THERMODYNAMICS

Synopsis:

1. Thermodynamics deals with the relation between heat energy and other forms of energy.
2. The thermodynamics coordinates of a system which are also called state variables are pressure, volume and temperature which are inter dependent.
3. The temperature of a system can be expressed as a function of pressure and volume is f(P, V)=T.

Calorimetry:

4. Calorimetery is the study of the measurement of quantities of heat.
5. Quantity of heat is the amount of molecular energy stored in a body.
6. **Calorie :** The quantity of heat required by one gram of water to raise its temperature from 14.5°C to 15.5°C is called one calorie.
7. British Thermal Unit : The amount of heat required by 1 Pound of water to raise its temperature by 1°F is called one British thermal unit.
8. Pound calorie : The amount of heat required by
   1 Pound of water to raise its temperature by 1°C is called one pound calorie.
   1 pound calorie=453.6 calories
   1 calorie=4.186 joule

Heat Capacity :

9. The amount of heat required to produce a specified change of temperature is directly proportional to the mass of the material.
10. For a given mass of material, the amount of heat absorbed is directly proportional to the temperature increase.
11. The amount of heat required to raise the temperature of the whole body by 1°C is called heat capacity or thermal capacity. Unit is J/K or Cal/°C.

$$C = \frac{dQ}{dT}$$

12. Specific heat : The quantity of heat required by one gram of a substance to raise its temperature by 1°C is called its specific heat.

    or

    Heat capacity per unit mass. Unit is J/Kg-K or Cal/g-°C.

$$s = \frac{dQ}{mdT}$$

$$dQ = msdT$$

13. If m is the mass and s is the specific heat of the material of the body, then the thermal capacity = ms cal/°C.
14. Of all solids and liquids, water has the highest specific heat or specific heat capacity. The value is 1 cal/g/°C or 4200 J/kg/K.
15. The specific heat of lead is the least among solids. (i.e., 0.03 cal/g/°C)
16. In liquids, mercury has least specific heat.

17. Of all solids, liquids and gases, hydrogen has the highest specific heat. It is equal to 3.5 cal/g/°C.
18. Specific heat depends upon the nature of the substance and does not depend upon mass, volume and heat supplied.
19. Specific heat of copper = 0.1 cal/g/°C.
    Specific heat of ice = 0.5 cal/g/°C
    Specific heat of steam = 0.45 cal/g/°C
    Specific heat of lead = 0.03 cal/g/°C.
20. Specific heat of a solid at its melting point is infinite.
21. Specific heat of a liquid at its boiling point is infinite.
22. The **water equivalent** of a body is the number of grams of water which require the same amount of heat as the substance for the same rise of temperature. Unit is grams.

    Water equivalent=ms grams.
23. Water equivalent is numerically equal to heat capacity.
24. **Latent heat (L)** is the quantity of heat required by unit mass of a substance to change its state at a constant temperature. Unit of L is cal/g or J/kg.
25. **Latent heat of fusion** is the quantity of heat required by unit mass of a solid to melt it at its melting point.
26. The latent heat of ice is 80 cal/g or 3.35×10^5 J/kg.
27. **Latent heat of vapourisation** is the quantity of heat required by unit mass of a liquid to vapourise it at its boiling point.
28. The latent heat of steam is 540 cal/g or 2.26×10^6 J/kg.
29. Latent heat of vapourisation of water decreases with the increase of pressure (i.e., increase of boiling point).
30. The latent heat of steam at boiling point t is given by $L=600-0.06t$.
31. Latent heat of vapourisation decreases with increase in temperature.
32. Latent heat of a substance becomes zero at critical temperature.
33. Latent heat depends on the nature of a substance and pressure.
34. During the change of state, the formula used to calculate the heat lost or heat gained is Q = mL.
35. When one gram of steam at 100°C is mixed with one gram of ice at 0°C, the resultant temperature will be 100°C and mass of steam condensed will be 1/3 gram.
36. When one gram of ice is mixed with one gram of water at 80°C, the resultant temperature will be 0°C and the composition of mixture will be 2 grams of water.
37. Steam causes more burns than water at 100°C. The reason is that steam while condensing to water at 100°C gives out heat at the rate of 540 cal/g.
38. Calorific value of a fuel is the quantity of heat liberated when one gram of the fuel is burnt completely. Unit is cal/g or J/kg. It is determined by using Bomb calorimeter or Bell calorimeter.
39. Calorific value of a food stuff is the quantity of heat liberated when a unit mass of the food stuff is completely utilised by the body. Unit is cal/g or J/kg.
40. Steam is used in heat engines as working substance because of its high latent heat.
41. Heavy water is used as coolant in nuclear reactors because of its high specific heat.

