfrac{V_2}{V_1}}{\dfrac{Q}{T}}$	$C_p \ln \dfrac{V_2}{V_1} + C_V \ln \dfrac{p_2}{p_1} = 0$

5.2 REAL GAS

Real gas, as opposed to a Perfect or Ideal Gas, effects refers to an assumption base where the following are taken into account:

• Compressibility effects
• Variable heat capacity
• Van der Waals forces
• Non-equilibrium thermodynamic effects
• Issues with molecular dissociation and elementary reactions with variable composition.

For most applications, such a detailed analysis is "over-kill" and the ideal gas approximation is used. Real-gas models have to be used near condensation point of gases, near critical point, at very high pressures, and in several other less usual cases.

4.3 VAN DER WAALS MODELISATION

Real gases are often modeled by taking into account their molar weight and molar volume

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

Where P is the pressure, T is the temperature, R the ideal gas constant, and Vm the molar volume. a and b are parameters that are determined empirically for each gas, but are sometimes estimated from their critical temperature (Tc) and critical pressure (Pc) using these relations:

$$a = \frac{27R^2T_c^2}{64P_c}$$

$$b = \frac{RT_c}{8P_c}$$

5.4 REDLICH–KWONG MODELISATION

The Redlich–Kwong equation is another two-parameters equation that is used to modelize real gases. It is almost always more accurate than the Van der Waals equation, and often more accurate than some equation with more than two parameters. The equation is

$$RT = P + \frac{a}{V_m(V_m + b)T^{\frac{1}{2}}}(V_m - b)$$

5.5 THERMODYNAMICS RELATIONS

Fundamental Equation of Thermodynamics

- $U = TS - pV + \mu N$

Enthalpy

- $H \equiv U + pV = \mu N + TS$

Helmholtz free energy

- $A \equiv U - TS = \mu N - pV$

Gibbs free energy

- $G \equiv U + pV - TS = H - TS = \mu N$

Maxwell relations

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial p}{\partial S}\right)_{V,N}$$

$$\left(\frac{\partial T}{\partial p}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{p,N}$$

$$\left(\frac{\partial T}{\partial V}\right)_{p,N} = -\left(\frac{\partial p}{\partial S}\right)_{T,N}$$

$$\left(\frac{\partial T}{\partial p}\right)_{V,N} = \left(\frac{\partial V}{\partial S}\right)_{T,N}$$

Maxwell relations.

The Maxwell's equations relate entropy to the three directly measurable properties p,v and T for pure simple compressible substances.

From first law of thermodynamics,

$$Q = W + U$$

Rearranging the parameters

$$Q = U + W \qquad \text{since } [ds = - \ , \ W = pdv \ ]$$

``

$$Tds = du + pdv$$

$$du = Tds - pdv \qquad ---------- (1)$$

We know that, $h = u + pv$

$$dh = du + d(pv)$$

$$= du + vdp + pdv \qquad ---------- (2)$$

Substituting the value du in equation (2),

$$dh = Tds + pdv + vdp - pdv$$

$$dh = Tds + vdp \qquad ---------- (3)$$

By Helmotz's function,

$$a = u - Ts$$

$$da = du - d(Ts)$$

$$= du - Tds - sdT \qquad ---------- (4)$$

Substituting the values of du in equation (4),

$$da = Tds - pdv - Tds - sdT$$

$$T = - pdv - sdT \qquad ---------- (5)$$

By Gibbs functions,

$$G = h - Ts$$

$$dg = dh - d(Ts)$$

$$dg = dh - Tds - sdT \qquad ----------- (6)$$

Substituting the value of dh in equation (6),

So, dg becomes

$$dg = Tds + vdp - Tds - sdT$$

$$dg = vdp - sdT \qquad ----------- (7)$$

By inverse exact differential we can write equation (1)

as, $du = Tds - pdv$

$$\overline{} \qquad \overline{} \qquad ----------- (8)$$

Similarly, equation (3) can be written as,

$$dh = Tds + vdp$$
$$\overline{} \qquad \overline{}$$

Similarly, equation (5) can be written as,

Similarly, equation (7) can be written as,

$$dg = vdp - sdT$$
$$\overline{} \qquad \overline{}$$

These equations 8, 9, 10 and 11 are Maxwell's equation.

Incremental processes

- $dU = T\, dS - p\, dV + \mu\, dN$
- $dA = -S\, dT - p\, dV + \mu\, dN$

- $dG = -S\, dT + V\, dp + \mu\, dN = \mu\, dN + N\, d\mu$
- $dH = T\, dS + V\, dp + \mu\, dN$

Proof #1

An example using the above methods is:

$$\left(\frac{\partial T}{\partial p}\right)_H = -\frac{1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T$$

$$\left(\frac{\partial T}{\partial p}\right)_H \left(\frac{\partial p}{\partial H}\right)_T \left(\frac{\partial H}{\partial T}\right)_p = -1$$

$$\left(\frac{\partial T}{\partial p}\right)_H = -\left(\frac{\partial H}{\partial p}\right)_T \left(\frac{\partial T}{\partial H}\right)_p$$

$$= \frac{-1}{\left(\frac{\partial H}{\partial T}\right)_p}\left(\frac{\partial H}{\partial p}\right)_T \quad C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

$$\Rightarrow \left(\frac{\partial T}{\partial p}\right)_H = -\frac{1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T$$

Tds relations in terms of temperature and pressure changes and temperature and volume changes.

The entropy (s) of pure substance can be expressed as a function of temperature (T) and pressure (p).

$$s = f(T,p)$$

We know that,
From Maxwell equation, we know that

$$— \qquad —$$

Substituting in ds equation,

$$ds = — \, dT \qquad — \, dp$$

Multiplying by T on both sides of the equation,

$$Tds = \quad dT \qquad — \, dp$$

This is known as the first form of entropy equation or the first Tds equation. By considering the entropy of a pure substance as a function of temperature and specific volume,

i.e. $s = f(T,v)$

From the Maxwell Equations, we know that

Substituting in ds Equation,

$$ds = - \, dT + \quad - \quad dv$$

Multiplying by T,

$$Tds = \quad dT + T \quad - \quad dv$$

This is known as the second form of entropy equation or the second Tds equation

4.6 THE JOULE-THOMSON COEFFICIENT OF AN IDEAL GAS IS ZERO

The Joule-Thomson coefficient is defined as the change in temperature with change in pressure, keeping the enthalpy remains constant. It is denoted by,

We know that the equation of state as,

$$pV = RT$$

Differentiating the above equation of state with respect to T by keeping pressure, p constant. $-\!\!-$ $\;\;$ $=$ $\;-$

$$\mu = 0.$$

It implies that the Joule-Thomson coefficient is zero for ideal gas.

