
UNIT 10 REAL GASES

Structure

- 10.1 Introduction
 - Objectives
- 10.2 Equations of State for Real Gases
 - 10.2.1 Real Gases and the Ideal Gas Equation of State
 - 10.2.2 Compressibility Factors
 - 10.2.3 Reduced Co-ordinates
 - 10.2.4 Other Equations of State
- 10.3 Specific Heats of Real Gases
- 10.4 Enthalpy and Entropy of Real Gases
- 10.5 Summary
- 10.6 Key Words and Phrases
- 10.7 Answers/Solutions to SAQs

10.1 INTRODUCTION

An ideal gas is a hypothetical substance because we define it simply as a substance that follows the equation of state $pV = RT$. Our definition is not based on any assumption that such a substance actually exists. Historically, the concept of an ideal gas resulted from the work of Boyle, Charles and Gay-Lussac, but we should remember that they actually measured properties of real gases. At low pressures and relatively high temperatures, the equation of state in the form $pV = RT$ is valid even for real gases.

In this Unit we shall see how a real gas differs from an ideal gas and what are the other equations of state that may be used to describe the real gas behaviour. We shall also see how the specific heats of a real gas vary from those of an ideal gas and deduce expressions for its enthalpy and entropy.

Objectives

After a study of this unit, you should be able to

- * distinguish between ideal and real gases,
- * examine the various equations of state available to describe the behaviour of a real gas, and
- * deduce expressions for the enthalpy and entropy of a real gas.

10.2 EQUATIONS OF STATE FOR REAL GASES

10.2.1 Real Gases and the Ideal Gas Equation of State

How closely does $pV = RT$ represent the characteristics of real gases is an important question. It is convenient to use such a simple equation of state, but we must know how much accuracy we sacrifice for the convenience. For air at room temperature, the error in $pV = RT$ is less than 1% for pressures as high as 2.7 MPa. For air at 1 atm, the error in $pV = RT$ is less than 1% for temperatures as low as -220°C . It is not very wrong to say that $pV = RT$ represents the characteristics of many real gases accurately enough for many engineering calculations as long as the gases are at pressures well below their critical pressures and at temperatures well above their critical temperatures.

10.2.2 Compressibility Factors

The simplest modification of the ideal gas equation of state to fit real gas behaviour is the introduction of a compressibility factor Z , which is defined as

$$Z = \frac{pV}{RT}$$

For an ideal gas, obviously, $Z = 1$. For a real gas, Z is a function of pressure and temperature and is usually determined empirically. Since RT/p is the ideal gas specific volume (v_{ideal}) of a gas, the compressibility factor may be considered a measure of the ratio of the actual specific volume to the ideal gas specific volume. That is

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

Z can be either less than or greater than unity for a real gas. Hence, the compressibility factor, measures the deviation of a real gas from ideal gas behaviour.

Figure 10.1 gives approximate compressibility factors for nitrogen in the form Z versus p for various values of T. Figure 10.2 (Source : National Bureau of Standards, Cryogenic Engineering Laboratory, U.S. Air Force WADD Technical Report 60-56, 17 Nov. 1960), gives more accurate values for nitrogen at low temperatures.

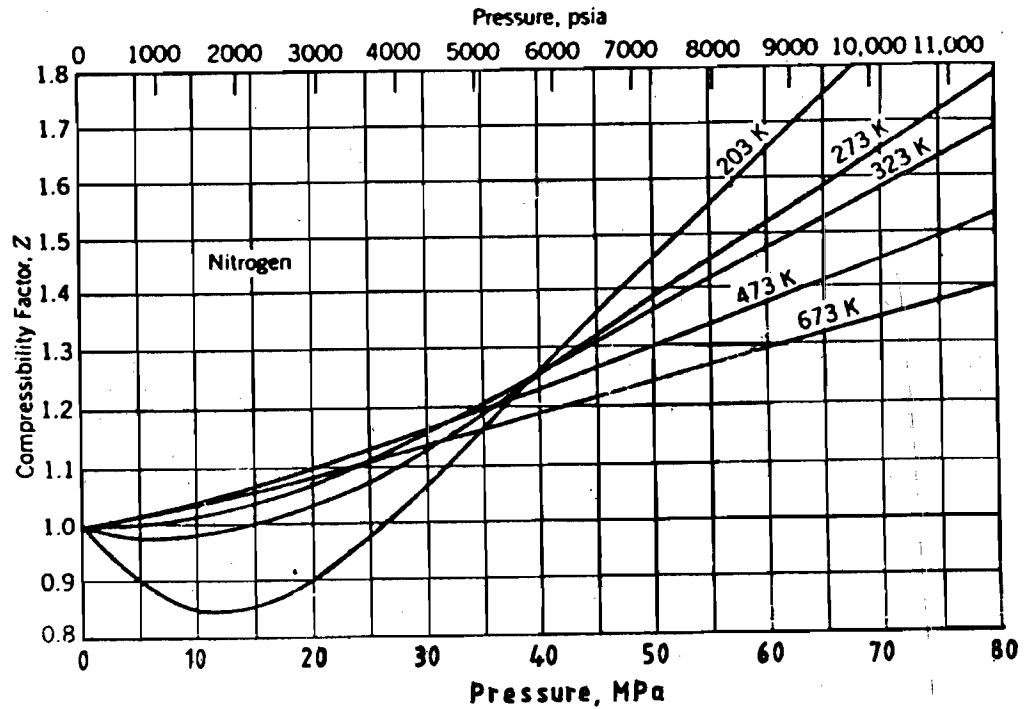


Figure 10.1 : Approximate compressibility factors for nitrogen

(Source : B.F. Dodge, Chemical Engineering Thermodynamics, McGraw Hill, New York 1944).

A few compressibility factor values for three other gases are given below in Table 10.1 which indicates the extent of error involved in using $p\nu = RT$ without correction.

Table 10.1 : Compressibility factors for three gases

Gas	Pressure		Temperature			
	atm	MPa	200 K	350 K	700 K	1400 K
Argon	1	0.101	0.997	1.00	1.00	1.000
	10	1.01	0.970	0.998	1.003	1.002
	100	10.13	0.692	0.988	1.029	1.021
Carbon dioxide	1	0.101		0.997	1.000	1.000
	10	1.01		0.970	1.000	1.003
	100	10.13		0.651	1.007	1.026
Hydrogen	1	0.101	1.001	1.001		
	10	1.01	1.007	1.005		
	100	10.13	1.076	1.054		

Let us consider now an example to illustrate the deviation in pressure that results when a given gas is assumed to be ideal instead of real.

