Section 6
Thermodynamic 2
Chapter 3
Ideal gas and real gases

Table 8.1. Constants of Van der Waals' Equation

S.No.	Substance	a $Nm^4/(kg\text{-}mol)^2$	b $m^3/kg\text{-}mol$
1.	Hydrogen (H_2)	25105	0.0262
2.	Oxygen (O_2)	139250	0.0314
3.	Carbon dioxide (CO_2)	362850	0.0423
4.	Helium (He)	3417620	0.0228
5.	Air	135522	0.0362
6.	Water (H_2O) vapour	551130	0.0300
7.	Mercury (Hg) vapour	2031940	0.0657

Table 8.2. Constants of the Beattie-Bridgeman Equation of State

Gas	A_0	a	B_0	b	$c \times 10^{-4}$
Hydrogen (H_2)	20.0117	−0.00506	0.02096	−0.04359	0.0504
Oxygen (O_2)	151.0857	0.02562	0.04624	0.004208	4.80
Carbon dioxide (CO_2)	507.2836	0.07132	0.10476	0.07235	66.0
Helium (He)	2.1886	0.05984	0.01400	0.0	0.0040
Air	131.8441	0.01931	0.04611	−0.001101	4.34
Nitrogen	136.2315	0.02617	0.05046	−0.00691	4.20
Argon	130.7802	0.02328	0.03931	0.0	5.99

Table 8.4. Properties of Gases

Gas	Molecular weight (M)	c_p (kJ/kg K)	c_v (kJ/kg K)	$R = c_p - c_v$ (kJ/kg K)	$\gamma = \frac{c_p}{c_v}$	$Z_c = \frac{p_c \bar{v}}{R_0 T_c}$
Air	28.97	1.005	0.718	0.287	1.4	0.284
Oxygen	32	0.920	0.660	0.260	1.4	0.307
Nitrogen	28	1.046	0.754	0.292	1.39	0.291
Hydrogen	2	14.40	10.40	4.0	1.38	0.304
Carbon monoxide	28	1.046	0.754	0.292	1.39	—

Problem 1

Example 8.4. *A vessel of capacity 3 m^3 contains 1 kg mole of N_2 at 90°C.*

(i) Calculate pressure and the specific volume of the gas.

(ii) If the ratio of specific heats is 1.4, evaluate the values of c_p and c_v.

(iii) Subsequently, the gas cools to the atmospheric temperature of 20°C ; evaluate the final pressure of gas.

(iv) Evaluate the increase in specific internal energy, the increase in specific enthalpy, increase in specific entropy and magnitude and sign of heat transfer.

Solution. Mass of N_2, m = 1 kg mole *i.e.*, 28 kg

Capacity of the vessel, $V_1 = 3\ m^3$

Temperature, $T_1 = 90 + 273 = 363$ K

(*i*) **Pressure (p_1) and specific volume (v_1) of the gas :**

Using the relation

$$p_1 V_1 = mRT_1$$

$$p_1 \times 3 = 28 \times \left(\frac{8314}{28}\right) \times 363 \qquad \left[\because \ R = \frac{R_0}{M} = \frac{8314}{28}\right]$$

$\therefore$ $\mathbf{p_1 = 1005994\ J/m^2}$ **or 10.06 bar. (Ans.)**

Specific volume, $\mathbf{v_1} = \dfrac{V_1}{m} = \dfrac{3}{28} = \mathbf{0.107\ m^3/kg.}$ **(Ans.)**

$$p_1V_1 = m_1RT_1 \qquad \left(\text{or } m_1 = \frac{p_1V_1}{RT_1}\right)$$

$$p_2V_2 = m_2RT_2 \qquad \left(\text{or } m_2 = \frac{p_2V_2}{RT_2}\right)$$

Mass of air removed during the process = $(m_1 - m_2)$ kg

$$(m_1 - m_2) = \frac{p_1V_1}{RT_1} - \frac{p_2V_2}{RT_2}$$

$$= \frac{1}{R}\left(\frac{p_1V_1}{T_1} - \frac{p_2V_2}{T_2}\right) = \frac{1}{287}\left[\frac{(1\times10^5)\times40}{298} - \frac{(0.4\times10^5)\times40}{278}\right]$$

$$= \mathbf{26.71\ kg.} \quad \textbf{(Ans.)}$$

Volume of this mass of gas at 1 bar and 25°C is given by

$$V = \frac{mRT}{p} = \frac{26.71\times287\times298}{1\times10^5} = \mathbf{22.84\ m^3.} \quad \textbf{(Ans.)}$$