4.7 CLAUSIUS–CLAPEYRON RELATION

The **Clausius–Clapeyron relation**, named after Rudolf Clausius and Émile Clapeyron, who defined it sometime after 1834, is a way of characterizing the phase transition between two phases of matter, such as solid and liquid. On a pressure–temperature (P–T) diagram, the line separating the two phases is known as the coexistence curve. The Clausius–Clapeyron relation gives the slope of this curve. Mathematically,

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{L}{T\,\Delta V}$$

where $\mathrm{d}P\,/\,\mathrm{d}T$ is the slope of the coexistence curve, L is the latent heat, T is the temperature, and V is the volume change of the phase transition.

Pressure Temperature Relations
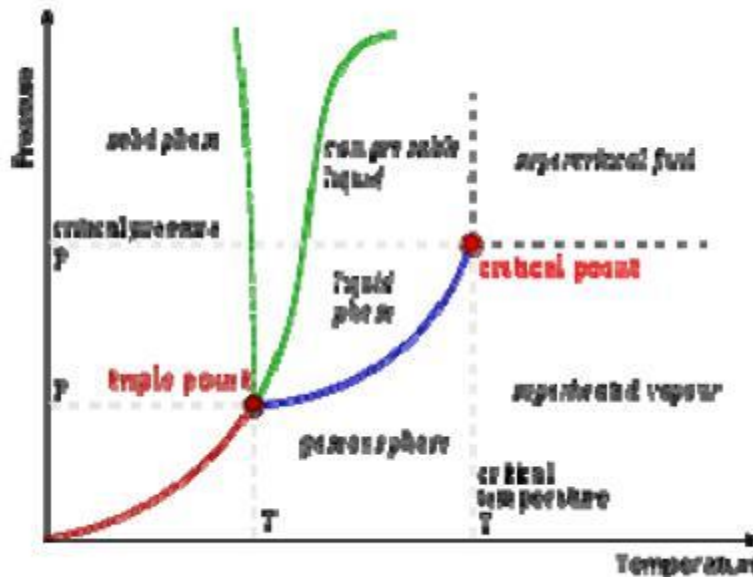
A typical phase diagram. The dotted line gives the anomalous behavior of water. The Clausius–Clapeyron relation can be used to (numerically) find the relationships between pressure and temperature for the phase change boundaries. Entropy and volume changes (due to phase change) are orthogonal to the plane of this drawing

Derivation

Using the state postulate, take the specific entropy, s, for a homogeneous substance to be a function of specific volume, v, and temperature, T.

$$ds = \frac{\partial s}{\partial v} dv + \frac{\partial s}{\partial T} dT.$$

During a phase change, the temperature is constant, so

$$ds = \frac{\partial s}{\partial v} dv.$$

Using the appropriate Maxwell relation gives

$$ds = \frac{\partial P}{\partial T} dv.$$

Since temperature and pressure are constant *during a phase change*, the derivative of pressure with respect to temperature is not a function of the specific volume. Thus the partial derivative may be changed into a total derivative and be factored out when taking an integral from one phase to another,

$$s_2 - s_1 = \frac{dP}{dT}(v_2 - v_1),$$

$$\frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{\Delta s}{\Delta v}.$$

is used as an operator to represent the change in the variable that follows it— final (2) minus initial (1) For a closed system undergoing an internally reversible process, the first law is

$$du = \delta q + \delta w = T ds - P dv.$$

This leads to a version of the Clausius–Clapeyron equation that is simpler to integrate:

$$\frac{dP}{P} = \frac{\Delta h}{R} \frac{dT}{T^2},$$

$$\ln P = -\frac{\Delta h}{R} \frac{1}{T} + C,$$

$$\ln \frac{P_2}{P_1} = \frac{\Delta h}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right).$$

C is a constant of integration

These last equations are useful because they relate saturation pressure and saturation temperature to the enthalpy of phase change, *without* requiring specific volume data. Note that in this last equation, the subscripts 1 and 2 correspond to different locations on the pressure versus temperature phase lines. In earlier equations, they corresponded to different specific volumes and entropies at the same saturation pressure and temperature.

The Joule–Thomson (Kelvin) coefficient

The rate of change of temperature T with respect to pressure P in a Joule– Thomson process (that is, at constant enthalpy H) is the Joule–Thomson (Kelvin) coefficient μJT. This coefficient can be expressed in terms of the gas's volume V, its heat capacity at constant pressure Cp, and its coefficient of thermal expansion α as

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial P}\right)_H = \frac{V}{C_P}(\alpha T - 1)$$

See the Appendix for the proof of this relation. The value of μJT is typically expressed in °C/bar (SI units: K/Pa) and depends on the type of gas and on the temperature and pressure of the gas before expansion.

All real gases have an inversion point at which the value of μJT changes sign. The temperature of this point, the Joule–Thomson inversion temperature, depends on the pressure of the gas before expansion. In a gas expansion the pressure decreases, so the sign of is always negative. With that in mind, the following table explains when the Joule–Thomson effect cools or warms a real gas:

If the gas temperature is	then μJT is	since ∂P is	thus ∂T must be	so the gas
below the inversion temperature	positive	always negative	negative	cools
above the inversion temperature	negative	always negative	positive	warms

Helium and hydrogen are two gases whose Joule–Thomson inversion temperatures at a pressure of one atmosphere are very low (e.g., about 51 K (−222 °C) for helium). Thus, helium and hydrogen warm up when expanded at constant enthalpy at typical room temperatures. On the other hand nitrogen and oxygen, the two most abundant gases in air, have inversion temperatures of 621 K (348 °C) and 764 K (491 °C) respectively: these gases can be cooled from room temperature by the Joule–Thomson effect.