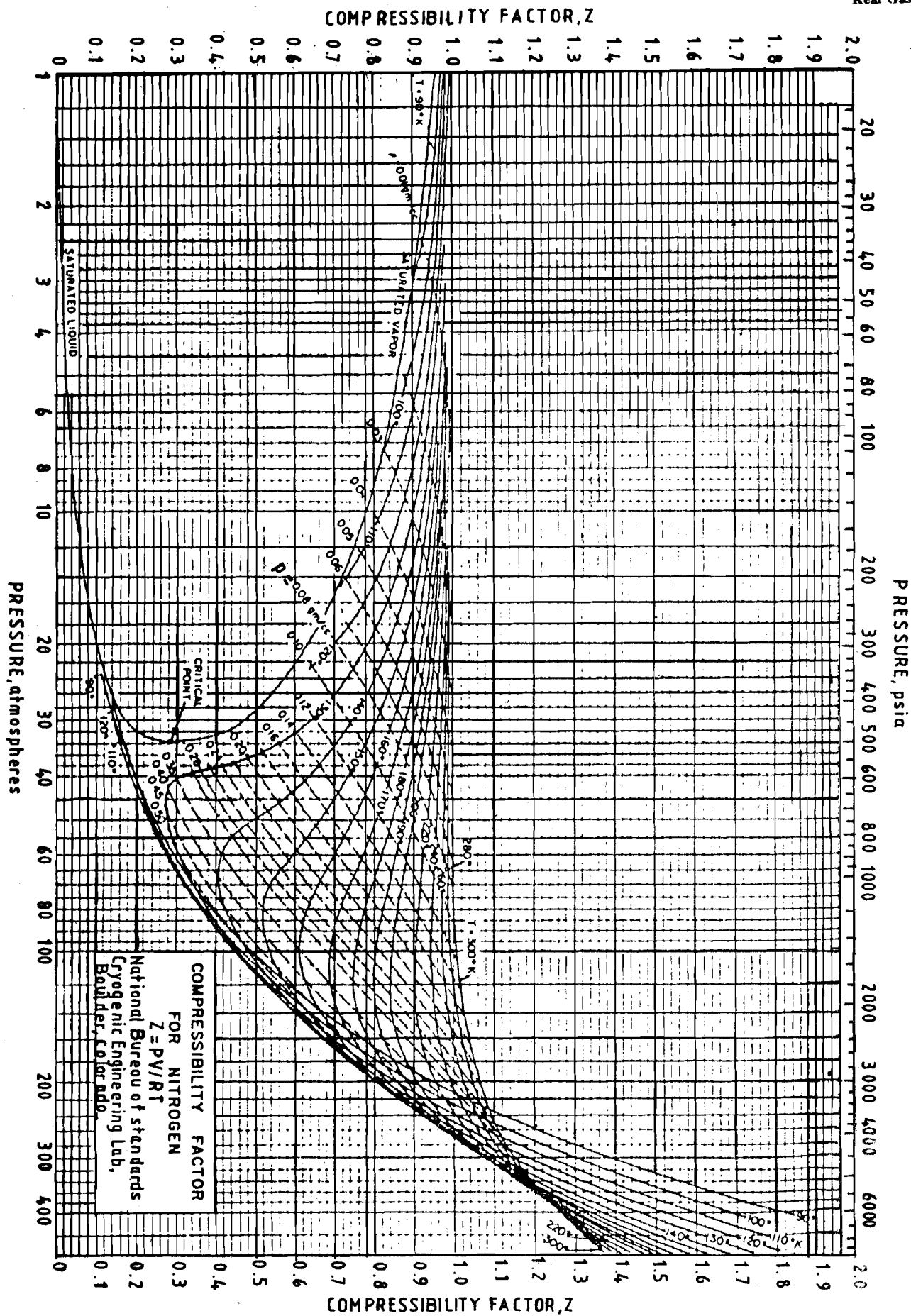


FIG. 10.2 : COMPRESSIBILITY FACTORS FOR NITROGEN AT LOW TEMPERATURES

Example 10.1 :

Determine the pressure in a steel vessel having a volume of 0.015 m³ and containing 3.4 kg of nitrogen at 400°C.

Solution :

As a first approximation let us assume that the ideal gas equation of state holds; hence the compressibility factor equals 1.

$$p = \frac{Zm RT}{V} = \frac{Zm R_u T}{MV}$$

$$= \frac{1 (3.40) 8.314 (673)}{28 (0.015) 1000} = 45.3 \text{ MPa}$$

Where R_u = universal gas constant = 8.314 kJ / kmol.K.

For this pressure and temperature, the value of Z from Figure 10.1 is 1.22. But this is not the true value as the pressure was obtained assuming ideal gas relationship. Therefore to arrive at the correct value of Z and pressure, a trial and error method is resorted to.

Assuming a new value for Z of 1.30 gives

$$p = \frac{1.30 (3.40) 8.314 (673)}{28 (0.015) 1000} = 58.9 \text{ MPa}$$

For this pressure, the value for Z is 1.29. It is evident that the pressure is between 45.3 and 58.9 MPa, and very close to 58.9 MPa; therefore assume that Z equals 1.28. Then

$$p = \frac{1.28 (3.40) 8.314 (673)}{28 (0.015) 1000} = 58.0 \text{ MPa}$$

The value of Z for this pressure and a temperature of 400°C is approximately 1.28; hence by trial the value for p is 58.0 MPa.

Example 10.2 :

Two kilograms of nitrogen in a closed system is compressed frictionlessly and isothermally from 28 MPa, 0°C to 56 MPa. Determine the amount of work required.

Solution :

For a frictionless process executed by a system

$$w = \int p dV$$

In order to integrate this expression, we must have the relationship between p and v at constant temperature. The pressures involved are too high for the ideal gas equation to be used accurately, but perhaps we can use $pV = ZmRT$. Z is usually a function of pressure and temperature, but for the constant temperature process, we have simply $Z = f(p)$. Referring to Figure 10.1 we see that between 28 MPa and 56 MPa, the 0°C isotherm is a straight line. Let $Z = a + bp$ and a and b can be determined from Figure 10.1. Since we know the pressure limits instead of the volume limits of the compression, let us replace V in the expression for work in terms of p . Thus

$$V = \frac{Zm RT}{p} = \frac{(a + bp) m RT}{p}$$

$$dV = - am RT \frac{dp}{p^2} + 0$$

$$w = \int_1^2 p dV = - \int_1^2 \frac{pam RT dp}{p^2} = - am RT \ln \frac{p_2}{p_1}$$

a is the $p = 0$ intercept of the 0°C isotherm between 28 and 56 MPa as it is extended. This gives on Figure 10.1 $a = 0.78$

$$\begin{aligned}
 \text{Therefore} \quad w &= -am RT \ln \frac{p_2}{p_1} \\
 &= -0.78 (2) \frac{8.314}{28} (273) \ln \frac{56}{28} \\
 &= -87.6 \text{ kJ}
 \end{aligned}$$

The minus sign indicates that work is done on the system.

Example 10.3 :

A closed tank contains 12 kg of nitrogen at 40 MPa and 200°C. Compute the pressure that results if the temperature is lowered to -75°C.

Solution :

The mass of nitrogen and the R value are constant; so we can write

$$\frac{p_1 V_1}{Z_1 T_1} = m R = \frac{p_2 V_2}{Z_2 T_2}$$

or

$$p_2 = \frac{p_1 Z_2 T_2}{Z_1 T_1}$$

From Figure 10.1 the value of Z_1 (at 40 MPa, 200°C) is approximately 1.23. Since the final temperature is lower than any shown in Figure 10.1, we must use Figure 10.2 for state 2. Since the final pressure is unknown, we make a first approximation on the basis of the ideal gas equation of state at state 2 so that $Z_2 = 1$ and

$$p_2 \approx \frac{p_1 Z_2 T_2}{Z_1 T_1} = \frac{40 (1) 198}{1.23 (473)} = 13.6 \text{ MPa}$$

For this pressure and 198 K, Figure 10.2 gives $Z_2 = 0.84$. Therefore, a better approximation is

$$p_2 \approx \frac{p_1 Z_2 T_2}{Z_1 T_1} = \frac{40 (0.84) 198}{1.23 (473)} = 11.4 \text{ MPa}$$

At 11.4 MPa, 198 K, Figure 10.2 shows that the compressibility factor remains 0.84 (the value used in the preceding step), so the final pressure is 11.4 MPa.