42. In extinguishing fire hot water is preferred than cold water since hot water becomes vapour quickly and vapours do not allow fire.

LAW OF MIXTRUES (OR)

CALORIMETRY PRINCIPLE :

43. If no heat is lost or gained otherwise, the quantity of heat gained by the cold body is equal to the quantity of heat lost by the hot body. This is called the principle of the method of mixtures.
44. The principle of method of mixtures is Heat lost = Heat gained.
45. Calorimeter is generally made up of copper because it has low specific heat and high conductivity and hence attains the temperature of contents quickly.
46. To calculate the heat gained or lost when there is no change of state, we use the formula Q=mst.
47. When three substances of different masses m_1, m_2 and m_3 specific heats s_1, s_2, s_3 and at different temperatures t_1, t_2 and t_3 respectively are mixed, then the resultant temperature is

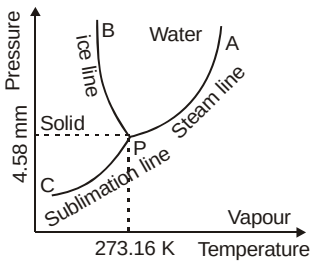
$$t = \frac{m_1s_1t_1 + m_2s_2t_2 + m_3s_3t_3}{m_1s_1 + m_2s_2 + m_3s_3}$$

48. When "x" gram of steam is mixed with "y" gram of ice, the resultant temperature is

$$t = \frac{80(8x - y)}{(x + y)}$$

TRIPLE POINT :

49. The temperature and pressure where solid, liquid and vapour states are co-exist is called triple point.
50. The triple point of water is 273.16 K (0.00750°C) and pressure 613.10 Pa (0.459 cm of Hg).



51. A graph drawn between the pressure and temperature representing the different states of matter is called the phase diagram.
52. PA is the steam line and along this line water and steam are in equilibrium state.
53. Above the line water exists and below steam exists.
54. The curve has positive slope showing the boiling point increases with pressure.
55. CP is called Hoar-frost line. Along this line ice and vapour coexist.
56. CP has positive slope.
57. PB is called ice line, along this line water and ice are in equilibrium.
58. Above the ice line water exists. The curve has negative slope showing the melting point decreases with increase of the pressure.

THERMODYNAMICS:

59. Internal energy depends only on temperature and is independent of pressure and volume.
60. Internal energy=P.E+K.E, where potential energy is due to molecular configuration and K.E is due to molecular motion.
61. Internal energy of an ideal gas consists of only the K.E of molecules (P.E is absent because there are no intermolecular forces among the molecules in an ideal or perfect gas).
62. Internal energy of a real gas consists of P.E and K.E.
63. The amount of work performed is directly proportional to the amount of heat produced ($W \alpha H$).

