

REAL GASES

7.1 REAL GAS

When a gas is found to disobey the perfect gas law, i.e. the equation of state for ideal gas, then it is called 'real gas'. Real gas behaviour can also be shown by a perfect gas at the changed thermodynamic states such as high pressure etc.

Deviation of real gas from ideal gas necessitates the suitable equation of state which can be used for interrelating the thermodynamic properties P , V , and T .

From the kinetic theory of gases it is obvious that the ideal gas equation of state suits the gas behaviour when intermolecular attraction and volume occupied by the molecules themselves is negligibly small in reference to gas volume. At high pressures intermolecular forces and volume of molecules both increase and so the gas behaviour deviates from ideal gas to real gas.

A number of mathematical equations of state suggested by Van der-Waals, Berthelot, Dieterici, Redlich-Kwong, Beattie-Bridgeman and Martin-Hou etc. are available for analysing the real gas behaviour.

Dalton's law and Amagat's law can also be used for real gases with reasonable accuracy in conjunction with modified equations of state.

As the ideal gas equation does not conform to the real gas behaviour in certain ranges of pressures and temperatures, so the perfect gas equation should be modified using compressibility factor for the gas at given pressure and temperature.

Such modified form of equations shall be;

$$P\bar{v} = Z \cdot \bar{R} \cdot T$$

Here Z is the compressibility factor, a function of pressure and temperature.

Thus, compressibility factor is like a correction factor introduced in ideal equation of state for suiting the real gas behaviour. Compressibility factor is an indication of deviation of a gas from ideal gas behaviour and can be mathematically given as;

$$Z = f(P, T)$$

or
$$Z = \frac{v_{\text{actual}}}{v_{\text{ideal}}}$$

Here, $v_{\text{ideal}} = \frac{RT}{P}$ i.e. $Z = 1$ for ideal gases while Z can be greater than or less than unity.

Individual graphical representations are available for getting the compressibility factor as shown in Fig 1.12. Compressibility factor charts are available for different substances.

Compressibility factors for various substances can also be shown on a generalized compressibility chart using reduced properties.

Reduced properties are non-dimensional properties given as ratio of existing property to critical property of substance. Such as reduced pressure is ratio of pressure of gas to critical pressure of gas. Similarly, reduced temperature can be given by ratio of temperature of gas to critical temperature of gas.

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Reduced pressure,
$$p_R = \frac{p}{p_c}$$