10.2.3 Reduced Co-ordinates

The disadvantage of compressibility charts such as Figures 10.1 and 10.2 is that a separate chart is needed for each gas. It would be convenient if one chart could be used for several gases. Two methods of doing this are often used. One is by means of the approximation sometimes called the law of corresponding states which states: If any two gases have equal values for the ratio of pressure to critical pressure and equal values for the ratio of temperature to critical temperature, then the ratio of specific volume to critical specific volume is the same for the two gases. The ratios of pressure, temperature and specific volume to the corresponding critical values are called reduced coordinates or reduced properties. Reduced pressure, reduced temperature and reduced specific volume are defined by

$$P_R = \frac{P}{P_c}, \quad T_R = \frac{T}{T_c}, \quad v_R = \frac{v}{v_c}$$

where the subscript R denotes a reduced property and the subscript c denotes a property at the critical state. Values of P_c and T_c are given in Table 10.2.

The law of corresponding states says that for all gases

$$v_R = f(P_R, T_R) \quad (a)$$

and the function is the same for all gases. If this approximation were accurate, a diagram of P_R versus T_R with v_R as a parameter plotted from data on any gas would apply to all others. Actually, the law of corresponding states is not sufficiently accurate over a wide range for much engineering work.

Table 10.2 : Critical State Properties, Vander Waal's Constants

Critical state properties				Van der Waal's constants		Gas
P_c MPa	T_c K	v_{Nc} $m^3 / kmol$	Z_c	a $\frac{MP_a m^6}{k mol^2}$	b $\frac{m^3}{k mol}$	
6.242	310	0.113	0.274	0.4472	0.0515	C ₂ H ₂
3.769	132			0.1352	0.0365	Air
3.780	425	0.255	0.274	1.3858	0.1162	C ₄ H ₁₀
7.387	304	0.094	0.275	0.3658	0.0428	CO ₂
3.496	133	0.093	0.294	0.1470	0.0395	CO
4.884	305	0.148	0.285	0.5573	0.06502	C ₂ H ₆
5.117	283	0.124	0.270	0.4573	0.0575	C ₂ H ₄
1.297	33.2	0.065	0.305	0.02481	0.0266	H ₂
4.641	191	0.099	0.290	0.2281	0.0427	CH ₄
3.394	126	0.090	0.291	0.1366	0.0386	N ₂
5.042	155	0.074	0.288	0.1380	0.0317	O ₂
4.266	370	0.200	0.277	0.9355	0.0901	C ₃ H ₈
22.09	647	0.051	0.230	0.5528	0.0305	H ₂ O

To illustrate the inaccuracy of the law of corresponding states, notice that the lefthand side of equation (a) can be written as

$$v_R = \frac{v}{v_c} = \frac{ZRT P_c}{P A_c RT_c} = \frac{Z}{Z_c} \left(\frac{T_R}{P_R} \right)$$

so that
$$\frac{Z}{Z_c} \cdot \frac{T_R}{P_R} = f(P_R, T_R)$$

and
$$\frac{Z}{Z_c} = \Phi(P_R, T_R)$$

Thus it follows that at the same values of P_R and T_R , all gases have the same value of Z/Z_c . However, at very low values of P_R , $Z = 1$ for all gases; so Z_c must be the same for all gases if the approximation stated in equation (a) holds. Experiments show that this is not the case. For example $Z_c = 0.230$ for water, 0.275 for carbon dioxide, and 0.305 for hydrogen. Consequently, this approximation is inaccurate at least at low pressures.

Another approach is based on the observation that at the same reduced pressure and reduced temperature all gases have approximately the same compressibility factor, except near the critical state. Thus

$$Z = f(P_R, T_R) \tag{b}$$

where the function is the same for all gases. (This is also sometimes called the law of corresponding states, but equations (a) and (b) are not the same). It is apparent that this does not hold for the critical state, where $P_R = 1$ and $T_R = 1$, because we have seen above that Z_c is not the same for all gases. For states well removed from the critical state, however, the generalised compressibility factor gives more accurate results than equation (a). Figure 10.3 is a generalised compressibility factor chart.

The generalised compressibility factor data should be resorted to only when compressibility factor data for the particular gas in question are unavailable.

Example 10.4 :

Determine the specific volume of water vapour in cm³/g, at 200 bar and 520°C by

- (a) the ideal gas equation of state
- (b) the law of corresponding states

Solution :

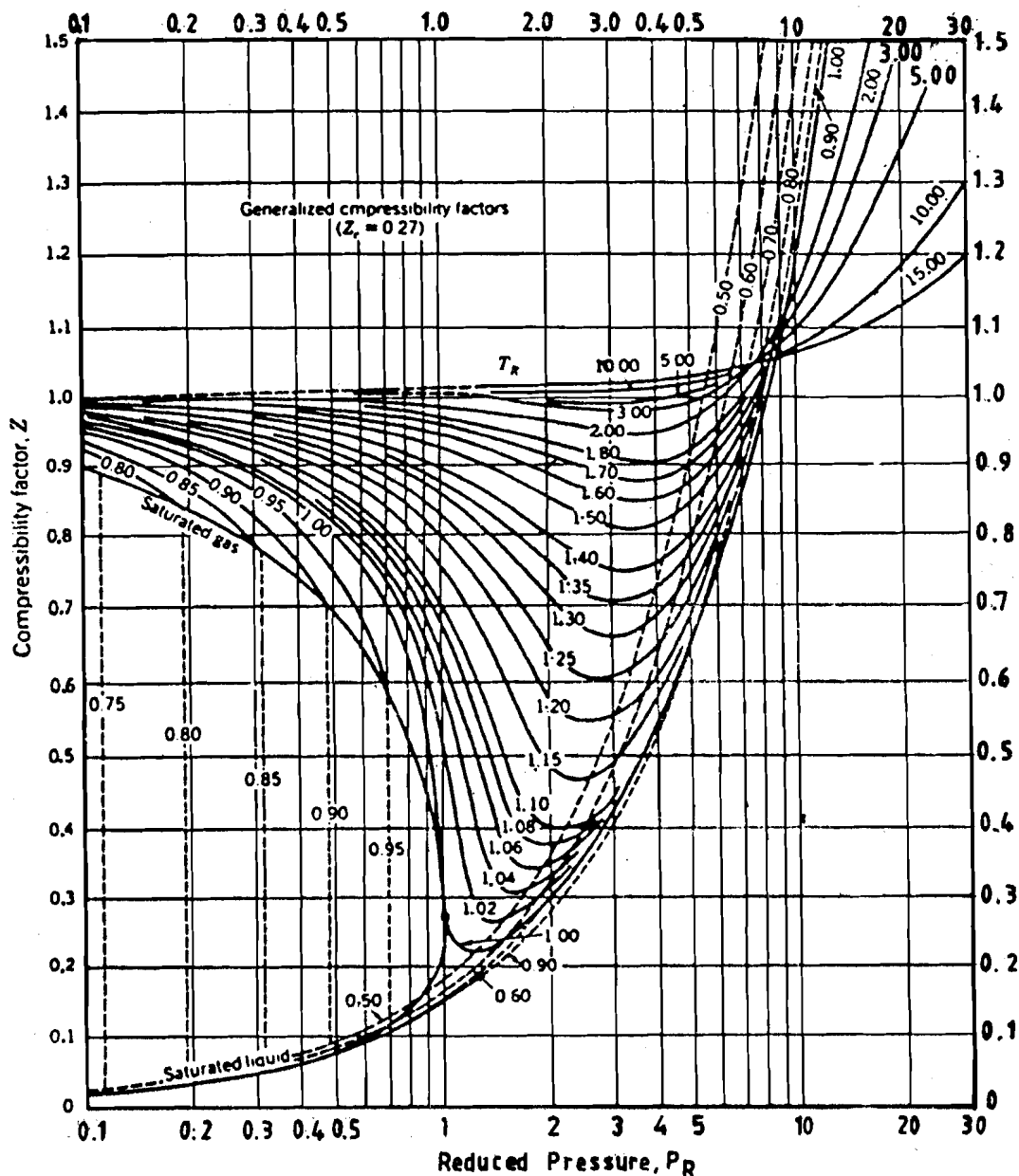


Figure 10.3 : Generalized compressibility factor chart

(Source : Gordon J. Van Wylen and Richard E Sonntag, Fundamentals of Classical Thermodynamics, 3rd ed. Wiley, New York 1985)