(*ii*) $\mathbf{c_p = ?, c_v = ?}$

$$\frac{c_p}{c_v} = 1.4 \text{ (given)} \qquad ...(i)$$

But $$c_p - c_v = R = \frac{8314}{28} \qquad ...(ii)$$

Solving for c_p and c_v between (*i*) and (*ii*)

$$\mathbf{c_p = 1.039 \text{ kJ/kg K}; \quad c_v = 0.742 \text{ kJ/kg K.}} \quad \textbf{(Ans.)}$$

(*iii*) **Final pressure of the gas after cooling to 20°C :**

Initially	*After cooling*
$p_1 = 10.06$ bar	$p_2 = ?$
$V_1 = 3 \text{ m}^3$	$V_2 = 3 \text{ m}^3$
$T_1 = 363$ K	$T_2 = 20 + 273 = 293$ K

Now, $$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

or $$\frac{p_1}{T_1} = \frac{p_2}{T_2} \qquad (\text{as } V_1 = V_2)$$

$\therefore$ $$\mathbf{p_2} = \frac{p_1T_2}{T_1} = \frac{10.06 \times 293}{363} = \mathbf{8.12 \text{ bar.}} \quad \textbf{(Ans.)}$$

(*iv*) **Δu, Δh, Δs, Q :**

For a perfect gas,

Increase in specific internal energy

$$\Delta \mathbf{u} = c_v(T_2 - T_1) = 0.742(293 - 363) = \mathbf{-\ 51.94\ kJ/kg.} \quad \textbf{(Ans.)}$$

Increase in specific enthalpy,

$$\Delta \mathbf{h} = c_p(T_2 - T_1) = 1.039(293 - 363) = \mathbf{-\ 72.73\ kJ/kg.} \quad \textbf{(Ans.)}$$

Increase in specific entropy,

$$\Delta \mathbf{s} = c_v \log_e \left(\frac{T_2}{T_1}\right) + R \log_e \left(\frac{v_2}{v_1}\right)$$

But $\quad v_1 = v_2$

$$\therefore \quad \Delta s = c_v \log_e \left(\frac{T_2}{T_1}\right) = 0.742 \log_e \left(\frac{293}{363}\right) = \mathbf{-\ 0.1589\ kJ/kg\ K.} \quad \textbf{(Ans.)}$$

Now, $\quad Q = \Delta u + W$

Here $W = 0$ as change in volume is zero

$\therefore \quad Q = \Delta u$

$\therefore$ **Heat transfer,** $\quad \mathbf{Q} = -\ 51.94\ \text{kJ/kg} = -\ 51.94 \times 28 = \mathbf{-\ 1454.32\ kJ.} \quad \textbf{(Ans.)}$

Problem 3

Example 8.5. *(a) 1 kg of air at a pressure of 8 bar and a temperature of 100°C undergoes a reversible polytropic process following the law $pv^{1.2}$ = constant. If the final pressure is 1.8 bar determine :*

(i) The final specific volume, temperature and increase in entropy ;

(ii) The work done and the heat transfer.

Assume R = 0.287 kJ/kg K and γ = 1.4.

(b) Repeat (a) assuming the process to be irreversible and adiabatic between end states.