Derivation of the Joule–Thomson (Kelvin) coefficent A derivation of the formula

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial P}\right)_H = \frac{V}{C_p}(\alpha T - 1)$$

for the Joule–Thomson (Kelvin) coefficient.

The partial derivative of T with respect to P at constant H can be computed by expressing the differential of the enthalpy dH in terms of dT and dP, and equating the resulting expression to zero and solving for the ratio of dT and dP. It follows from the fundamental thermodynamic relation that the differential of the enthalpy is given by:

$$dH = TdS + VdP$$

$$dH = C_p dT + \left[V + T\left(\frac{\partial S}{\partial P}\right)_T\right]dP$$

The remaining partial derivative of S can be expressed in terms of the coefficient of thermal expansion via a Maxwell relation as follows. From the fundamental thermodynamic relation, it follows that the differential of the Gibbs energy is given by:

$$dG = -SdT + VdP$$

The symmetry of partial derivatives of G with respect to T and P implies that:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -V\alpha$$

where α is the coefficient of thermal expansion. Using this relation, the differential of H can be expressed as

$$dH = C_p dT + V(1 - T\alpha)dP$$

Expressing dS in terms of dT and dP gives:

$$dH = T \left(\frac{\partial S}{\partial T} \right)_P dT + \left[V + T \left(\frac{\partial S}{\partial P} \right)_T \right] dP$$

Using

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_{P \text{(see Specific heat capacity)}}, \text{ we can write:}$$

4.8 SOLVED PROBLEMS

1. **A mixture of ideal gases consists of 7kg ofand 2kg ofat a pressure of 4bar and a temperature of 27°C. Determine:**
    i.   **Mole fraction of each constituent,**
    ii.   **Equivalent molecular weight of the mixture,**
    iii.   **Equivalent gas constant of the mixture,**
    iv.   **The partial pressure and partial volumes,**
    v.   **The volume and density of the mixture**

    Given data:

    M1=7kg

    = M22kg

    p = 4bar   ‾‾‾‾‾‾

    T = 27°C

    Solution: ‾‾‾‾‾‾

Describe Joule Kelvin effect with the help of T-p diagram

The Joule Kelvin effect or Joule Thomson effect is an efficient way of cooling gases. In this, a gas is made to undergo a continuous throttling process. A constant pressure is

maintained at one side of a porous plug and a constant lower pressure at the other side. The apparatus is thermally insulated so that the heat loss can be measured.

Joule – Thomson co – efficient is defined as the change in temperature with change in pressure, keeping the enthalpy remains constant. It is denoted by,

$$\mu = \quad —$$

Throttling process:

It is defined as the fluid expansion through a minute orifice or slightly opened valve. During this process, pressure and velocity are reduced. But there is no heat transfer and no work done by the system. In this process enthalpy remains constant.

Joule Thomson Experiment:

The figure shows the arrangement of porous plug experiment. In this experiment, a stream of gas at a pressure and temperature is allowed to flow continuously through a porous pig. The gas comes out from the other side of the porous pig at a pressure and temperature .

Throttle
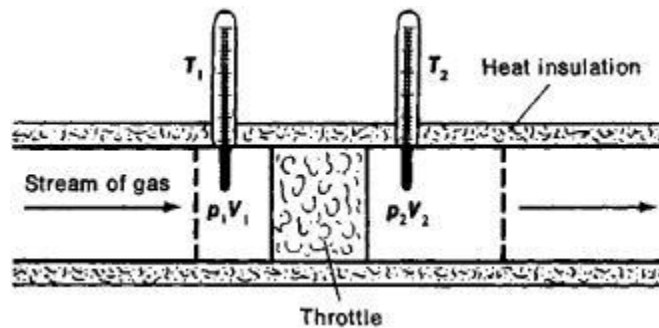
The whole apparatus is insulated. Therefore no heat transfer takes place. Q = 0.

The system does not exchange work with the surroundings.

So, W=0 from steady flow energy equation we know that

$$g + \quad — \quad + (+ \quad) + Q = g + \quad — \quad + (+ \quad) + W$$

Since there is no considerable change velocity, and , Q=0,W=0, are applied in steady flow energy equation. Therefore,

It indicates that the enthalpy is constant for throttling process.
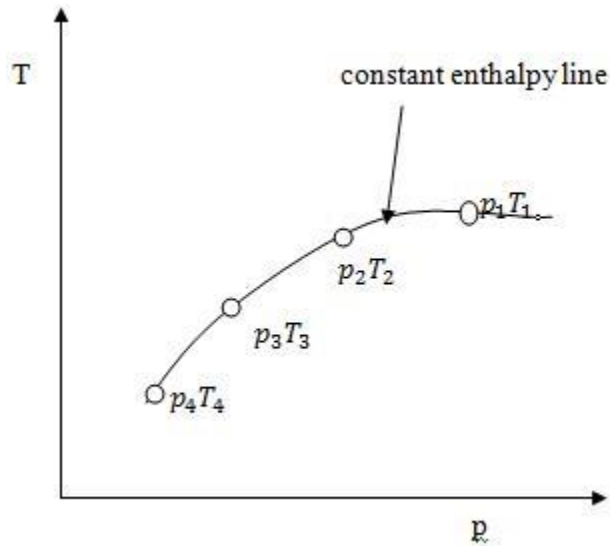
It is assumed that a series of experiments performed on a real gas keeping the initial pressure and temperature constant with various down steam pressures ( ). It is found that the down steam temperature also changes. The results from these experiments can be plotted as enthalpy curve on T-p plane.

The slope of a constant enthalpy is known as Joule Thomson Coefficient. It is denoted by μ.

For real gas, μ may be either positive or negative depending upon the thermodynamic state of the gas.

Example . *Find the increase in entropy when 2 kg of oxygen at 60°C are mixed with 6 kg of nitrogen at the same temperature. The initial pressure of each constituent is 103 kPa and is same as that of the mixture.*

Solution.