(a) On the basis of the ideal gas equation

$$v = \frac{RT}{p}$$

R = the gas constant - $\frac{R_u}{M}$

$$R_u = 8.314 \text{ kJ/kmol.K} = 8.314 \times 10^3 \frac{\text{N} \cdot \text{m} \times 10^3}{\text{m}^2 \cdot \text{kmol} \cdot \text{K}}$$

$$= 0.08314 \frac{\text{bar} \cdot \text{m}^3}{\text{kmol} \cdot \text{K}}$$

$$\begin{aligned} \text{Therefore, } R &= \frac{R_u}{M} = \frac{0.08314 \text{ bar} \cdot \text{m}^3/\text{kmol} \cdot \text{K}}{18 \text{ kg/kmol}} \times \frac{10^6 \text{ cm}^3}{\text{m}^3} \times \frac{\text{kg}}{10^3 \text{ g}} \\ &= 4.62 \frac{\text{bar} \cdot \text{cm}^3}{\text{g} \cdot \text{K}} \end{aligned}$$

$$\begin{aligned} \text{Hence } v &= \frac{RT}{p} = 4.62 \frac{\text{bar} \cdot \text{cm}^3}{\text{g} \cdot \text{K}} \times \frac{793 \text{ K}}{200 \text{ bars}} \\ &= 18.3 \text{ cm}^3/\text{g} \end{aligned}$$

(b) The specific volume based on the law of corresponding states is given by

$$v_{\text{actual}} = Z \cdot v_{\text{ideal}}$$

The value of Z is found by computing T_R and P_R and then using Figure 10.3 to find Z . The critical data for water is found in Table 10.2. Based on these data

$$T_R = \frac{793 \text{ K}}{647 \text{ K}} = 1.23, \quad P_R = \frac{200 \text{ bars}}{220.9 \text{ bars}} = 0.904$$

From Figure 10.3, the Z value is approximately 0.83.

$$\text{Therefore, } v = 0.83 \times 18.3 = 15.2 \text{ cm}^3/\text{g}.$$

SAQ 1

What is wrong in using equation of state for real gases?

SAQ 2

What are the limitations of using compressibility charts for all ranges of temperatures and pressures?

SAQ 3

Compute the compressibility factor for steam at 14 MPa and 500°C. The specific volume under these conditions is 0.02252 m³/kg.

10.2.4 Other Equations of State

a) The Van der Waals Equation of State

In 1873 Van der Waals proposed an equation of state which was an attempt to correct the ideal gas equation so that it would be applicable to real gases. On the basis of simple kinetic theory, particles are assumed to be point masses, and there are no intermolecular forces between particles. However, as the pressure increases on a gaseous system, the volume occupied by the particles may become a significant part of the total volume. In addition the intermolecular attractive forces become important under this condition. To account for the volume occupied by the particles, Van der Waals proposed that the specific volume in the ideal gas equation of state be replaced by the term $v - b$. At the same time the ideal pressure

was to be replaced by the term $p + \frac{a}{v_N^2}$. The constant b is the covolume of the particles, and the constant a is a measure of the attractive forces. Thus the Van der Waals equation in the molar form is

$$\left(p + \frac{a}{v_N^2}\right)(v_N - b) = R_u T \quad \text{or} \quad p = \frac{R_u T}{v_N - b} - \frac{a}{v_N^2}, \quad v_N = \frac{V}{N} = \frac{V.M}{m}$$

The units of a and b being consistent with those used for p , v_N and T . As the pressure approaches zero and the specific volume approaches infinity, the correction terms are negligible and the equation reduces to $p v = RT$. Empirically, it is observed that as the pressure increases, the $\frac{a}{v_N^2}$ term usually becomes important sooner than the b correction factor.

The Van der Waals equation is only an approximation and could be sometimes in error. It is of historical interest as one of the first attempts to correct the ideal gas equation so as to apply it to a real gas. Table 10.2 lists some typical values for the Van der Waals constants.

b) Beattie - Bridgeman Equation

This is another widely used equation of state

$$p = \frac{R_u T (1 - \epsilon)}{v_N^2} (v_N + B) - \frac{A}{v_N^2}$$

where

$$A = A_0 \left(1 - \frac{a}{v_N}\right)$$

$$B = B_0 \left(1 - \frac{b}{v_N}\right)$$

$$\epsilon = \frac{a}{v_N T^3}$$

This is a five - constant equation. A_0 , a , B_0 , b and c for 10 gases are given in Table 10.3/ ϵ is a function of molar volume and temperature as shown. The Beattie - Bridgeman equation has been used for formulating properties of the vapour close to the liquid phase at pressures less than the critical pressure. In general, the equation is accurate when the specific volumes involved are greater than twice the critical specific volume.

Table 10.3 : Beattie - Bridgeman constants

Gas	A_0 $\frac{\text{atm m}^6}{\text{kmol}^2}$	a $\frac{\text{m}^3}{\text{kmol}}$	B_0 $\frac{\text{m}^3}{\text{kmol}}$	b $\frac{\text{m}^3}{\text{kmol}}$	c (10^{-4}) $\frac{\text{m}^3 \cdot \text{K}^3}{\text{kmol}}$
Air	1.301	0.0193	0.0461	-0.00110	4.35
Ar	1.294	0.0233	0.0393	0	5.99
CO	1.345	0.0262	0.0504	-0.00693	4.21
CO ₂	5.008	0.0712	0.1055	0.0724	66.05
H ₂	0.198	-0.0051	0.0210	-0.0436	0.050
He	0.022	0.0598	0.0140	0	0.040
N ₂	1.345	0.0262	0.0504	-0.00693	4.21
Ne	0.213	0.0220	0.0206	0	0.101
N ₂ O	5.008	0.0712	0.1049	0.0724	66.05
O ₂	1.493	0.0257	0.0463	0.00421	4.81

Note for A_0 units of $\frac{\text{atm} \cdot \text{m}^6}{\text{kmol}^2}$, $R_u = 0.0820 \frac{\text{atm} \cdot \text{m}^3}{\text{kmol} \cdot \text{K}}$

c) **Virial Equations**

For the purpose of preparing extensive tables of properties and for computational purposes, it is often convenient to have an equation of state in the form

$$\frac{Pv}{RT} = A_0 + A_1 P + A_2 P^2 + A_3 P^3 + \dots$$

or

$$\frac{Pv}{RT} = B_0 + \frac{B_1}{v} + \frac{B_2}{v^2} + \frac{B_3}{v^3} + \dots$$

where A 's and B 's are functions of temperature only. These equations are called virial equations, and the A 's and B 's are called virial coefficients. One of the advantages of virial equations of state is that it is relatively easy to determine the virial coefficients from experimental $p v t$ data.