Solution. (*a*) Mass of air, $m = 1$ kg

Pressure, $p_1 = 8$ bar

Temperature, $T_1 = 100 + 273 = 373$ K

The law followed : $pv^{1.2} = \text{constant}$

Final pressure, $p_2 = 1.8$ bar

Characteristic gas constant, $R = 0.287$ kJ/kg K

Ratio of specific heats, $\gamma = 1.4$

(*i*) **v_2, T_2 and Δs :**

Assuming air to be a perfect gas,

$$p_1 v_1 = RT_1$$

$$\therefore \quad v_1 = \frac{RT_1}{p_1} = \frac{(0.287 \times 1000) \times 373}{8 \times 10^5} = 0.1338 \text{ m}^3/\text{kg}$$

Also, $$p_1 v_1^{1.2} = p_2 v_2^{1.2}$$

or $$\frac{v_2}{v_1} = \left(\frac{p_1}{p_2}\right)^{1/1.2}$$

or $$v_2 = v_1 \left(\frac{p_1}{p_2}\right)^{1/1.2} = 0.1338 \left(\frac{8}{1.8}\right)^{1/1.2} = 0.4637 \text{ m}^3/\text{kg}$$

i.e., Final specific volume, $\mathbf{v_2 = 0.4637 \text{ m}^3/\text{kg}}$. **(Ans.)**

Again, $$p_2 v_2 = RT_2$$

$$T_2 = \frac{p_2 v_2}{R} = \frac{1.8 \times 10^5 \times 0.4637}{(0.287 \times 1000)} = 290.8 \text{ K}$$

i.e., Final temperature, $\mathbf{t_2} = 290.8 - 273 = \mathbf{17.8°C}$. **(Ans.)**

Increase in entropy Δs is given by,

$$\Delta s = c_v \log_e \left(\frac{T_2}{T_1}\right) + R \log_e \left(\frac{v_2}{v_1}\right)$$

But $$\gamma = \frac{c_p}{c_v} = 1.4 \text{ (given)}$$

and $$c_p - c_v = R \text{ (= 0.287 kJ/kg K for air)}$$

Solving for c_v between (*i*) and (*ii*),

$$c_v = 0.717 \text{ kJ/kg K}$$

$$\therefore \quad \Delta s = 0.717 \log_e \left(\frac{290.8}{373}\right) + 0.287 \log_e \left(\frac{0.4637}{0.1338}\right)$$

$$= -0.1785 + 0.3567 = 0.1782 \text{ kJ/kg K}$$

i.e., Increase in entropy, $\mathbf{\Delta s = 0.1782 \text{ kJ/kg K}}$. **(Ans.)**

(*ii*) **Work done and heat transfer :**

The work done in a polytropic process is given by,

$$W = \frac{p_1 v_1 - p_2 v_2}{n-1} = \frac{R(T_1 - T_2)}{n-1}$$

$$= \frac{0.287\,(373 - 290.8)}{(1.2 - 1)} = 117.96 \text{ kJ/kg}$$

i.e., **Work done = 117.96 kJ/kg. (Ans.)**

Heat transfer, $Q = \Delta u + W$

where $\Delta u = c_v(T_2 - T_1)$

$= 0.717\,(290.8 - 373) = -58.94$ kJ/kg

$\therefore$ $Q = -58.94 + 117.96 = 59.02$ kJ/kg

Hence **heat transfer = 59.02 kJ/kg. (Ans.)**

(*b*) (*i*) Though the process is assumed now to be irreversible and adiabatic, the end states are given to be the same as in (*a*). Therefore, **all the properties at the end of the process are the same as in (a). (Ans.)**

(*ii*) As the process is adiabatic, Q (heat transfer) = **0. (Ans.)**

$\Delta u = \Delta u$ in (*a*)

Applying first law for this process

$$Q = \Delta u + W$$

$$0 = \Delta u + W$$

or $W = -\Delta u$

$= -(-58.94) = 58.94$

$\therefore$ **Work done = 58.94 kJ/kg. (Ans.)**

Problem 6

Example 8.7. *CO_2 flows at a pressure of 10 bar and 180°C into a turbine, located in a chemical plant, and there it expands reversibly and adibatically to a final pressure of 1.05 bar. Calculate the final specific volume, temperature and increase in entropy. Neglect changes in velocity and elevation.*

If the mass flow rate is 6.5 kg/min. evaluate the heat transfer rate from the gas and the power delivered by the turbine.