Given: Mass of oxygen, m_{O_2} = 2 kg

Temperature of oxygen, T_{O_2} = 60°C = 60 + 273 = 333 K

Mass of nitrogen, m_{N_2} = 6 kg

Initial pressure of each constituent,

$$p_{O_2} = p_{N_2} = 103 \text{ kPa}$$

We know that number of moles of oxygen,

$$n_{O_2} = \frac{\text{Mass of oxygen } (m_{O_2})}{\text{Molecular mass of oxygen } (M_{O_2})} = \frac{2}{32} = 0.0625$$

and number of moles of nitrogen,

$$n_{N_2} = \frac{m_{N_2}}{M_{N_2}} = \frac{6}{28} = 0.2143$$

Total number of moles in the mixture,

$$n = n_{O_2} + n_{N_2} = 0.0625 + 0.2143 = 0.2768$$

We know that mole fraction of oxygen,

$$x_{O_2} = \frac{n_{O_2}}{n} = \frac{p_{O_2}}{p} = \frac{0.0625}{0.2768} = 0.2258$$

and mole fraction of nitrogen,

$$x_{N_2} = \frac{n_{N_2}}{n} = \frac{p_{N_2}}{p} = \frac{0.2143}{0.2768} = 0.7742$$

We know that increase in entropy,

$$ds = -2.3 \, n_{O_2} R_u \log \left(\frac{p_{O_2}}{p} \right) - 2.3 \, n_{N_2} R_u \log \left(\frac{p_{N_2}}{p} \right)$$

$$= -2.3 \times 0.0625 \times 8.314 \log (0.2258) - 2.3 \times 0.2143 \times 8.314 \log (0.7742)$$

$$= 0.7724 + 0.4555 = 1.2279 \text{ kJ/kg } \textbf{Ans.}$$

Compressibility factor
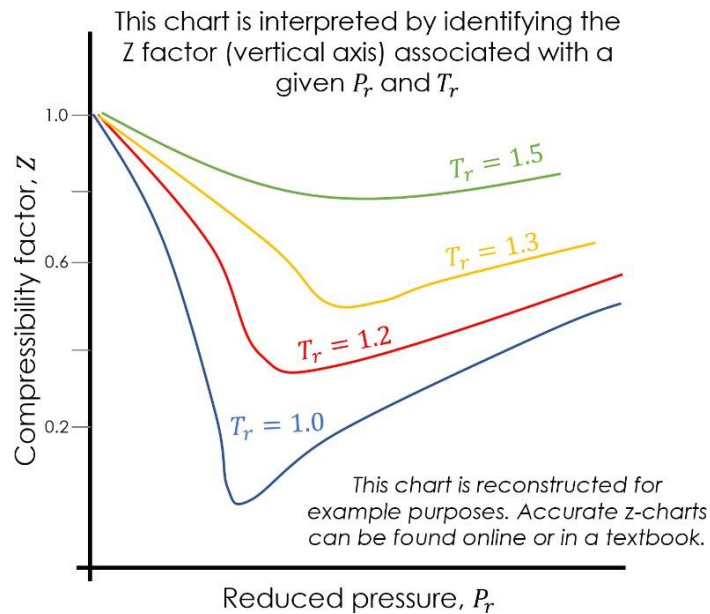
Ideal gasses follow the formula $PV = mRT$, but real gasses fall on a spectrum of compressibility, denoted by z. This is a ratio of the actual volume of a gas to the volume that is predicted by an ideal gas version at a given temperature and pressure.

Z may be greater than or less than 1. A value of 1 indicates an ideal gas.

$$z = \frac{P}{v} = \frac{PV}{rmT}$$
$$\frac{}{\frac{R}{T}}$$

Subscript R indicates "reduced", and subscript C indicates "critical". These are used to create a general graph that can be applied to any gas, rather than graphs specifically for each type of gas.

$$P_R = \frac{P}{T_c} reduced\ pressure$$
$$T_R = \frac{T}{T_c} = reduced\ temperature$$

This chart is interpreted by identifying the Z factor (vertical axis) associated with a given P_r and T_r

$T_r = 1.5$

$T_r = 1.3$

$T_r = 1.2$

$T_r = 1.0$

Compressibility factor, Z

1.0

0.6

0.2

This chart is reconstructed for example purposes. Accurate z-charts can be found online or in a textbook.

Reduced pressure, P_r

$$v' = \underline{p}suedo - reduced\ specific\ volume$$

Once the compressibility factor is known, the modified ideal gas equation can be used tocontinue solving a given problem:

$$Pv = zRT$$

The ideal-gas equation is very simple and thus very convenient to use. Gases deviate from ideal-gas behavior significantly at states near the saturation region and the critical point. This deviation from ideal-gas behavior at a given temperature and pressure can accurately be accounted for bythe introduction of a correction factor called the compressibility factor *Z*. It is defined as:

$$Z = \frac{Pv}{RT} \qquad \text{(2-17)}$$

$$Pv = ZRT \qquad \text{(2-18)}$$

or, it can also be expressed as:

$$Z = \frac{v_{\text{actual}}}{v_{\text{ideal}}} \qquad \text{(2-19)}$$

where v_{ideal} = *RT/P*. Obviously, *Z* = 1

For ideal gases. For real gases *Z* can be greater than or less than unity(Fig. 2-55).