Example 10.5 :

Determine the pressure in a steel vessel having a volume of 0.0150 m^3 and containing 3.40 kg of nitrogen at 400°C by means of

- the Van der Waals equation and
- the Beattie - Bridgeman equation

Solution :

We know that $R_u = 8.314 \text{ kJ/kmol.K}$ and it is given $T = 673 \text{ K}$ and

$$v_N = \frac{V}{N} = v \cdot \frac{M}{m} = \frac{0.0150(28)}{3.40} \text{ m}^3 / \text{kmol}.$$

- a) The Van der Waals equation

$$P = \frac{R_u T}{(v_N - b)} - \frac{a}{v_N^2}$$

with $a = 136.6 \text{ kPa.m}^6/\text{kmol}^2$ and $b = 0.0386 \text{ m}^3/\text{kmol}$ from Table 10.2

$$P = 56.9 \text{ MPa}$$

- b) The Beattie - Bridgeman equation is

$$P = \frac{R_u T (1 - \epsilon)}{v_N^2} (v_N + B) - \frac{A}{v_N^2}$$

with

$$A = A_0 \left(1 - \frac{a}{v_N} \right), \quad B = B_0 \left(1 - \frac{b}{v_N} \right)$$

and

$$\epsilon = \frac{c}{v_N \cdot T^3}$$

Table 10.3 gives $A_0 = 136 \text{ kPa m}^6 / \text{kmol}^2$

$$a = 0.0262 \text{ m}^3 / \text{kmol}$$

$$B_0 = 0.0504 \text{ m}^3 / \text{kmol}$$

$$b = -0.00693 \text{ m}^3 / \text{kmol}$$

and

$$c = 4.21 \text{ m}^3 \cdot \text{k}^3 / \text{kmol}$$

$$P = 57.8 \text{ MPa}$$

These results should be compared with the more accurate result of example 10.1.

SAQ 4

Estimate the pressure which would be exerted by 3.7 kg of CO in a 0.030 m^3 container at 215 K employing (a) the ideal gas equation of state (b) Van der Waal's equation

SAQ 5

Compute the pressure of neon for a temperature of 50°C and a specific volume of $0.01 \text{ m}^3/\text{kg}$ by means of the Beattie-Bridgeman equation of state

10.3 SPECIFIC HEATS OF REAL GASES

We have seen earlier in Unit 9 that the specific heats of ideal gases are functions of temperature only. The specific heats of real gases are functions of both pressure and temperature. From the definition of c_p ,

$$c_p = \left(\frac{\delta h}{\delta T} \right)_P,$$

we see that c_p is equal to the slope of a constant pressure line on an h - T diagram.

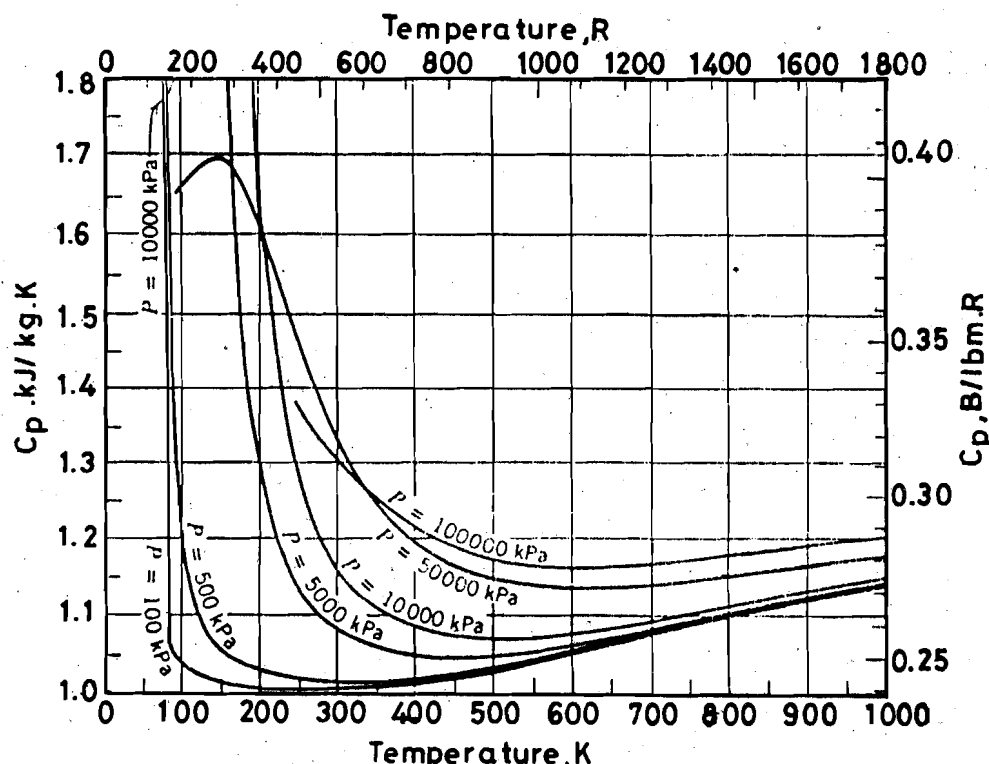


Figure 10.4 : Plot of c_p versus T for air

Figure 10.4 is a plot of c_p versus T for air. For a real gas, pressure has less influence on the value of c_p than it does on the value of c_v . The quantity $(c_p - c_v)$ is not a constant as it is for ideal gases.

10.4 ENTHALPY AND ENTROPY OF REAL GASES

We have seen that the equations of state developed for real gases are merely extensions of the ideal gas equation of state, $pv = RT$. We also know that the enthalpy of any substance that follows the ideal gas equation of state is a function of temperature only. For other gases, the relationship involving enthalpy is more complex, but again it is convenient to formulate it as an extension of the relationship for ideal gas.

Let us consider now the determination of the enthalpy change for a process of a real gas from state 1 to state 2 as shown on the T - s diagram of Figure 10.5(a). At state 1, $P_R > 1$. At state 2, $T_R < 1$ and P_R is less than 1 but not very low. Therefore, it is unlikely that the ideal gas equation of state would be accurate for these states.

For any gas, the change in enthalpy is given by

$$h_2 - h_1 = \int_1^2 c_p dT - \int_1^2 \left[T \left(\frac{\delta v}{\delta T} \right)_p - v \right] dp \quad (A)$$

(From Maxwell's Equations)

The second term on the right-hand side can be evaluated from pvT data; the first one requires a knowledge of the $c_p T$ relationship along the process 1 to 2.

Since the value of any property change between two states is the same for any process between them, a fruitful approach is to evaluate the enthalpy change by using the path $1 - 1^* - 2^* - 2$ shown in Figure 10.5(b). This path consists of a constant temperature process from state 1 to state 1^* at a low pressure, a constant pressure process from state 1^* to a state 2^* , and a constant temperature process from state 2^* to state 2. States 1^* and 2^* are at such a low pressure that the ideal gas equation of state applies. Thus we evaluate the enthalpy change between states 1 and 2 as

$$h_2 - h_1 = (h_2 - h_2^*) + (h_2^* - h_1^*) + (h_1^* - h_1)$$

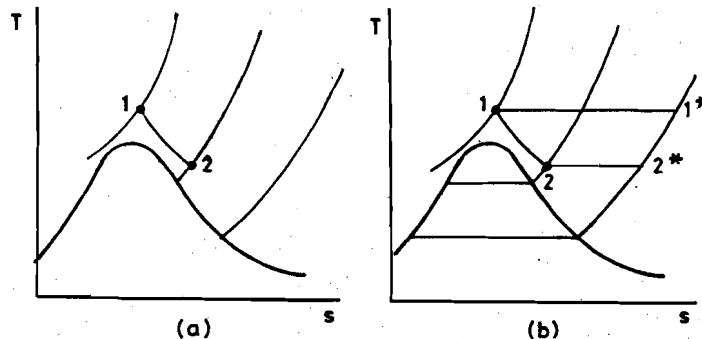


Figure 10.5 : Process of real gas from state 1 to state 2

Each of the three terms on the right-hand side can be evaluated by means of equation (A).

For process $1^* - 2^*$, the pressure is constant.

