

Mechanical Engineering

Thermodynamics

Comprehensive Theory

with Solved Examples and Practice Questions



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Publications



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Thermodynamics

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Contents

Thermodynamics

Chapter 1

Basic Concepts & Zeroth Law of Thermodynamics 1

1.1	Introduction.....	1
1.2	System, Surroundings and Properties.....	1
1.3	State of the System & Process	3
1.4	Pure Substances	4
1.5	Zeroth Law of Thermodynamics	5
	<i>Objective Brain Teasers</i>	9
	<i>Student Assignments</i>	10

Chapter 2

Energy and Energy Interactions 11

2.1	Introduction.....	11
2.2	Work	12
2.3	Closed System Analysis	13
2.4	Ideal Gas.....	22
2.5	Heat	25
	<i>Objective Brain Teasers</i>	30
	<i>Student Assignments</i>	33

Chapter 3

First Law of Thermodynamics 35

3.1	Introduction.....	35
3.2	First Law of Thermodynamics	35
3.3	Enthalpy	40
3.4	Heat-Transfer in Various Processes	40
3.5	Free Expansion	54
	<i>Objective Brain Teasers</i>	62
	<i>Student Assignments</i>	67

Chapter 4

Open System Analysis by First Law 68

4.1	An Open System (or Control Volume)	68
4.2	Steady Flow Systems	68
4.3	Mass Balance and Energy Balance for Steady Flow Systems.....	69
4.4	SFEE Applied to Various Devices	73
4.5	Comparison of SFEE with Euler and Bernoulli's Equation.....	83
4.6	Unsteady Flow Process	84
	<i>Objective Brain Teasers</i>	104
	<i>Student Assignments</i>	108

Chapter 5

Second Law of Thermodynamics..... 109

5.1	Introduction.....	109
5.2	Thermal Energy Reservoir.....	110
5.3	Heat Engine	110
5.4	Kelvin - Planck Statement of Second Law.....	112
5.5	Refrigerators and Heat Pumps.....	113
5.6	Clausius Statement of the Second Law	116
5.7	Equivalence of Kelvin-Planck and Clausius Statement	116
5.8	Reversible and Irreversible Processes.....	117
5.9	The Carnot Cycle	122
5.10	The Carnot Principles	124
5.11	The Thermodynamic Temperature Scale	127
5.12	Maximum Performance Measures for Cycles Operating between Two Reservoirs Operating between two Reservoirs.....	129
	<i>Objective Brain Teasers</i>	146
	<i>Student Assignments</i>	151

Chapter 6

Entropy152

6.2	Clausius Inequality.....	152
6.3	The Property of Entropy.....	155
6.4	Principle of Entropy Increase	157
6.5	Temperature-Entropy Diagram.....	159
6.6	The T-dS Relations:.....	162
6.7	Entropy change for an Ideal Gas.....	164
6.8	Entropy Change of An Incompressible Substance.....	172
6.9	Finite Body Analysis.....	173
6.10	Reversible Steady-Flow Work.....	179
6.11	Second Law Analysis of a Control Volume	183
6.12	Available Energy	190
6.13	Available Energy Referred to a Cycle.....	191
6.14	Heat Transfer Through a Finite Temperature Difference.....	192
6.15	Availability and Availability function	196
6.16	Irreversibility	198
6.17	Second Law Efficiency	199
	<i>Objective Brain Teasers</i>	217
	<i>Student Assignments</i>	223

Chapter 7

Properties of Pure Substances225

7.1	Introduction.....	225
7.2	Phase Change of a Pure Substance.....	225
7.3	Property Diagrams	227
7.4	Quality and Saturated Liquid Vapour Mixture	229
7.5	Enthalpy and Entropy of Pure Substances	232
7.6	Steam Tables.....	233
7.7	Reference State and Reference Values	238
	<i>Objective Brain Teasers</i>	248
	<i>Student Assignments</i>	251

Chapter 8

Thermodynamic Relations.....253

8.1	Mathematical Theorems	253
8.2	The Maxwell Relations	254
8.3	Tds Partial Differential Equations	255
8.4	Specific Heats c_p and c_v	256
8.5	Energy Equations.....	261
8.6	The Joule-Thomson Coefficient.....	264
8.7	Clausius - Clapeyron Equation	267
8.8	Compressibility Factor	270
8.9	Van der Waal's equation of State.....	271
	<i>Objective Brain Teasers</i>	283
	<i>Student Assignments</i>	287