Gases behave differently at a given temperature and pressure, but they behave very much the same at temperatures and pressures normalized with respect to their critical temperatures and pressures.
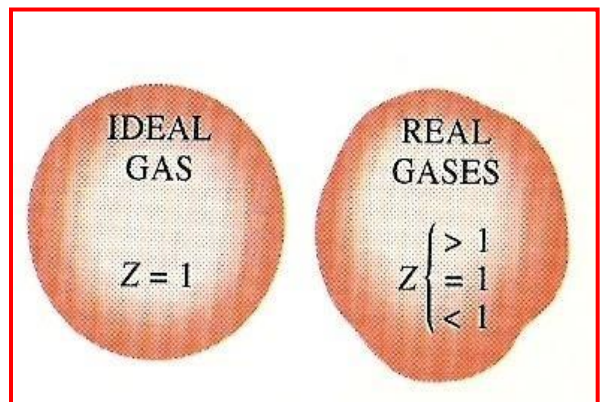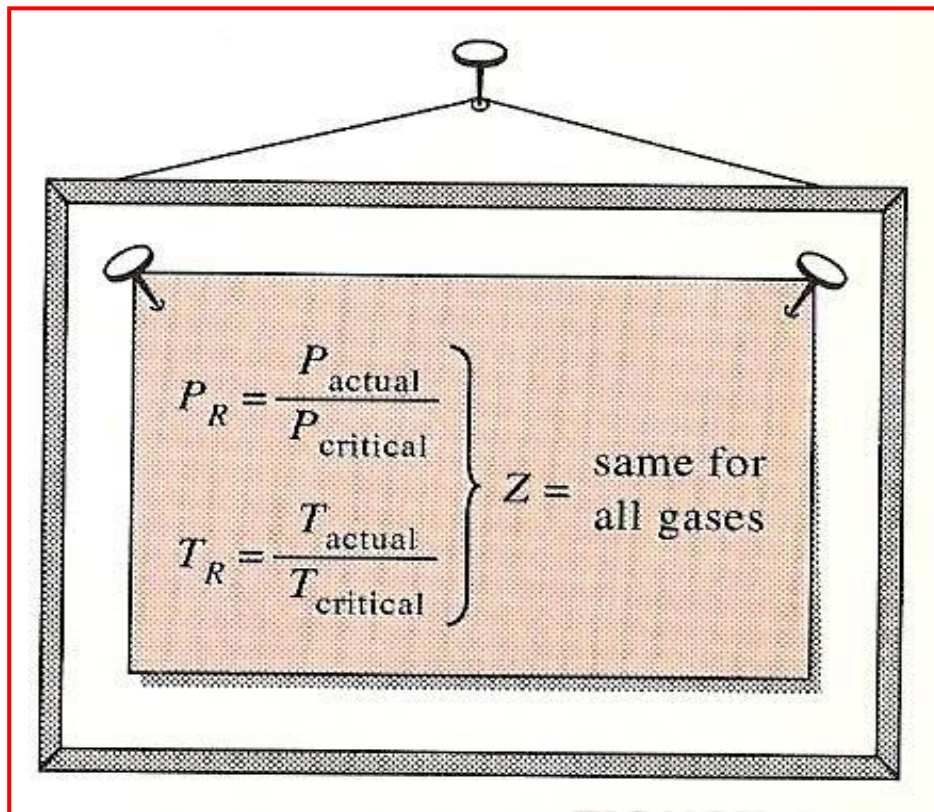

Figure 2-55. The compressibility factor is unity for ideal gases.

$$P_R = \frac{P}{P_{cr}} \quad \text{and} \quad T_R = \frac{T}{T_{cr}} \qquad\qquad (2\text{-}20)$$

Here, P_R = reduced pressure, T_R = reduced temperature

The Z factor for all gases is approximately the same at the same reduced pressure and temperature (Fig. 2-56). This is called the principle of corresponding states.


$$P_R = \frac{P_{actual}}{P_{critical}}$$
$$T_R = \frac{T_{actual}}{T_{critical}} \Biggr\} \quad Z = \begin{array}{l}\text{same for}\\ \text{all gases}\end{array}$$

Figure 2-56. The compressibility factor is the same for all gases at the reduced pressure and temperature   (principle of corresponding states).

In Fig. 2-57, the experimentally determined Z values are plotted against P_R and T_R for several gases. The gases seem to obey the

principle of corresponding states reasonably well. By curve-fitting all the data, we obtain the generalized compressibilitychart which can be used for all gages.
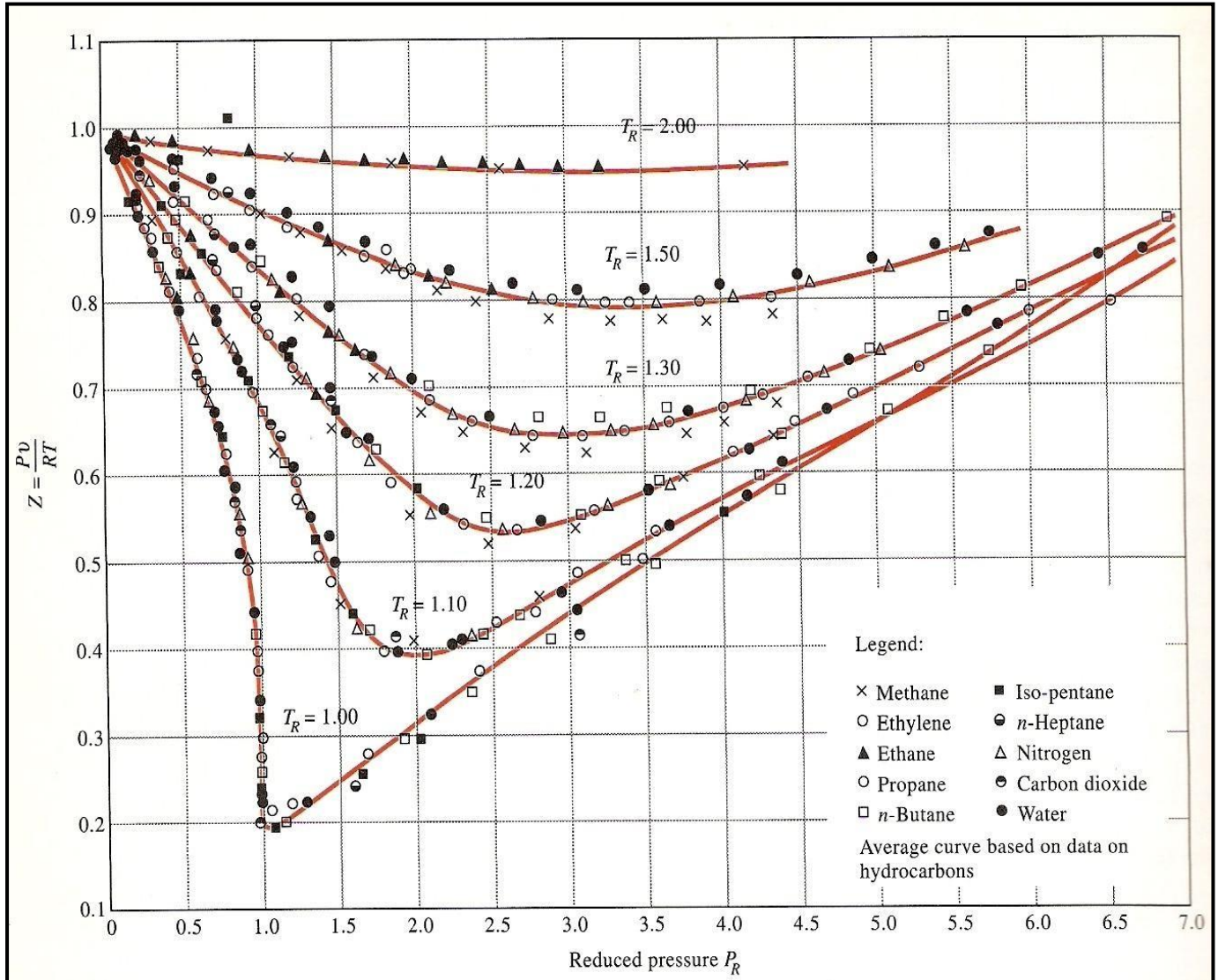