Therefore equation (A) gives $h_2^* - h_1^* = \int_1^{2^*} c_p dT$

Process $1 - 1^*$ is a constant temperature process

Therefore equation (A) gives

$$h_1^* - h_1 = \int_1^{1^*} \left[v - T \left(\frac{\delta v}{\delta T} \right)_p \right] dp$$

This expression can be evaluated from a pvT relationship. In a like manner, the enthalpy change between states 2^* and 2 can be calculated. Consequently, for evaluating the enthalpy change between any two states of a real gas we can use the same procedure illustrated here.

The difference between h and h^* (sometimes called the enthalpy departure or enthalpy residual) is obtained by equation (A) which for the constant temperature process connecting these two states is

$$h^* - h = \int_p^o \left[v - T \left(\frac{\delta v}{\delta T} \right)_p \right] dp$$

(where h = enthalpy of the real gas at the given state and h^* = enthalpy at the same temperature but very low pressure, low enough for the equation of state to be valid).

In the absence of any other pVT relationship for the gas at hand, we use a compressibility factor so that in this equation we make the substitution $v = ZRT/p$ to obtain

$$h^* - h = -R \int_P^0 \frac{T^2}{P} \left(\frac{\delta Z}{\delta T} \right)_P dP$$

If ZTp data are available for the gas, this expression can be evaluated graphically or numerically. If ZpT data are not available, we can use the approximation of a generalised compressibility factor or $Z p_R T_R$ chart. Substituting $p = P_R P_C$ and $T = T_R T_C$ into the equation results in

$$\frac{h^* - h}{R_u T_C} = \int_0^{P_R} T_R^2 \left(\frac{\delta Z}{\delta T_R} \right)_{P_R} d(\ln P_R) \tag{B}$$

where the h^s are molar specific enthalpies to permit the introduction of R_u instead of R . Again, the integral can be evaluated numerically or graphically from a table or chart of generalised compressibility factors. A resulting plot of $(h^* - h)/R_u T_C$ in terms of P_R and T_R , called a generalised compressibility chart, is given as Figure 10.6. This chart is based on a generalized compressibility factor chart with a value of $Z = 0.27$. We should note here that it is an approximation based on properties of many gases. A generalized entropy chart can be developed in a similar manner, starting with the general equation for entropy change

$$S_2 - S_1 = \int_1^2 c_p \left(\frac{dT}{T} \right) - \left(\frac{\delta v}{\delta T} \right)_P dp \tag{C}$$

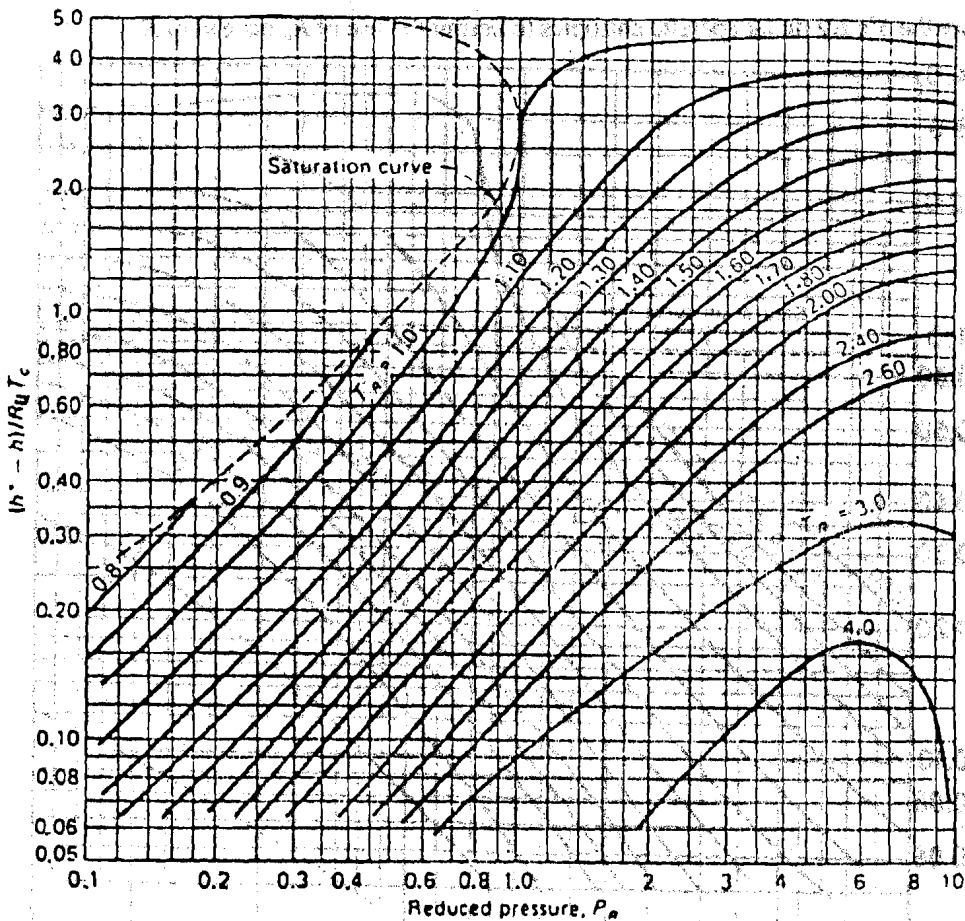


Figure 10.6 : Generalized enthalpy chart

(Source : Kenneth Wark, Thermodynamics, 4th ed. McGraw-Hill, New York 1983).

One difference between the development of the generalized entropy chart and the development of the generalized enthalpy chart is that for an ideal gas, entropy is not a function of pressure. Further for an ideal gas $c_p \rightarrow \infty$ as $n \rightarrow 0$ at

constant temperature. The difficulty this introduces can be avoided by using some arbitrary low pressure, P_{ar} , as a standard. This way we can eliminate the arbitrary low pressure from the calculations. Applying equation (C) to a constant temperature process between the state of the real gas (at p, T) and a state (at P_{ar}, T) at a low enough pressure for the gas to behave as an ideal gas gives

$$S_{p, T} - S_{P_{ar}, T}^* = - \int_{P_{ar}}^P \left(\frac{\delta v}{\delta T} \right)_P dp \tag{i}$$

where the asterisk indicates an ideal gas property.

If the gas could exist as an ideal gas at state p, T the change in entropy between the state at P_{ar}, T and that at p, T would be

$$S_{p, T}^* - S_{P_{ar}, T}^* = - \int_{P_{ar}}^P \left(\frac{\delta v}{\delta T} \right)_P dp = -R \int_{P_{ar}}^P \left(\frac{dp}{p} \right) \tag{ii}$$

subtracting equation (i) from equation (ii) gives

$$S_{p, T}^* - S_{p, T} = - \int_{P_{ar}}^P \left[\frac{R}{p} - \left(\frac{\delta v}{\delta T} \right)_P \right] dp$$

which is the difference in entropy between the hypothetical state of the gas as an ideal gas at p and T and the real gas state at the same p and T . (state P_{ar}, T has been eliminated). This entropy difference depends only on the pvT relationship, so by using a generalised compressibility factor and letting P_{ar} approach 0 it can be expressed as

$$\frac{S_p^* - S_p}{R_u} = - \int_0^{P_R} \frac{1-Z}{P_R} dP_R + T_R \int_0^{P_R} \left(\frac{\delta Z}{\delta T_R} \right)_{P_R} d(\ln P_R)$$

where the S 's are molar specific entropies to permit the use of R_u instead of R .