Thermodynamic Relations

8.1 Mathematical Theorems

Let three variables are represented by x , y and z . Their functional relationship may be expressed in the forms:

$$\begin{aligned} f(x, y, z) &= 0 \\ x &= x(y, z) \\ y &= y(x, z) \\ z &= z(x, y) \end{aligned}$$

Let x is a function of two independent variables y and z i.e.

$$x = x(y, z)$$

Then the differential of the dependent variable x is given by

$$dx = \left(\frac{\partial x}{\partial y} \right)_z dy + \left(\frac{\partial x}{\partial z} \right)_y dz$$

Where dx is called the exact differential

Let $\left(\frac{\partial x}{\partial y} \right)_z = M$ and $\left(\frac{\partial x}{\partial z} \right)_y = N$

then

$$dx = Mdy + Ndz$$

Partial differential of M and N with respect to z and y , respectively gives

$$\frac{\partial M}{\partial z} = \frac{\partial^2 x}{\partial y \partial z}$$

and

$$\frac{\partial N}{\partial y} = \frac{\partial^2 x}{\partial z \partial y}$$

or

$$\left(\frac{\partial M}{\partial z} \right)_y = \left(\frac{\partial N}{\partial y} \right)_z$$

This is the condition of exact or perfect differential

Similarly if, $y = y(x, z)$ and $z = z(x, y)$

then from these two relations we have

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz$$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

or it can be written for dy as

$$\begin{aligned} dy &= \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x \left[\left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \right] \\ &= \left[\left(\frac{\partial y}{\partial x}\right)_z + \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y \right] dx + \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial y}\right)_x dy \\ &= \left[\left(\frac{\partial y}{\partial x}\right)_z + \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y \right] dx + dy \end{aligned}$$

So we can conclude that the coefficient of dx should be zero in order to have above equation true

$$\begin{aligned} \therefore \left(\frac{\partial y}{\partial x}\right)_z + \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y &= 0 \\ \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y &= -\left(\frac{\partial y}{\partial x}\right)_z \\ \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y &= -1 \end{aligned}$$

In terms P , v and T , the following relation holds good

$$\left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial T}{\partial P}\right)_v \left(\frac{\partial v}{\partial T}\right)_P = -1$$

NOTE



Chain rule: If f is a function of x , y and z then

$$\left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f \left(\frac{\partial z}{\partial x}\right)_f = 1$$

8.2 The Maxwell Relations

The equations that relate the partial derivatives of properties P , v , T and s of a simple compressible system to each other are called the Maxwell relations. They are obtained from the four Gibbs equations by exploiting the exactness of the differential of thermodynamic properties.

Two of the Gibbs relations we have already seen

$$du = Tds - PdV \quad \dots (i)$$

$$\text{and} \quad dh = Tds + vdP \quad \dots (ii)$$

The other two Gibbs relations are based on two new combination properties the Helmholtz function f and the Gibbs function g , defined as

$$f = u - Ts$$

$$\text{and} \quad g = h - Ts$$

NOTE



- For any natural process the value of Gibbs function and Helmholtz function decreases and attains a minimum value.
- The rate of chemical reactions and their degree of completion is determined using the second law of thermodynamics

Differentiating the two new functions, we get

$$df = du - Tds - sdT$$

$$dg = dh - Tds - sdT$$

the above relations are simplified with the help of first two Gibbs relations, to obtain the other two Gibbs relations for simple compressible systems as

$$df = -sdT - Pdv \quad \dots \text{(iii)}$$

$$dg = -sdT + vdP \quad \dots \text{(iv)}$$

A careful examination of the four gibbs relations [(i) to (iv)] reveals that they are of the form

$$dx = Mdy + Ndz$$

with

$$\left(\frac{\partial M}{\partial z}\right)_y = \left(\frac{\partial N}{\partial y}\right)_z \quad \dots \text{(v)}$$

Since u , h , f and g are properties and thus have exact differentials. Applying equation (v) to each of them, we obtain

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v$$

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$$

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$

$$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$$

The above four relations are called the Maxwell relations. They are extremely valuable in thermodynamics because they provide a means of determining the change in entropy, which cannot be measured directly, by simply measuring the changes in properties P , v and T .

8.3 Tds Partial Differential Equations

Since entropy may be expressed as a function of any other two properties, e.g. Temperature T and specific volume v ,

Hence writing

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

i.e.

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$$

or
$$Tds = T\left(\frac{\partial s}{\partial T}\right)_v dT + T\left(\frac{\partial s}{\partial v}\right)_T dv \quad \dots (i)$$

But for a reversible constant volume change

$$dq = c_v(dT)_v = T(ds)_v$$

or
$$c_v = T\left(\frac{\partial s}{\partial T}\right)_v$$

But,
$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v \quad \text{(From Maxwell equations)}$$

Hence, substituting in equation (i), we get

$$Tds = c_v dT + T\left(\frac{\partial P}{\partial T}\right)_v dv$$

This is known as the first form of entropy equation, or the **First Tds equation**.