Figure 2-57. Comparison of *Z* factors for various gases.

The following observations can be made from generalized compressibility chart:

1. At very low pressures ($P_R \ll 1$), the gases behave as an ideal gas regardless of temperature (Fig. 2-58).

2. At high temperatures ($T_R > 2$), ideal-gas behavior canassumed with good accuracy regardless of pressure (exceptwhen $P_R \gg 1$).

3. The deviation of a gas from ideal-gas behavior is greatest in the vicinity of the critical point (Fig. 2-59).
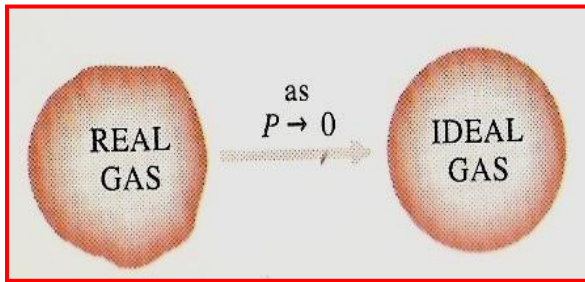
Figure 2-58. At very low pressures, all gases approach ideal-gas behavior (regardless of their temperature).
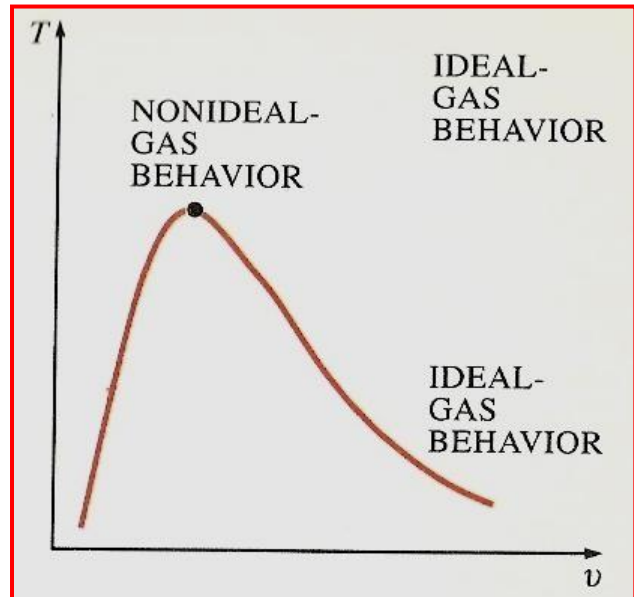
Figure 2-59. Gases deviate from the ideal-gas behavior most in the neighborhood of the critical point.

Example 2-10.

Determine the specific volume of refrigerant-12 at 1 MPa and 50℃, using (*a*) the refrigerant-12 tables, (*b*) the ideal-gas equation of state, and (*c*) the generalized compressibility chart. Also determine the error involved in parts (*b*) and (*c*).
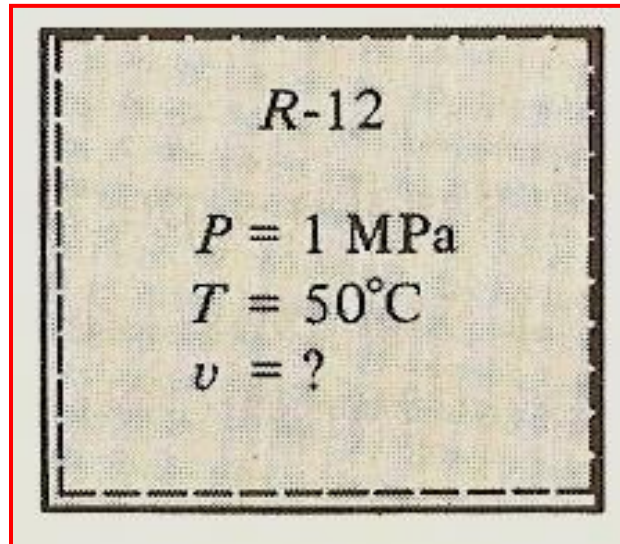
Solution

A sketch of the system is given in Fig. 2-60. The gas constant, the critical pressure, and the critical temperature of refrigerant-12 are determined from Table A-1 to be:

$R = 0.0688$ kPa.m^3/(kg.K)

$P_{cr} = 4.01$ MPa

$T_{cr} = 384.7$ K

R-12

$$P = 1 \text{ MPa}$$
$$T = 50°C$$
$$v = ?$$

Figure 2-60. Schematic for **Example 2-10**.

(a) The specific volume of refrigerant-12 at the specified state is determined from Table A-13 to be:

$$\left.\begin{array}{l} P = 1 \text{ MPa} \\ T = 50°C \end{array}\right\} \quad v = 0.01837 \text{ m}^3/\text{kg}$$

This is the experimentally determined value, and thus it is the most accurate.