64. W=JH, where J is known as mechanical equivalent of heat or **Joule's constant**. J is equal to the amount of work required to produce one calorie of heat. Its value is equal to 4.186 joule/calorie. SI unit is J/kcal. The statement W=JH is also called the non-differential form of the first law of thermodynamics.
65. J=4.186 J/cal=4.186x10^7 erg/cal=4186 J/Kcal
66. When heat and work are in Joule then J=1.
67. The height form which ice is to be dropped to melt it completely is
    $h=\frac{JL}{g}$ where L=latent heat of ice.
68. The rise in temperature of water when it falls from a height h to the ground is
    $\Delta\theta=\frac{gh}{Js}$ where 's' is specific heat of water.
69. When a body of mass m moving with a velocity v is stopped and all of its energy is retained by it, then the increase in temperature is
    $\Delta\theta=\frac{v^2}{2Js}$
70. When a block of ice of mass M is dragged with constant velocity on a rough horizontal surface of coefficient of friction μ, through a distance d, then the mass of ice melted is
    $m=\frac{\mu Mgd}{JL}$ where m=mass of ice melted.
71. When a block of mass m is dragged on a rough horizontal surface of coefficient of friction μ, then the rise in temperature of block is
    $\Delta\theta=\frac{\mu gd}{Js}$
72. If a bullet just melts when stopped by an obstacle and if all the heat produced is absorbed by the bullet then
    $ms\Delta\theta+mL=\frac{1}{2}\frac{mv^2}{J}$
    where L=latent heat of the material of the bullet
    s=specific heat
73. A metal ball falls from a height 'h_1', and bounces to height 'h_2'. The rise in temperature of the ball is
    $\Delta\theta=\frac{g(h_1-h_2)}{Js}$
74. Joule's law or Mayer's hypothesis : It states that there is no change in internal energy during the free expansion of gas.

SPECIFIC HEAT OF GASES :

75. A gas will have two specific heats.
    a) specific heat at constant volume (C_V)
    b) specific heat at constant pressure (C_P)
76. Specific heat depends only on the nature of material and temperature.
77. Water has largest specific heat among solids and liquids.
78. Among solids, liquids and gases specific heat is maximum for hydrogen.
79. Specific heat slightly increases with increase of temperature.
80. In liquids specific heat is minimum for mercury.

81. The value of specific heat may lie between 0 and ∞.
82. In isothermal process, the value of specific heat is ∞ but in adiabatic process its value is zero.
83. Specific heat of water is maximum at 15°C and minimum at 37°C.
84. Specific heat of all substances is zero at 0 K.
85. Substances with highest specific heat are bad conductors of heat and with low specific heat are good thermal and electrical conductors.
86. The substance with large specific heat warms up slowly and cools down slowly.
87. C_P is greater than C_V and
$\frac{C_P}{C_V} = \gamma$
88. $C_P - C_V = R$ (for 1 mole of gas) where R is universal gas constant
R=8.3 J/mol-K
89. $C_P - C_V = r$ (for 1 g of gas)
where r is specific gas constant.
$C_P - C_V = R/J$ (in heat units)

C_V, C_P and values of different gases :

S.No.	Nature of gas	C_P	C_V	$\gamma = C_P/C_V$
1.	Monoatomic	$\frac{5}{2}R$	$\frac{3}{2}R$	$\frac{5}{3}$=1.67
2.	Diatomic	$\frac{7}{2}R$	$\frac{5}{2}R$	$\frac{7}{5}$=1.4
3.	Tri (or) Polyatomic	4R	3R	$\frac{4}{3}$=1.33

90. γ value is always greater than one. It depends upon the atomicity of a gas. It decreases with increase in atomicity.
$C_P = \gamma \frac{R}{\gamma - 1}$ and $C_V = \frac{R}{\gamma - 1}$
91. γ of mixture of gases : When n_1 moles of a gas with specific heat at constant volume C_{V_1} is mixed with n_2 moles of another gas of specific heat at constant volume C_{V_2} then

$(C_V)_{mixture} = \frac{n_1 C_{V_1} + n_2 C_{V_2}}{n_1 + n_2}$

$(C_P)_{mixture} = (C_V)_{mixture} + R = \frac{n_1 C_{P_1} + n_2 C_{P_2}}{n_1 + n_2}$

$\gamma_{mixture} = \frac{C_{P(mixture)}}{C_{V(mixture)}}$; $\frac{n_1 + n_2}{\gamma_{mix} - 1} = \frac{n_1}{\gamma_1 - 1} + \frac{n_2}{\gamma_2 - 1}$

Fraction of heat absorbed that is converted into internal energy is $\frac{dU}{dQ} = \frac{C_V}{C_P} = \frac{1}{\gamma}$