Reduced temperature,
$$T_R = \frac{T}{T_c}$$

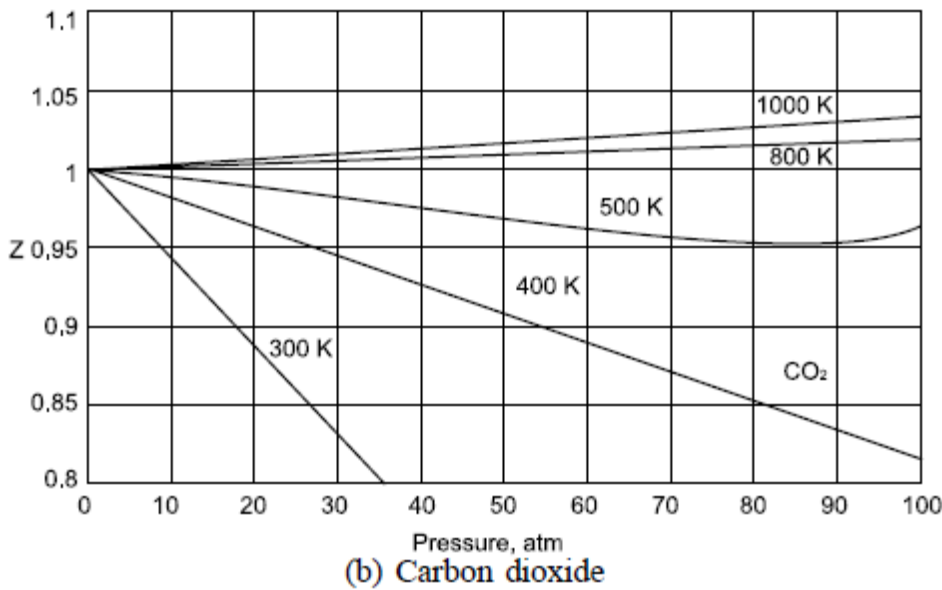
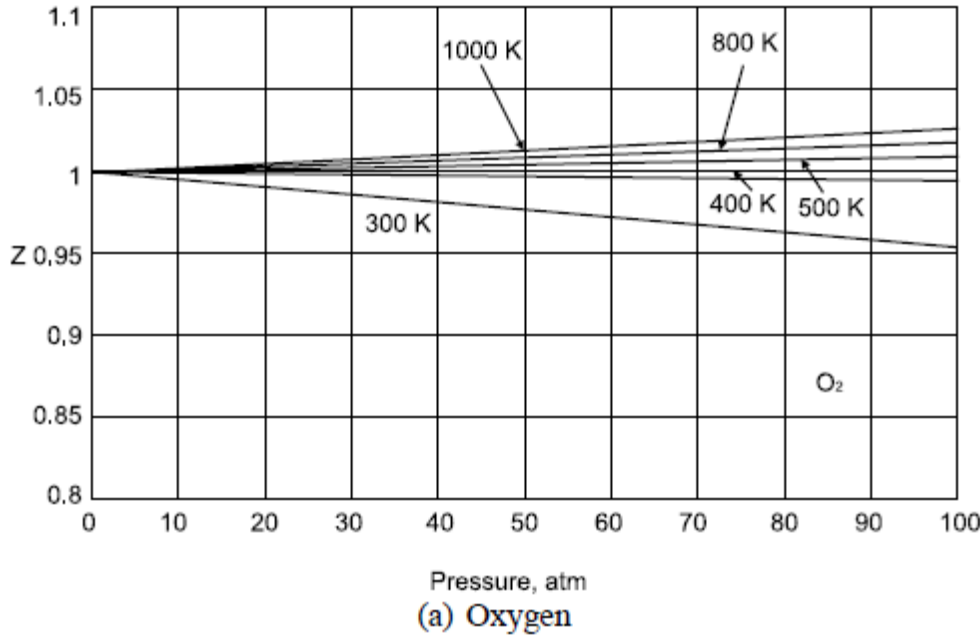


Fig. 1.12 Compressibility factors, Z

where P_c and T_c denote critical pressure and critical temperature respectively. These reduced pressure and reduced temperature are used for getting the generalized compressibility chart of the form, $Z = f(p_R, T_R)$ where Z for all gases is approximately same. This similar behaviour of compressibility correction factor for different gases in respect to reduced pressures and temperatures is called "principle of corresponding states." Fig. 1.13 shows a generalized compressibility chart. In generalized compressibility chart a set of curves is fitted through a set of experimentally determined Z values plotted against reduced

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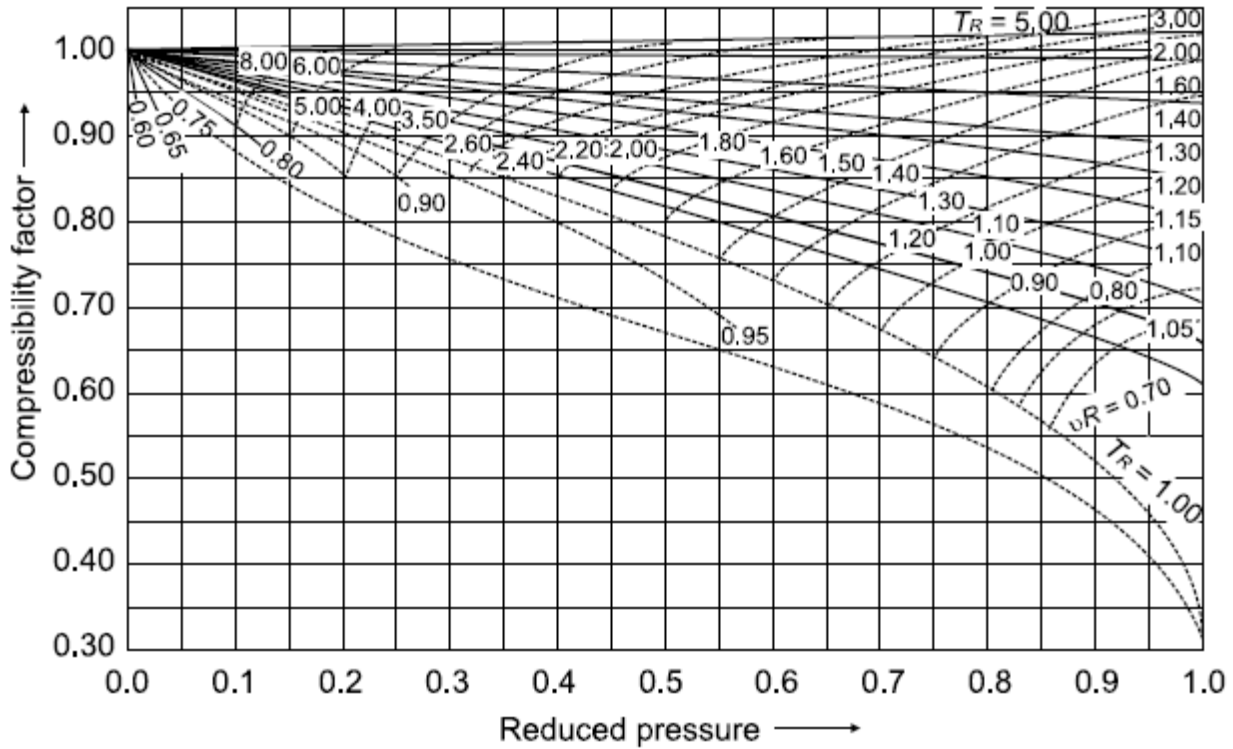