(b) The specific volume of the refrigerant-12 under the ideal-gas assumption is determined from the idea-gas relation (Eq.2-9) to:

$$v = \frac{RT}{P} = \frac{[(0.0688 \text{ kPa.m3})/(\text{kg.K})](323 \text{ K})}{1000 \text{ kPa}} = 0.02222 \text{ m}^3/\text{kg}$$

Therefore, treating the refrigerant-12 vapor as an ideal gas would result in as error of:

$$\% \text{ error} = \frac{0.02222 - 0.01837}{0.01837} \times 100 = 20.8\ \%$$

(c) To determine the correction factor *Z* from the compressibility chart, we first need to calculate the reduce pressure and temperature:

$$P_R = \frac{P}{P_{cr}} = \frac{1\ \text{MPa}}{4.01\ \text{MPa}} = 0.249$$

$$Z = 0.83$$

(Fig. A-30)

$$T_R = \frac{T}{T_{cr}} = \frac{323\ \text{K}}{384.7} = 0.840$$

Thus, $\quad v = Zv_{\text{ideal}} = (0.83)(0.02222\ \text{m}^3/\text{kg}) = 0.01844\ \text{m}^3/\text{kg}$

$$\% \text{ error} = \frac{0.01844 - 0.01837}{0.01837} \times 100 = 0.38\ \%$$

When *P* and v, or *T* and v, are given instead of *P* and *T*, the generalized compressibility chart can still be used to determine the third property, but it word involve tedious trial and error, Therefore, it is very convenient to define one more reduced property called the pseudo-reduced specific volume v_R as:

$$v_R = \frac{v_{\text{actual}}}{RT_{cr}/P_{cr}} \qquad\qquad \textbf{(2-21)}$$

v_R is defined differently from P_R and T_R. It is related to T_{cr} and P_{cr} instead of v_{cr}. Lines of constant v_R are also added to the compressibility charts, and this enables one to determine T or P without having to resort to time-consuming iterations (Fig. 2-61).

$$P_R = \frac{P}{P_{cr}}$$
$$v_R = \frac{v}{RT_{cr}/P_{cr}} \left.\begin{array}{l} \\ \\ \end{array}\right\} \begin{array}{l} Z = \dots \\ \text{(Fig. A-30)} \end{array}$$

Figure 2-61. The compressibility factor can also be determining from a knowledge of P_R and v_R.

Example 2-11.

Determine the pressure of water vapor at 600°F and 0. 514 ft³/lbm, using (*a*) the steam tables, (*b*) the ideal-gas equation, and (*c*) the generalized compressibility chart?.

H_2O

$T = 600°F$
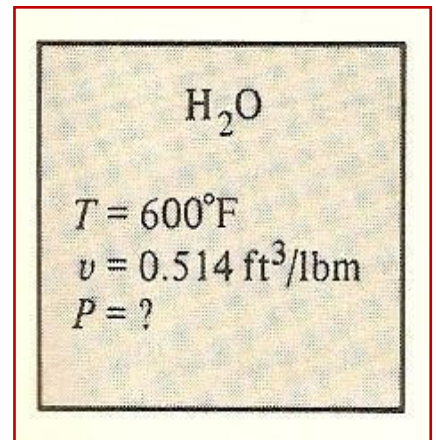$v = 0.514 \text{ ft}^3/\text{lbm}$
$P = ?$

Solution

A sketch of the system is given in Fig. 2-62. The gas constant, the critical pressure, and the critical temperature of steam are determined from Table A-1E to be:

Figure 2-62 Schematic for **Example 2-11**.

$$R = 0.5956 \text{ psia.ft}^3/(\text{lbm.R})$$

$$P_{cr} = 3204 \text{ psia}$$

$$T_{cr} = 1165.3 \text{ R}$$

(a) The pressure of steam at the specified state is determined

from Table A-6E to be:

$$v = 0.514 \text{ ft3/lbm} \atop T = 600°F \Big\} \quad P = 1000 \text{ psia}$$

This is the experimentally value, and thus it is the most accurate.

(b) The pressure of steam under the ideal-gas assumption is determined from the ideal-gas relation (Eq.2.9) to be:

$$P = \frac{RT}{v} = \frac{[0.5956 \text{ psia.ft3/(lbm.R)}](1060 \text{ R})}{0.514 \text{ ft3/lbm}} = 1228.3 \text{ psia}$$

Therefore, treating the steam as an ideal gas would result in an error of :

$$\% \text{ error} = \frac{1228.2 - 1000}{1000} \text{ x } 100 = 22.8 \%$$

(c) To determine the correction *Z* from the compressibility chart (Fig.A-30), we first need to calculate the pseudo-reducedspecific volume and the reduced temperature:

$$v_R = \frac{v_{acual}}{RT_{cr}/P_{cr}} = \frac{(0.514 \text{ ft}^3/\text{lbm})(3204 \text{ psia})}{[0.5056 \text{ psia.ft}^3/(\text{lbm.R})](1165.3 \text{ R})]}$$

$$= 2.373 \qquad\qquad\qquad P_R = 0.33$$

$$T_R = \frac{T}{T_{cr}} = \frac{1060 \text{ R}}{11653 \text{ R}} = 0.91$$

Thus, $\quad$ **$P = P_R P_{cr} = (0.33)(3204 \text{ psia}) = 1057.3 \text{ psia}$**

$$\% \text{ error} = \frac{1057.3 - 1000}{1000} \text{ x } 100 = 5.7 \%$$

Using the compressibility chart reduced the error from 22.8 to 5.7 percent, which is acceptable for most engineering purposes (Fig. 2-63). A bigger chart, of course, would give better resolution and reduce the reading errors. Notice that we did not have to determine Z in this problem since we could read P_R directly from the chart.

	P, psia
Exact	1000.0
Z chart	1057.3
Ideal gas	1228.3

(from Example 2-11)

Figure 2-63 Results obtained by using the compressibility chart are usually within a few percent of the experimentally determined values.