Fraction of heat absorbed that is converted into workdone= $\frac{dW}{dQ} = \frac{R}{C_P} = 1 - \frac{1}{\gamma}$

Isothermal Process :

92. In this process, the pressure and volume of gas changes but temperature remains constant.

93. The system is in thermal equilibrium with the surroundings.
94. It is a slow process.
95. The internal energy of the system remains constant i.e, du = 0.
96. It obeys the Boyle's law i.e., PV=K.
97. The work done during isothermal expansion at constant temperature is

    $W=2.303RT\log_{10}\left(\frac{V_2}{V_1}\right)$

    $=2.303RT\log_{10}\left(\frac{P_1}{P_2}\right)$

98. The isothermal elasticity $=-\frac{dP}{dV/V}=P$.

    The –ve sign represents, as pressure increases volume decreases.
99. It takes place in a conducting vessel.

Adiabatic Process :

100. The pressure, volume and temperature of a gas change but total heat remains constant. i.e., dQ=0 (Q=constant)
101. It is a quick process.
102. The internal energy changes as temperature changes.
103. The adiabatic process is represented by the equations

    PV^{γ}=constant

    $TV^{\gamma-1}$=constant

    $P^{1-\gamma}T^{\gamma}$=constant
104. The work done by the system during the adiabatic expansion is

$$W=\frac{R}{\gamma-1}(T_1-T_2)=nC_V(T_1-T_2)$$

$$=n\frac{C_P}{\gamma}(T_1-T_2)$$

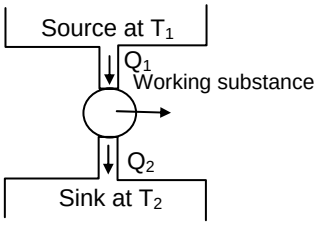
$$=\frac{P_2V_2-P_1V_1}{\gamma-1}$$

105. The adiabatic elasticity of gas is γP.
106. The slope of adiabatic curve is γ times greater than the isothermal curve.
107. It takes place in a non conducting vessel.
108. Adiabatic expansion causes cooling and contraction causes heating.
109. If two samples of gases are compressed so that their pressures have the same increase, one sample isothermally and the other adiabatically, final volume is more in adiabatic change. If their pressures decrease by the same factor the final volume is more in isothermal change.
110. **Isochoric process :** It is a process in which the volume of the system remains constant.
    i.e., $\Delta V=0$ for such process $\Delta W=0$.
111. **Isobaric process :** It is a process in which the pressure of the system remains constant. i.e., $\Delta P=0$.
112. The equation of state for different types of processes :

Sl. No	Name of the process	Quantity remains constant	Quantity which becomes zero	Result in I law
1.	Isothermal	temperature	dU	dQ=dW
2.	Isobaric	pressure	None	dQ=dU+dW
3.	Isochoric	volume	dW	dQ=dU
4.	Adiabatic	heat energy	dQ	dU=–dW

113. Work done is maximum during isobaric process and minimum in adiabatic process.

HEAT ENGINES :



114. Heat engine is a device used to convert heat into mechanical work.

115. Heat engines are of two types namely internal combustion engine and external combustion engine.

a) Internal combustion engine is an engine in which heat is produced in the engine itself.

Ex : Otto engine and Diesel engine.

b) In external combustion engine, heat is produced outside the engine.

Ex : steam engine.

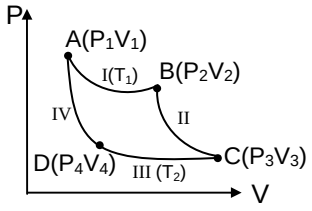
116. Heat engine absorbs a quantity of heat Q_1 from a source, performs an amount of work W, and returns to the initial state after rejecting some heat Q_2 to a sink. The working substance, which is a gas or liquid undergoes a cyclic thermodynamic process. The source is at a higher temperature than the sink.