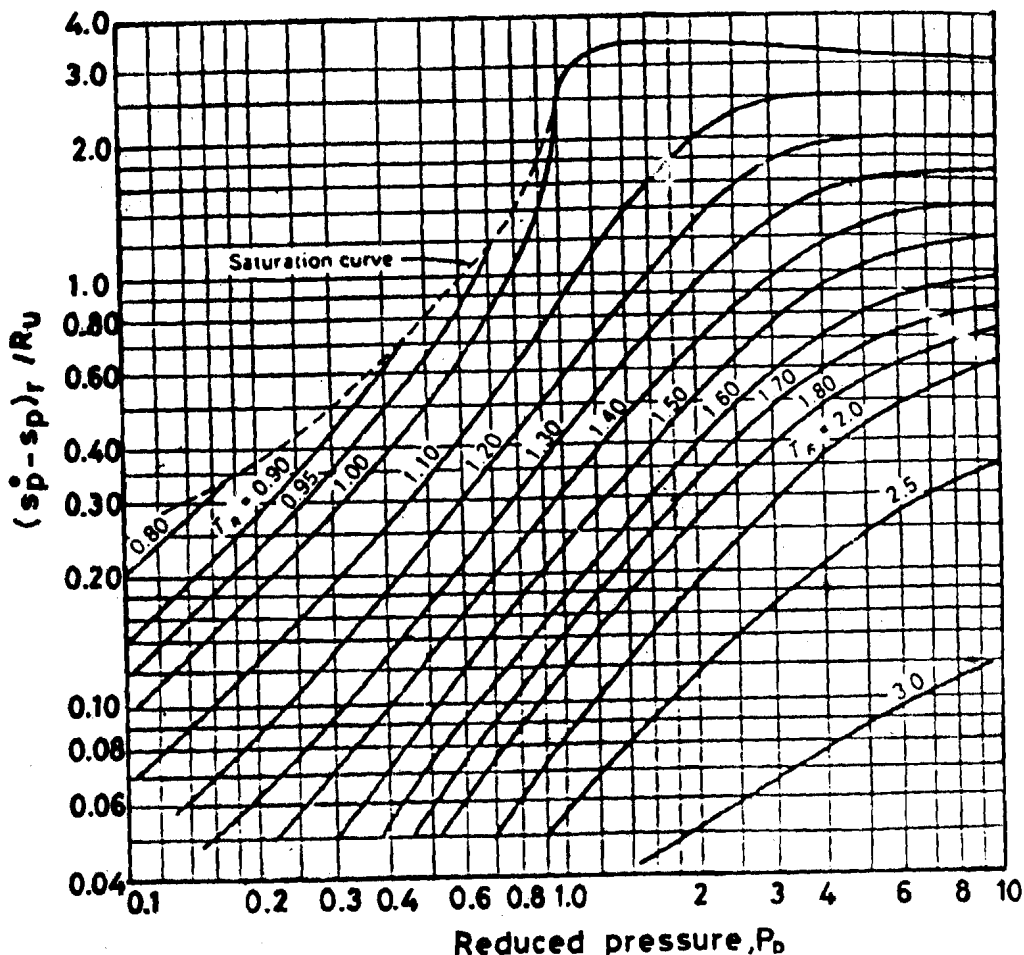


Figure 10.7 : Generalized entropy chart

(Source : Kenneth Wark, Thermodynamics, 4th ed. McGraw-Hill, New York 1983).

This expression can be evaluated by numerical or graphical integration using $Z_{P_R} T_R$ data to produce a generalized entropy chart as shown in Figure 10.7. Again, we must remember that the accuracy of results based on such a chart is limited by the approximations involved in the generalized compressibility factor chart.

The calculation of entropy change of a real gas between states 1 and 2 is carried out by

$$S_2 - S_1 = (S_2 - S_2^*) + (S_2^* - S_1^*) + (S_1^* - S_1) \quad (\text{iii})$$

The first term on the right hand side is the entropy difference between the real gas and the hypothetical ideal gas, both at p_2 and T_2 . The second term is the entropy difference of the hypothetical ideal gas between states 1 and 2. The third term is the entropy difference between the real gas and the hypothetical ideal gas, both at p_1 and T_1 .

Example 10.6 :

Methane expands adiabatically through a turbine at a rate of 0.32 kg/s from 10 MPa, 27°C to 2 MPa, -45°C. Kinetic energy changes are negligible. Determine the turbine power output and the change in entropy of the methane during the expansion.

Analysis: The first law must be applied here to determine the power, and it will require enthalpy values for the methane. At the conditions specified, methane is unlikely to behave as an ideal gas. As a check on this point, we obtain values of $p_c = 4.641$ MPa and $T_c = 191$ K for methane (from Table 10.2) and then calculate P_{R1} and T_{R1} for each state. Then we obtain values of Z from Figure 10.3

$$P_{R1} = 2.17 \quad T_{R1} = 1.57 \quad Z_1 = 0.87$$

$$P_{R2} = 0.43 \quad T_{R2} = 1.20 \quad Z_2 = 0.92$$

This much departure from the ideal gas value of $Z = 1$ confirms that we cannot treat the methane as an ideal gas. Therefore, we will use the generalised enthalpy and generalised entropy charts in the calculations.

Solution :

From the first law

$$w = h_1 - h_2$$

and we evaluate the enthalpy change by means of the generalized enthalpy chart Figure 10.6

$$w = h_1 - h_2 = h_1^* - h_2^* - (h_1^* - h_1) + (h_2^* - h_2)$$

using a mean specific heat for the term $h_1^* - h_2^*$ and arranging the other two terms on the right hand side in a form suitable for using the generalized enthalpy chart

$$w = c_p (T_1 - T_2) - \frac{R_u T_c}{M} \left(\frac{h_1^* - h_1}{R_u T_c} - \frac{h_2^* - h_2}{R_u T_c} \right)$$

Taking c_p for methane as 2.22 kJ/kg.K (from properties of gases Table) and numerical values corresponding to P_R and T_R from Figure 10.6, gives

$$w = 2.2 (300 - 228) - \frac{8.314 (191.0)}{16.04} (0.92 - 0.32)$$

$$= 99 \text{ kJ/kg}$$

$$\dot{W} = \dot{m} w = 0.32 (99) = 31.68 \text{ kW}$$

In a similar manner, the entropy change is

$$S_2 - S_1 = S_2^* - S_1^* - (S_2^* - S_2) + (S_1^* - S_1)$$

The first term on the right hand side is the entropy change of methane as an ideal gas between states 1 and 2, and each of the other two terms is the difference between the entropy of an ideal gas and that of a real gas at the same pressure and temperature. For the ideal gas term we integrate the Tds equation, $Tds = dh - vdp$, for an ideal gas with constant c_p . The other two terms we arrange for convenient use of the generalized entropy chart Figure 10.7 which we enter with the p_R and T_R values already determined. Thus

$$S_2 - S_1 = c_p \ln \frac{T_2}{T_1} - R \ln \frac{p_2}{p_1} - \frac{R_u}{M} \left[\frac{S_2^* - S_2}{R_u} - \frac{S_1^* - S_1}{R_u} \right]$$

$$= 2.22 \ln \left(\frac{228}{300} \right) - \left(\frac{8.131}{16.04} \right) \ln \left(\frac{2}{10} \right) - \left(\frac{8.314}{16.04} \right) (0.20 - 0.47)$$

$$= 0.347 \text{ kJ / kg.K}$$

SAQ 6

Determine the power required to compress ethane steadily, and adiabatically at a rate of 0.31 kg/s from 10 MPa, 27°C to 40 MPa, 300°C.

10.5 SUMMARY

For real gases in many applications especially at higher pressures and lower temperatures, the equation of state $pv = RT$ is not sufficiently accurate.