2-9. Other Equations of State

The ideal-gas equation of state is very simple, but its range of applicability is limited. It is desirable to have equations of state that represent the $P - v - T$ behavior of substances accurately over a larger region with no limitations. Several equations have been proposed for this purpose (Fig. 2-64).
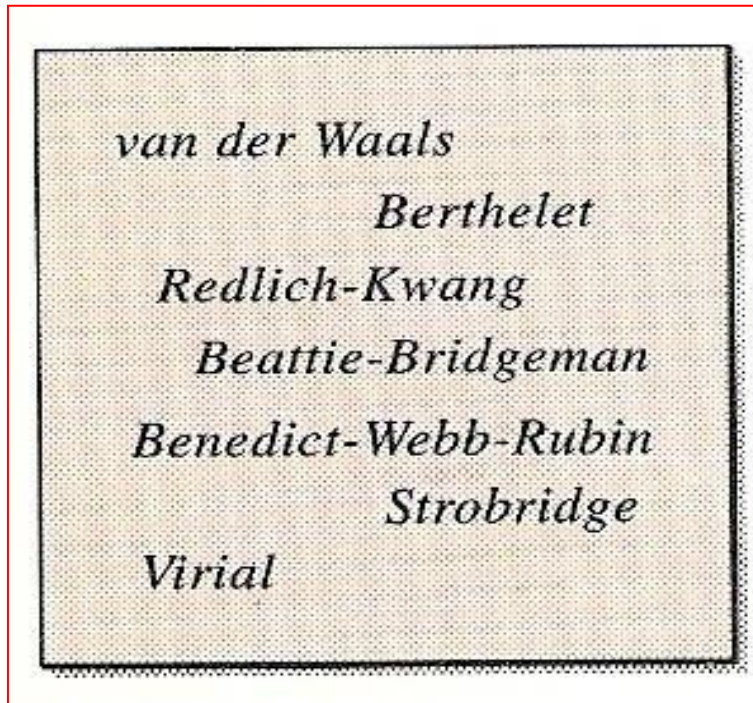
Figure 2-64 Several equations of state are proposed throughout the history.

Van der Waals Equation of State

The van der Waals equation of state is one of the earliest equations was proposed in 1873, and it has two constants which are determined from the behavior of a substance at the critical point. The van der Waals equation of state is given by:

$$\left(P + \frac{a}{v^2}\right)\left(v - b\right) = RT \qquad (2\text{-}22)$$

Van der Waals intended to improve the ideal-gas equation of state by including two of the effects not considered in the ideal-gas model: The intermolecular attraction forces and the volume occupied by the molecules themselves. a/v^2 accounts for the intermolecular attraction forces, and b accounts for the volume occupied by the gas molecules. Van der Waals proposed to correct this by replacing v in ideal-gas relation with the quality v

– b, where *b* represents the volume by the gas molecules per unit mass.

The equation determination of the two constants appearing in this equation is based on the observation that the critical isotherm on a *P-v* diagram has a horizontal inflection point at the critical point (Fig. 2-65). Thus the first and second derivatives of *P* with respect to v at the critical point must be zero. That is,

$$= 0 (2\text{-}23) = \text{const}$$

The costants *a* and *b* can be determined for any substance from the critical-point data alone (Table A-1).The van der Waals equation of state can also be expreeed on a unitmole basis by replacing the v in Eq. 2-22 by $\bar{v}$ and the *R* in Eq. 2-23 and 2-24 by R_u.
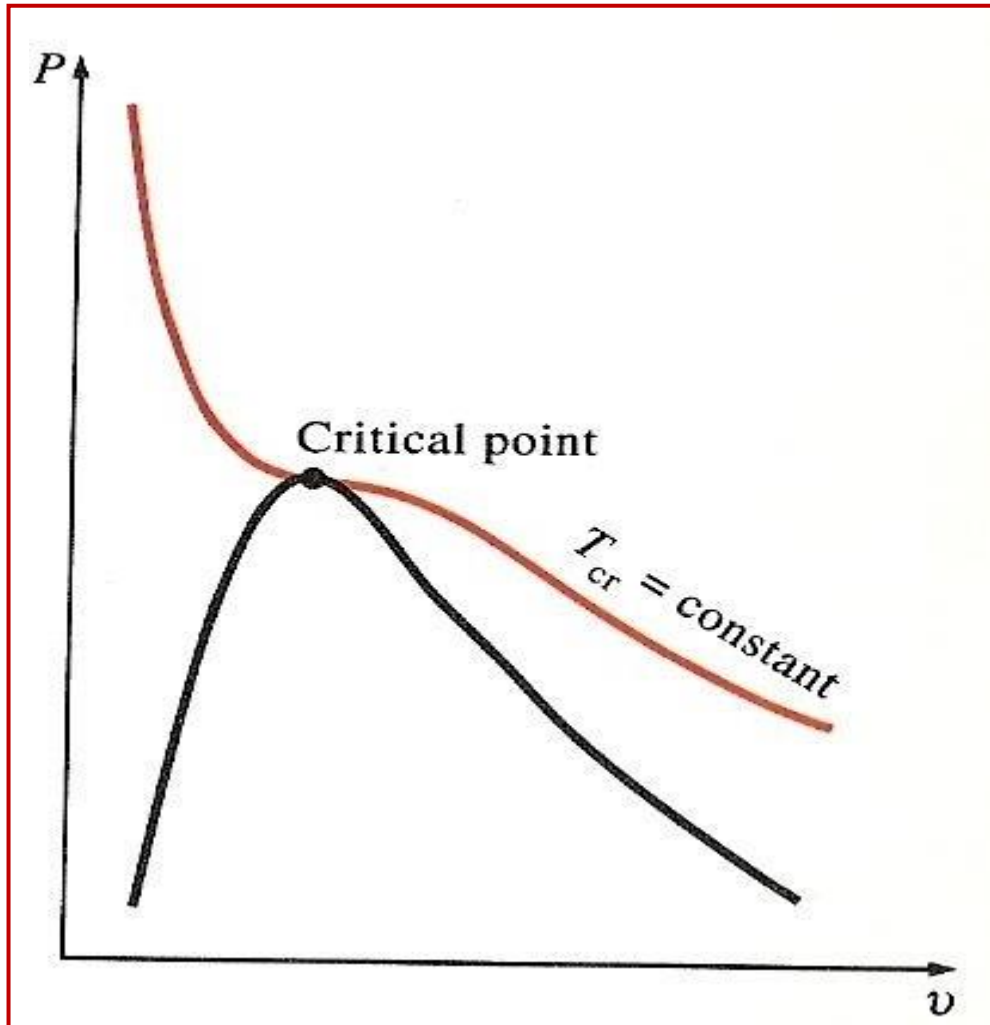
Figure 2-65 Critical isotherm of a pure substance has an inflection at the critical state.