Similarly writing,

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

i.e.
$$ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP$$

or
$$Tds = T\left(\frac{\partial s}{\partial T}\right)_P dT + T\left(\frac{\partial s}{\partial P}\right)_T dP \quad \dots (ii)$$

But for a reversible constant pressure change

$$dq = c_p(dT)_P = T(ds)_P$$

or
$$c_p = T\left(\frac{\partial s}{\partial T}\right)_P$$

Also,
$$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P \quad \text{(From Maxwell relations)}$$

Substituting in equation (ii), we get,

$$Tds = c_p dT - T\left(\frac{\partial v}{\partial T}\right)_P dP$$

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

8.4 Specific Heats c_p and c_v

Equating the first and second Tds equations, we get

$$Tds = c_p dT - T\left(\frac{\partial v}{\partial T}\right)_P dP = c_v dT + T\left(\frac{\partial P}{\partial T}\right)_v dv$$

$$(c_p - c_v)dT = T\left(\frac{\partial P}{\partial T}\right)_v dv + T\left(\frac{\partial v}{\partial T}\right)_P dP$$

$$dT = \frac{T}{c_p - c_v} \left[\left(\frac{\partial P}{\partial T} \right)_v dv + \left(\frac{\partial v}{\partial T} \right)_P dP \right] \quad \dots (i)$$

Now temperature may be expressed as a function of any other two properties

so let $T = f(P, v)$

$$\therefore dT = \left(\frac{\partial T}{\partial P} \right)_v dP + \left(\frac{\partial T}{\partial v} \right)_P dv \quad \dots (ii)$$

Comparing equations (i) and (ii), we get

$$\frac{T}{c_p - c_v} \left(\frac{\partial v}{\partial T} \right)_P = \left(\frac{\partial T}{\partial P} \right)_v \text{ and } \frac{T}{c_p - c_v} \left(\frac{\partial P}{\partial T} \right)_v = \left(\frac{\partial T}{\partial v} \right)_P$$

Both these equations give

$$c_p - c_v = T \left(\frac{\partial P}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_P$$

$$\text{But, } \left(\frac{\partial T}{\partial P} \right)_v \cdot \left(\frac{\partial P}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_P = -1 \quad (\text{as } T = f(P, v))$$

\therefore We get,

$$c_p - c_v = -T \left(\frac{\partial P}{\partial v} \right)_T \left[\left(\frac{\partial v}{\partial T} \right)_P \right]^2$$

This relation can be expressed in terms of two other thermodynamic properties called the volume expansivity (β) and isothermal compressibility (K_T), which are defined as

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P$$

and

$$K_T = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T$$

Substituting these two relations, we obtain another relation for $c_p - c_v$ as:

$$c_p - c_v = \frac{TV\beta^2}{K_T}$$

It is called **Mayer's relation**.

Conclusions which can be drawn from the above equation are:

- (i) The isothermal compressibility K_T is a positive quantity for all substances in all phases. The volume expansivity β could be negative for some substance (such as liquid water below 4°C), but its square is always positive or zero. The temperature T in this relation is thermodynamic temperature which is also positive. Therefore we conclude that the constant pressure specific heat is always greater than or equal to the constant volume specific heat i.e.

$$c_p \geq c_v$$

- (ii) The difference between c_p and c_v approaches zero as the absolute temperature approaches zero.
- (iii) The difference between the two specific heats is very small and is usually disregarded for substances that are nearly incompressible, such as liquids and solids.

Example 8.1Show that $c_p - c_v = R$ for an ideal gas**Solution :**

We know for any gas

$$c_p - c_v = -T \left(\frac{\partial P}{\partial v} \right)_T \left[\left(\frac{\partial v}{\partial T} \right)_P \right]^2$$