Assume CO_2 to be a perfect gas and c_v = 0.837 kJ/kg K.

Solution. *At entry to turbine* *At exit of turbine*

Pressure, p_1 = 10 bar Pressure, p_2 = 1.05 bar

Temperature, T_1 = 180 + 273 = 453 K

Since the expansion is reversible and adiabatic, therefore, the equation pv^γ = constant is applicable.

$$\therefore \quad p_1 v_1^\gamma = p_2 v_2^\gamma \qquad \ldots(i)$$

Eliminating v_1 and v_2 using the perfect gas equation

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

We can write equation (*i*) as

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{(\gamma-1)/\gamma}$$

$$\therefore \quad \frac{453}{T_2} = \left(\frac{10}{105}\right)^{(\gamma-1)/\gamma}$$

$$c_v = 0.837 \text{ kJ/kg K} \quad \text{(given)}$$

$$R = \frac{R_0}{M} = \frac{8.314}{44} \quad \text{(Molecular weight of } CO_2 = 44)$$

$$= 0.1889 \text{ kJ/kg K}$$

Also $\quad c_p - c_v = R$

$$\therefore \quad c_p - 0.837 = 0.1889$$

$$c_p = 1.0259 \text{ kJ/kg K}$$

$$\therefore \quad \gamma = \frac{c_p}{c_v} = \frac{1.0259}{0.837} = 1.23$$

Substituting for γ in equation (ii)

$$\frac{453}{T_2} = \left(\frac{10}{105}\right)^{(1.23-1)/1.23}$$

$$\therefore \quad T_2 = 297 \text{ K}$$

Final temperature $= 297 - 273 =$ **24°C. (Ans.)**

$$p_2 v_2 = RT_2$$

$$\therefore \quad 1.05 \times 10^5 \times v_2 = (0.1889 \times 1000) \times 297$$

$$\therefore \quad v_2 = \frac{(0.1889 \times 1000) \times 297}{1.05 \times 10^5} = 0.5343 \text{ m}^3/\text{kg}$$

Final specific volume $=$ **0.5343 m³/kg. (Ans.)**

As the process is reversible and adiabatic

$$\Delta s = 0$$

Increase in entropy = 0. (Ans.)

Since the process is adiabatic, therefore, **heat transfer rate from turbine = 0. (Ans.)**

Applying steady flow energy equation (S.F.E.E.) on unit time basis,

$$\dot{m}\left[h_1 + \frac{C_1^2}{2} + Z_1\right] + \dot{Q} = \dot{m}\left[h_2 + \frac{C_2^2}{2} + Z_2\right] + W$$

By data changes in velocity and elevation are negligible, and $Q = 0$.

$\therefore$ S.F.E.E. reduces to

$$W = \dot{m}(h_1 - h_2)$$

$$= \dot{m}\, c_p (T_1 - T_2) \qquad \left[as\ \frac{dh}{dT} = c_p, h_1 - h_2 = c_p (T_1 - T_2)\right]$$

$$= \frac{6.5}{60} \times 1.0259\,(453 - 297) = 17.34 \text{ kW}$$

Hence power delivered by the turbine = 17.34 kW. (Ans.)

Problem 9

Example 8.9. *One kg of CO_2 has a volume of 1 m^3 at 100°C. Compute the pressure by*
(i) Van der Waals' equation
(ii) Perfect gas equation.

Solution. (*i*) **Using Van der Waals' equation** :

Molar specific volume, $\bar{v} = 1 \times 44 = 44$ m³/kg-mol $\quad (\because \; M \text{ for } CO_2 = 44)$

Temperature, $T = 100 + 273 = 373$ K

The values of a and b for CO_2 (from Table 8.1)

$$a = 362850 \text{ Nm}^4/(\text{kg-mol})^2$$

and $$b = 0.0423 \text{ m}^3/\text{kg-mol}$$

$$R_0 = 8314 \text{ Nm/kg-mol K}$$

Van der Waals' equation is written as

$$\left(p + \frac{a}{\bar{v}^2}\right)(\bar{v} - b) = R_0 T$$

or $$p = \left(\frac{R_0 T}{\bar{v} - b} - \frac{a}{\bar{v}^2}\right)$$

Substituting the values in the above equation, we get

$$\therefore \quad \mathbf{p} = \frac{8314 \times 373}{44 - 0.0423} - \frac{362850}{44^2}$$

$$= 70548 - 187 = \mathbf{70361 \text{ N/m}^2 \text{ or } 0.7036 \text{ bar.}} \quad \textbf{(Ans.)}$$