Fig. 1.13 (a) Generalized compressibility chart, $p_R \leq 1.0$

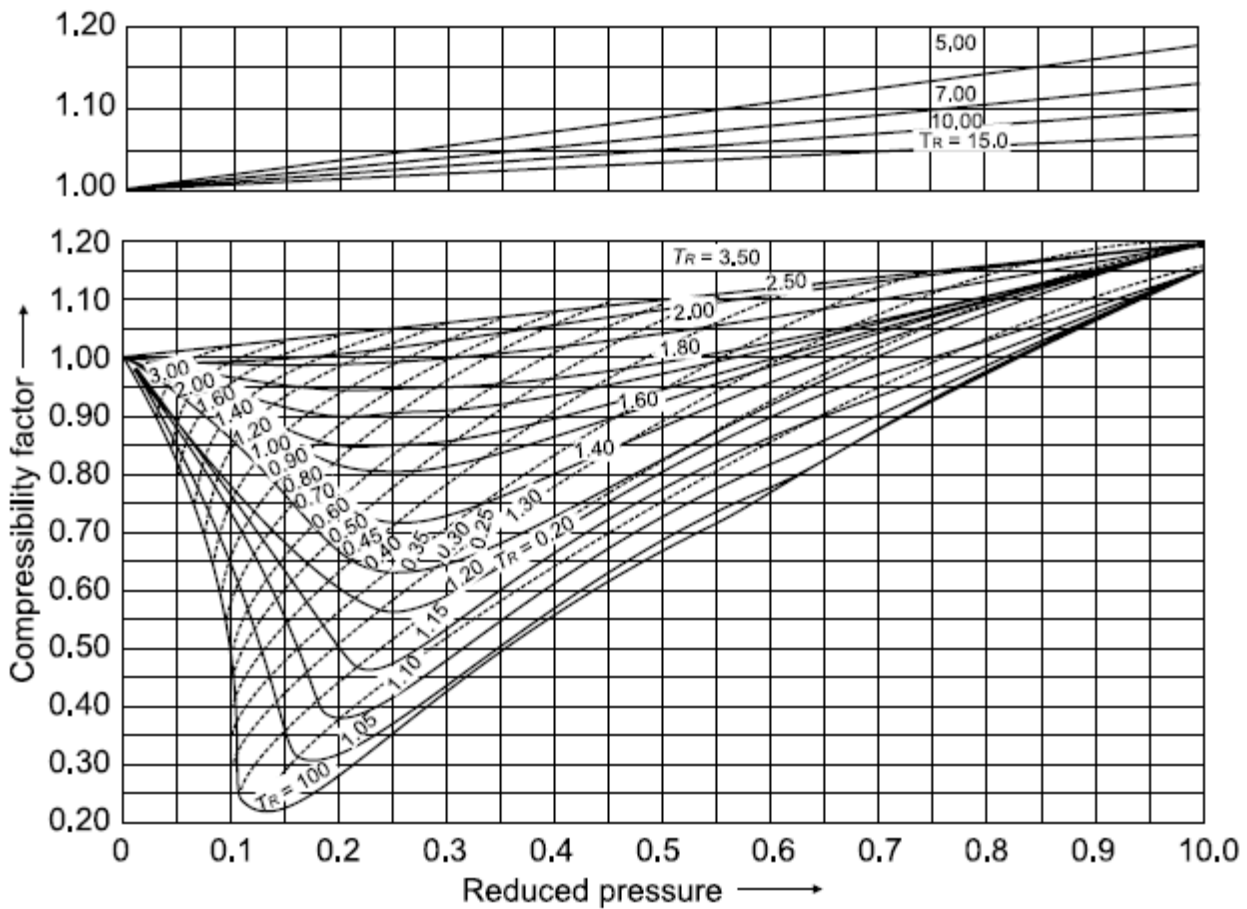


Fig. 1.13 (b) Generalized compressibility chart, $p_R \leq 10.0$

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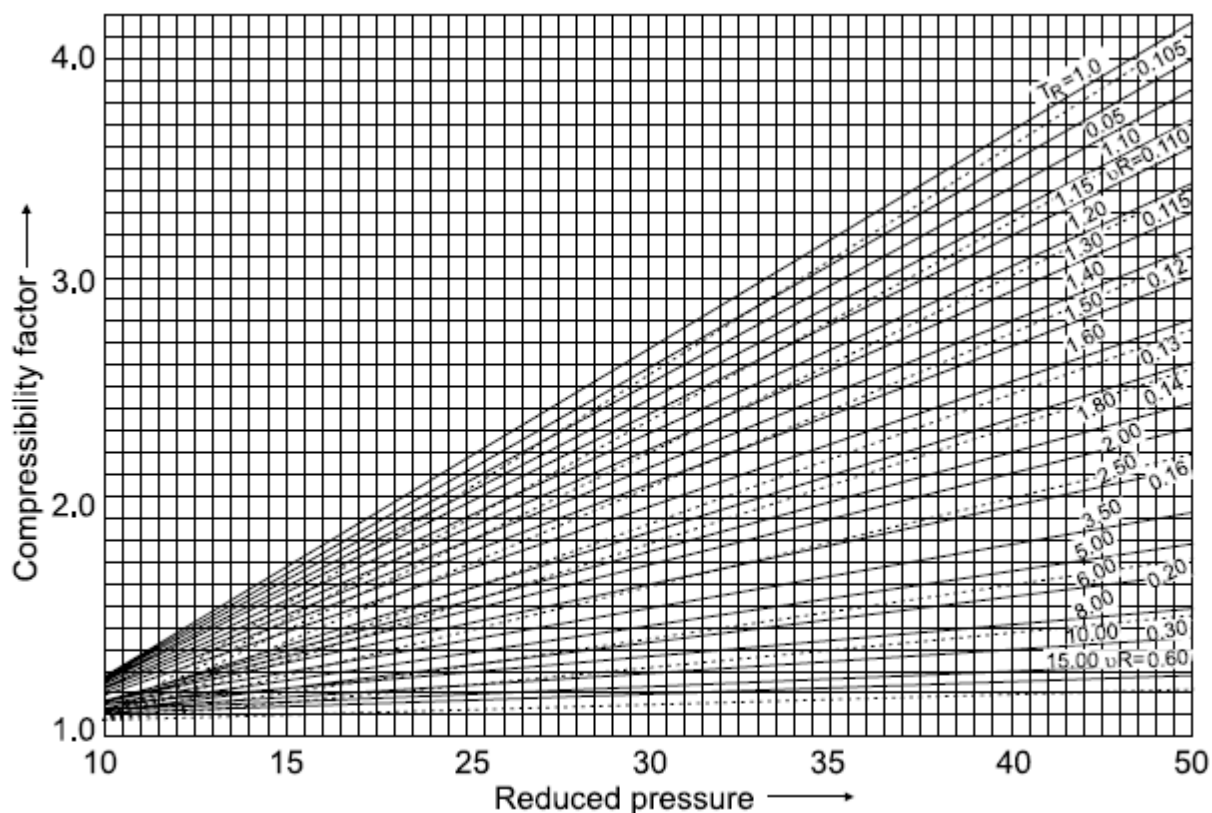


Fig. 1.13 (c) Generalized compressibility chart, $10 \leq p_R \leq 40$

pressure and reduced temperatures for several gases. On the generalized compressibility chart it could be seen that at “very small pressures the gases behave as an ideal gas irrespective of its temperature” and also at “very high temperatures the gases behave as ideal gas irrespective of its pressure”

7.2 VANDER' WAALS AND OTHER EQUATIONS OF STATE FOR REAL GAS

Vander' Waals suggested the equation of state for real gas in 1873. The equation has been obtained applying the laws of mechanics at molecular level and introducing certain constants in the equation of state for ideal gas. This equation agrees with real gas behaviour in large range of gas pressures and temperatures.