The ideal gas equation of state gives us

$$Pv = RT \text{ or } P = \frac{RT}{v}$$

$$\therefore \left(\frac{\partial P}{\partial v} \right)_T = \frac{-RT}{v^2} = \frac{-P}{v}$$

and also,
$$v = \frac{RT}{P}$$

$$\therefore \left(\frac{\partial v}{\partial T} \right)_P = \frac{R}{P}$$

Substituting,
$$c_p - c_v = -T \left(\frac{-P}{v} \right) \times \left(\frac{R}{P} \right)^2 = \frac{T}{Pv} \times R^2 = \frac{1}{R} \times R^2 \quad (\text{as } Pv = RT)$$

$$\therefore c_p - c_v = R$$

Hence proved

Example 8.2

For a perfect gas, shown that

$$c_p - c_v = \left[P + \left(\frac{\partial u}{\partial v} \right)_T \right] \left(\frac{\partial v}{\partial T} \right)_P = Pv\beta + v\beta \left(\frac{\partial u}{\partial v} \right)_T$$

where β is the coefficient of cubical/volume expansion.**Solution :**

The first law of thermodynamics applied to a closed system undergoing a reversible process states as follows:

$$\delta Q = du + Pdv$$

and as per second law

$$ds = \left(\frac{\delta Q}{T} \right)_{\text{rev}}$$

Combining above two equation we have

$$Tds = du + Pdv$$

also we know,

$$h = u + Pv$$

$$\therefore dh = du + Pdv + v dP$$

- The change of temperature of a fluid during a throttling process is described by the

Joule-Thomson coefficient defined as $\mu = \left(\frac{\partial T}{\partial P} \right)_h$

and also $\mu = \frac{1}{c_p} \left[T \left(\frac{\partial v}{\partial T} \right)_P - v \right]$ for any substance

- The Clapeyron equation enables us to determine the enthalpy change associated with a phase change from a knowledge of P , v and T data alone. It is expressed as

$$\left(\frac{dP}{dT} \right)_{\text{sat}} = \frac{h_{fg}}{T_{\text{sat}} v_{fg}}$$

It can be further expressed as Clausius Clapeyron equation as

$$\left(\frac{dP}{dT} \right)_{\text{sat}} = \frac{(h_{fg})P_{\text{sat}}}{R(T_{\text{sat}})^2} \quad (\text{Assuming } v_g \gg v_f)$$

- The deviation from ideal gas behaviour can be properly accounted for by using the compressibility factor Z , defined as

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

The Z factor is approximately the same for all gases at the same reduced temperature and reduced pressure, which are defined as

$$T_r = \frac{T}{T_C} \text{ and } P_r = \frac{P}{P_C}$$

Where T_C and P_C are critical temperature and pressure respectively.

- The approximate behaviour of real gases was taken into consideration by Van der Waal in his equation of state for a gas given as

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

Where $a = \frac{27R^2T_C^2}{64P_C}$ and $b = \frac{RT_C}{8P_C}$



Objective Brain Teasers

Q.1 For a given volume of dry saturated steam, Clapeyron's equation is given by

(a) $v_g - v_f = \frac{dT_s}{dP} \times \frac{T_s}{h_g - h_f}$

(b) $v_g - v_f = \frac{dT_s}{dP} \times \frac{h_g - h_f}{T_s}$

(c) $v_g - v_f = \frac{dP}{dT_s} \times \frac{h_g - h_f}{T_s}$

(d) $v_g - v_f = \frac{dP}{dT_s} \times \frac{T_s}{h_g - h_f}$

Q.2 To get the cooling effect for a refrigerant, it has to be precooled at least below the



STUDENT'S ASSIGNMENTS

- Q.1** Using Maxwell's relations, show that for a pure substance

$$\begin{aligned} Tds &= c_p dT - T\beta dP \\ &= c_v dT + \frac{T\beta}{K} dv \\ &= \frac{Kc_v dP}{\beta} + \frac{c_p}{\beta} dv \end{aligned}$$

where β is the coefficient of cubical expansion, K is the coefficient of isothermal compressibility and c_p , c_v are specific heats at constant pressure and constant volume respectively.

- Q.2** Derive expressions for Δu , Δh and Δs for a gas that obeys the Van der Waal's equation of state for an isothermal process.

- Q.3** For a substance with volume expansivity, $\beta > 0$, show that at every point of a single phase region (vapour region) on a Mollier diagram, the slope of constant pressure line is greater than the slope of constant temperature line but less than that of constant volume line.

- Q.4** Show that for a Van der Waal's gas

(a) $\left(\frac{\partial c_v}{\partial v}\right)_T = 0$

(b) $(s_2 - s_1)_T = R \ln \left(\frac{v_2 - b}{v_1 - b} \right)$

(c) $T(v - b)^{R/c_v} = \text{Constant}$ for an isentropic process

(d) $c_p - c_v = \frac{R}{1 - \frac{2a(v - b)^2}{RTv^3}}$

(e) $(h_2 - h_1)_T = (P_2 v_2 - P_1 v_1) + a \left(\frac{1}{v_1} - \frac{1}{v_2} \right)$

■■■■