(*ii*) **Using perfect gas equation :**

$$p\bar{v} = R_0 T$$

$$\therefore \quad \mathbf{p} = \frac{R_0 T}{\bar{v}} = \frac{8314 \times 373}{44} = \mathbf{70480 \text{ N/m}^2 \text{ or } 0.7048 \text{ bar.}} \quad \textbf{(Ans.)}$$

Problem 10

Example 8.10. *A container of 3 m³ capacity contains 10 kg of CO_2 at 27°C. Estimate the pressure exerted by CO_2 by using :*

(i) *Perfect gas equation*

(ii) *Van der Waals' equation*

(iii) *Beattie Bridgeman equation.*

Solution. Capacity of the container, $V = 3\ m^3$

Mass of CO_2, $m = 10$ kg

Temperature of CO_2, $T = 27 + 273 = 300$ K

Pressure exerted by CO_2, p :

(i) **Using perfect gas equation :**

Characteristic gas constant, $R = \dfrac{R_0}{M} = \dfrac{8314}{44} = 188.95$ Nm/kg K (for CO_2)

Using perfect gas equation

$$pV = mRT$$

$$\therefore \quad \mathbf{p} = \frac{mRT}{V} = \frac{10 \times 188.95 \times 300}{3}$$

$$= \mathbf{188950\ N/m^2 \text{ or } 1.889 \text{ bar. (Ans.)}}$$

(ii) **Using Van der Waals' equation :**

$$\left(p + \frac{a}{\bar{v}^2}\right)(\bar{v} - b) = R_0 T$$

$$p = \frac{R_0 T}{\bar{v} - b} - \frac{a}{\bar{v}^2}$$

From Table 8.1

For CO_2 :

$a = 362850$ Nm⁴/(kg-mol)²

$b = 0.0423$ m³/(kg-mol)

$$\bar{v} = \text{Molar specific volume} = \frac{3 \times 44}{10} = 13.2 \text{ m}^3\text{/kg-mol}$$

Now substituting the values in the above equation, we get

$$p = \frac{8314 \times 300}{13.2 - 0.0423} - \frac{362850}{(13.2)^2}$$

$$= 189562 - 2082.5 = \mathbf{187479.5\ N/m^2 \text{ or } 1.875 \text{ bar. (Ans.)}}$$

(*iii*) **Using Beattie Bridgeman equation :**

$$p = \frac{R_0 T(1-e)}{(\bar{v})^2}(\bar{v}+B) - \frac{A}{\bar{v}^2}$$

where p = pressure, $A = A_0\left(1-\frac{a}{\bar{v}}\right)$, $B = B_0\left(1-\frac{b}{\bar{v}}\right)$ and $e = \frac{c}{\bar{v}T^3}$

From Table 8.2 $A_0 = 507.2836,\ a = 0.07132$

$B_0 = 0.10476,\ \ b = 0.07235$

$C = 66 \times 10^4$

$$\therefore \quad A = 507.2836\left(1-\frac{0.07132}{13.2}\right) = 504.5$$

$$B = 0.10476\left(1-\frac{0.07235}{13.2}\right) = 0.1042$$

$$C = \frac{66\times10^4}{13.2\times(300)^3} = 0.001852$$

Now substituting the various values in the above equation, we get

$$\mathbf{p} = \frac{8314\times300(1-0.001852)}{(13.2)^2}(13.2+0.1042) - \frac{504.5}{(13.2)^2}$$

$$= 190093 - 2.89 \simeq 1.9\times10^5\ \text{N/m}^2 = \mathbf{1.9\ bar.}\quad \textbf{(Ans.)}$$