Vander' Waals equation of state for real gas is as follows,

$$\left(p + \frac{a}{\bar{v}^2} \right) (\bar{v} - b) = \bar{R}T$$

where ‘a’ is the constant to take care of the mutual attraction amongst the molecules and

thus $\left(\frac{a}{\bar{v}^2} \right)$ accounts for cohesion forces.

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Table 1.6 Vander' Waals constant

Gas	Constant a , $N.m^4/(kg. mol)^2$	Constant b , $m^3/kg.mol$
Helium	34176.2×10^2	2.28×10^{-2}
Hydrogen	251.05×10^2	2.62×10^{-2}
Oxygen	1392.5×10^2	3.14×10^{-2}
Air	1355.22×10^2	3.62×10^{-2}
Carbon dioxide	3628.50×10^2	3.14×10^{-2}

Constant 'b' accounts for the volumes of molecules which are neglected in perfect gas equation, thus it denotes "co-volume", Mathematicall

$$a = \frac{27\bar{R}^2 T_c^2}{64p_c}, \quad b = (\bar{R} \cdot T_c) / (8p_c)$$

Here, p_c , T_c are critical point pressures and temperatures having values as given in appendix.

Thus these constants 'a' & 'b' are determined from behaviour of substance at the critical point.

In general it is not possible to have a single equation of state which conforms to the real gas behaviour at all pressures and temperatures.

A few more equations of state for real gas as suggested by various researchers are as follows.

Redlich-Kwong equation of state for real gas,

$$p = \frac{\bar{R}T}{(\bar{v} - b)} - \frac{a}{\bar{v} \cdot (\bar{v} + b) \cdot \sqrt{T}}$$

where

$$a = 0.4278 \left(\frac{\bar{R}^2 \cdot T_c^{2.5}}{p_c} \right) \text{ and } b = 0.08664 \left(\frac{\bar{R} \cdot T_c}{p_c} \right)$$

Berthelot equation of state for real gas,

$$p = \frac{\bar{R}T}{(\bar{v} - b)} - \frac{a}{T \cdot \bar{v}^2},$$

where

$$a = \left(\frac{27 \cdot \bar{R}^2 \cdot T_c^3}{64 \cdot p_c} \right) \text{ and } b = \left(\frac{\bar{R} \cdot T_c}{8 p_c} \right)$$

Here a and b refer to the constants as suggested in respective equations.

Beattie-Bridgeman equation of state given in 1928, for real gas has five constants determined experimentally. It is

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$$p = \frac{\bar{R} \cdot T}{(\bar{v})^2} \left(1 - \frac{C}{\bar{v} \cdot T^3} \right) (\bar{v} + B) - \frac{A}{(\bar{v})^2}$$

$$A = A_0 \left(1 - \frac{a}{\bar{v}} \right) \text{ and } B = B_0 \left(1 - \frac{b}{\bar{v}} \right)$$

Constants used in Beattie – Bridgeman equation are given in Table 1.7 when p is in $k\text{ pa}$, v is in $\text{m}^3/\text{k mol}$, T is in K , and $R = 8.314\text{ k pa m}^3/\text{k mol.K}$.

Table 1.7. Beattie -Bridgeman constants

Gas	A_0	a	B_0	b	c
Helium	2.1886	0.05984	0.01400	0.0	40
Hydrogen	20.0117	-0.00506	0.02096	-0.04359	504
Oxygen	151.0857	0.02562	0.04624	0.004208	4.80×10^4
Air	131.8441	0.01931	0.04611	-0.001101	4.34×10^4
Carbon dioxide	507.2836	0.07132	0.10476	0.07235	6.60×10^5

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1. Determine the pressure of 5 kg carbon dioxide contained in a vessel of 2 m³ capacity at 27° C,

considering it as

(i) perfect gas

(ii) real gas

Solution:

Given : Volume, $V = 2 \text{ m}^3$, Universal gas constt. = 8.314 kJ/kg · K

Temperature, $T = 27^\circ\text{C}$
 $= (273 + 27) \text{ K}$
 $T = 300 \text{ K}$

Mass, $m = 5 \text{ kg}$

Let pressure exerted be 'p'.