The simplest modification of the ideal gas equation of state to fit real gas behaviour is the introduction of a compressibility factor Z which is defined as

$$Z = \frac{pv}{RT}$$

For an ideal gas, $Z = 1$. For a real gas, Z is a function of pressure and temperature. The value of Z for any state is a direct indication of the error involved in using $pv = RT$ for that state.

In this unit you have also learnt the use of a single generalized compressibility chart of Z versus reduced pressure p_R at various T_R for all gases. This is a better approximation, except near the critical state, than Z versus p .

The other equations of state introduced in this unit are

- i) Van der Waals equation of state
- ii) The Beattie - Bridgeman equation
- iii) Virial equations

The specific heats of real gases are functions of both pressure and temperature. In the absence of specific data on real gases, properties such as h , u and s can be approximated by means of generalized property charts based on generalized compressibility factors.

10.6 KEY WORDS AND PHRASES

- Compressibility factor** : It is a measure of the deviation of a real gas from ideal gas behaviour.
- Reduced properties** : These are the ratios of pressure, temperature and specific volume to the corresponding critical values.
- Generalized compressibility factor** : For states well removed from critical states, it is observed that at the same reduced pressure and reduced temperature, all gases have approximately the same compressibility factor. This is called the generalized compressibility factor.
- Vander waals equation of state** : This is an equation of state that attempts to correct the ideal gas equation to make it applicable to a real gas.
- Beattie-Bridgeman equation of state** : This is another modified form of the ideal gas equation that can be applied to vapours close to the liquid phase at pressures less than the critical pressure.
- Virial coefficients** : These coefficients are used in formulating an alternate form of equation of state, that is ideally suited for preparing property tables.
- Enthalpy Departure** : The difference between the enthalpy of a real gas at the given state and the enthalpy at the same temperature but very low pressure (low enough for the equation of state to be valid) is called the enthalpy departure.

10.7 ANSWERS/SOLUTIONS TO SAQs

SAQ 1

An ideal gas is a hypothetical substance that follows the equation of state $pv = RT$. A real gas deviates from $pv = RT$ and therefore we modify this equation with correction factors. Also, if $pv \neq RT$, specific heats are usually functions of both pressure and temperature so that relations for u and h are not as simple as they are for ideal gases. At low pressures and relatively high temperatures, real gases follow $pv = RT$ very nearly.

SAQ 2

The general trend of increasing accuracy of $pv = RT$ as pressure decreases and temperature increases does not hold for all ranges. We can see this clearly in Figure 10.1. For example at 273 K, there is less error in $pv = RT$ at 15 MPa than at 5 MPa.

SAQ 3

$$Z = \frac{pv}{RT}, \quad R \text{ for steam} = \frac{R_u}{M} = \frac{8.314}{18}$$

$$T = 500 + 273 = 773 \text{ K}$$

Therefore

$$Z = 14 \times 10^6 \left(\text{N/m}^2 \right) \times \frac{0.02252}{773} \left(\text{m}^3/\text{kg} \right) \times \frac{18}{8.314} \left(\text{kgK/kJ} \right)$$

$$= 14 \times 10^3 \times \frac{0.02252}{773} \times \frac{18}{8.314}$$

$$= 0.88$$

SAQ 4

The calculations are made using the following values:

$$R_u = 8.314 \text{ kJ/kmol} \cdot \text{K}, \quad T = 215 \text{ K}$$

$$v_N = \frac{V}{N} = \frac{VM}{m} = \frac{0.030 \times 28}{3.7} \text{ m}^3/\text{kmol}$$

a) Ideal gas equation of state

$$pv = RT \quad v = \frac{V}{m}$$

$$p = \frac{RT}{v} = \frac{R_u \cdot T m}{m V} = \frac{8.314 \times 215 \times 3.7}{28 \times 0.030 \times 1000}$$

$$= 7.87 \text{ MPa}$$

b) The Van der Waals equation

$$p = \frac{R_u T}{(v_N - b)} - \frac{a}{(v_N)^2}$$

$$a = 0.147 \frac{\text{MPa} \cdot \text{m}^6}{\text{kmol}^2}, \quad b = 0.0395 \frac{\text{m}^3}{\text{kmol}}$$

(From Table 10.2)

$$p = \frac{8.314 \times 215}{\left(\frac{0.03 \times 28}{3.7} - 0.0395 \right)} - \frac{0.147}{\left(\frac{0.03 \times 28}{3.7} \right)^2}$$

$$= 9.533 - 2.854 = 6.679 \text{ MPa}$$

SAQ 5

Gas is neon, temperature $T = 273 + 50 = 323 \text{ K}$

$$v = 0.01 \text{ m}^3/\text{kg}, \quad m = 1 \text{ kg}$$

The Beattie-Bridgeman equation is

$$p = \frac{R_u T (1 - \epsilon)}{(v_N)^2} (v_N + B) - \frac{A}{(v_N)^2}$$

with
$$A = A_o \left(1 - \frac{a}{v_N} \right), \quad B = B_o \left(1 - \frac{b}{v_N} \right) \text{ and}$$

$$\epsilon = \frac{c}{(v_N \cdot T^3)}$$

From Table 10.3 : $A_o = 0.213 \times 10^5 \frac{\text{Pa} \cdot \text{m}^6}{\text{kmol}^2}$

$$a = 0.0220 \frac{\text{m}^3}{\text{kmol}}$$

$$B_o = 0.0206 \frac{\text{m}^3}{\text{kmol}}$$

$$b = 0$$

$$c = 0.101 \frac{\text{m}^3 \cdot \text{k}^3}{\text{kmol}}$$

$$M \text{ for Neon} = 20.18 \text{ kg/kmol}$$

Therefore
$$v_N = \frac{V.M.}{m} = \frac{0.01 \times 20.18}{1} = 0.2018 \frac{\text{m}^3}{\text{kmol}}$$

$$p = \frac{8.314 \times 323}{(0.2)^2} \times (0.2 + 0.02) - \frac{18978}{(0.2)^2}$$

$$= 13.56 - 0.0189 = 13.54 \text{ MPa}$$

SAQ 6

Power to compress ethane C_2H_6 under steady, adiabatic conditions.

$m = 0.31 \text{ kg/s}$, 10 MPa, 27°C to 40 MPa, 300°C

Neglecting kinetic and potential energy changes we need enthalpy and entropy values for ethane. At the conditions specified, ethane is unlikely to behave as an ideal gas we will have to use the generalised enthalpy and generalised entropy charts in the calculations.

From the first law

$$Q - w_x = \Delta h, \quad Q = 0$$

$$+ w_x = (h_2 - h_1)$$

First we evaluate the enthalpy change using the generalized enthalpy chart Figure 10.6

$$h_2 - h_1 = h_2^* - h_1^* - (h_2^* - h_2) + (h_1^* - h_1)$$

Using mean specific heat for the term $h_2^* - h_1^*$ and arranging the other terms in a form suitable for using generalised enthalpy chart

$$h_2 - h_1 = c_p (T_2 - T_1) - \frac{R_u T_c}{M} \left(\frac{h_2^* - h_2}{R_u T_c} - \frac{h_1^* - h_1}{R_u T_c} \right)$$

From Table 10.2 $T_c = 305 \text{ K}$. Taking a mean value for c_p of ethane as 1.8 kJ/kg K and substituting other numerical values from Figure 10.6

$$+ w_x = h_2 - h_1 = 1.8 (573 - 300) - \frac{8.314 \times 305}{30} (1.25 - 4.5)$$

$$= 1.8 (273) - 84.5 (-3.25)$$

$$= 482.4 + 274.625$$

$$= 757.02 \text{ kJ/kg}$$

Therefore
$$\dot{W} = \dot{m} w = 757.02 \times 0.31$$

$$= 234.67 \text{ kW}$$