(i) Considering it as perfect gas,

$$pV = mR_{\text{CO}_2}T$$

$$R_{\text{CO}_2} = \frac{\text{Universal gas constt.}}{\text{Molecular weight of CO}_2}$$

$$R_{\text{CO}_2} = \frac{8.314 \times 10^3}{44.01}$$

$$R_{\text{CO}_2} = 188.9 \text{ J/kg} \cdot \text{K}$$

Substituting in perfect gas equation,

$$p = \frac{5 \times 188.9 \times 300}{2} = 141675 \text{ N/m}^2$$

$$\text{Pressure} = \mathbf{1.417 \times 10^5 \text{ N/m}^2} \quad \text{Ans.}$$

(ii) Considering it as real gas let us use Vander-Waals equation;

$$\left(p + \frac{a}{\bar{v}^2} \right) (\bar{v} - b) = \bar{R}T$$

where 'v' is molar specific volume and constants 'a' and 'b' can be seen from Table 1.6.

$$\bar{R} = 8.314 \times 10^3$$

$$\text{Molar specific volume, } \bar{v} = \frac{2 \times 44.01}{5}$$

$$\bar{v} = 17.604 \text{ m}^3/\text{kg} \cdot \text{mol}$$

Vander-Waals Constant,

$$a = 3628.5 \times 10^2 \text{ N} \cdot \text{m}^4/(\text{kg} \cdot \text{mol})^2$$

$$b = 3.14 \times 10^{-2} \text{ m}^3/\text{kg} \cdot \text{mol}$$

Substituting values in Vander Waals equation,

$$\left(p + \frac{3628.5 \times 10^2}{(17.604)^2} \right) (17.604 - 3.14 \times 10^{-2}) = (8.314 \times 10^3 \times 300)$$

$$p + 1170.86 = 141936.879$$

$$p = 140766.019 \text{ N/m}^2$$

$$\text{Pressure} = \mathbf{1.408 \times 10^5 \text{ N/m}^2}$$

$$\text{For CO}_2 \text{ as perfect gas} = 1.417 \times 10^5 \text{ N/m}^2$$

$$\text{For CO}_2 \text{ as real gas} = \mathbf{1.408 \times 10^5 \text{ N/m}^2} \quad \text{Ans.}$$

(using Vander-Waals equation)

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2. Determine the specific volume of steam at 17672 kPa and 712 K considering it as (a) perfect gas,

(b) considering compressibility effects. Take critical pressure = 22.09 MPa, critical temperature = 647.3 K,

$R_{\text{steam}} = 0.4615 \text{ kJ/kg}\cdot\text{K}$.

Solution:

(a) Considering steam as perfect gas,

$$\begin{aligned}\text{Sp. volume} &= \frac{R_{\text{steam}} \cdot T}{p} \\ &= \frac{0.4615 \times 712}{17672}\end{aligned}$$

Specific volume = **0.0186 m³/kg** Ans.

(b) Considering compressibility effects, the specific volume can be given by product of compressibility factor 'Z' and "specific volume when perfect gas".

$$\begin{aligned}\text{Reduced pressure} &= \frac{p}{\text{Critical pressure}} \\ &= \frac{17672}{22.09 \times 10^3}\end{aligned}$$

Reduced pressure = 0.8

$$\begin{aligned}\text{Reduced temperature} &= \frac{T}{\text{Critical temperature}} \\ &= \frac{712}{647.3}\end{aligned}$$

Reduced temperature = 1.1

From generalized compressibility chart compressibility factor 'Z' can be seen for reduced pressure and reduced temperatures of 0.8 and 1.1. We get,

$$Z = 0.785$$

$$\begin{aligned}\text{Actual specific volume} &= 0.785 \times 0.0186 \\ &= \mathbf{0.0146 \text{ m}^3/\text{kg}} \quad \text{Ans.}\end{aligned}$$