117. The efficiency η of a heat engine is given by

$$\eta = \frac{\text{heat converted to work}}{\text{total heat absorbed}} = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}.$$

From the above expression it is clear that the efficienty of a heat is always less than 1 or 100%.

118. Carnot heat engine essentially consists of four components. They are



i) a cylinder with perfect thermal insulating walls, perfect conducting base and a tight fitting perfect insulating and frictionless piston (It consists of a working substance).

ii) a hot body of infinitely large heat capacity at a constant temperature serving as a source.

iii) a cold body of infinitely large heat capacity at a constant temperature serving as a sink and

iv) a perfectly thermal insulating stand.

119. **Carnot Engine** : Carnot developed, ideal heat engine that has maximum possible efficiency consistent with the second law. The working substance is imagined to go through a cycle of four processes known as **Carnot cycle**. The working substance, an ideal gas, undergoes a cycle which consists of two isothermal and two adiabatic processes as follows.

i) Step I (AB) : The gas expands isothermally at source temperature T_1 and absorbs heat Q_1.

$W_1 = Q_1 = nRT_1 \cdot \ln\left(\frac{V_2}{V_1}\right)$.

ii) Step II (BC) : The gas expands adiabatically until its temperature decreases to the sink temperature T_2. $W_2 = \frac{nR(T_1 - T_2)}{\gamma - 1}$.

iii) Step III(CD) : The gas is compressed isothermally at T_2, rejecting heat Q_2.

$W_3 = Q_2 = nRT_2 \ln\left(\frac{V_3}{V_4}\right)$

iv) Step IV(DA) : The gas is compressed adiabatically until it returns to its initial state A.

$W_4 = \frac{nR(T_1 - T_2)}{\gamma - 1}$.

v) All the steps are carried out very slowly so that there are no dissipative effects.

vi) The process is reversible.

vii) $W = Q_1 - Q_2$.

viii) $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$

It can be shown that the efficiency of Carnot engine is $\eta = 1 - \frac{T_2}{T_1}$.

120. η can be 100% only if $T_2 = 0$. i.e., the sink is maintained at absolute zero which is impossible.

121. A decreases in T_2 is more effective than an equal increase in T_1 in increasing the efficiency.

122. The efficiency of engine depends upon the temperature of source and sink.

123. The efficiency of the engines working between same source and sink is same.

124. The efficiency of a reversible engine is independent of the nature of the working substance.

125. The net external work done obtained is the area enclosed.

126. **Carnot theorem :** No engine working between two given temperatures can be more efficient than a reversible engine working between the same two temperatures have the same efficiency, whatever may be the working substance.

127. If many heat engines are operating in series in such a way that the first engine absorbs a quantity of heat Q_1 at T_1 and the last engine rejects heat Q_n at the lowest temperature T_n the efficiency of the combination is given by

$\eta = \sum\frac{W}{Q_1} = \frac{Q_1 - Q_n}{Q_1} = 1 - \frac{T_n}{T_1}$.

128. The Carnot's cycle working in the opposite direction can perform the following two functions.

i) It can further root the colder body.

ii) It can further heat the hot body.

a) When reversed heat engine is used to further cool the colder system the arrangment is called a **refrigerator**.

b) When the reversed heat engine is used to further heat the hotter system it is known as **Heat pump**.

129. **Principle of Refrigerator :**

a) It will absorb an amount of heat Q_2 from the sink (contents of refrigerator) at lower temperature T_2.

b) As heat is to be removed from the sink at lower temperature, an amount of work equal to $Q_1 - Q_2$ is performed by the compressor of refrigerator and then it rejects the total heat Q to the same (atmosphere) through the radiator fixed at its back.

130. **Coefficient of performance :**

The ratio of the quantity of heat removed per cycle from the contents of the refrigerator to the work done by the external agency to remove it is called **co-efficient of performance** of the refrigerator. It is denoted by 'β'.

$$\beta = \frac{Q_2}{w} = \frac{Q_2}{Q_1 - Q_2}$$

$$\Rightarrow \beta = \frac{1}{\frac{Q_1}{Q_2} - 1}$$

But $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$

$$\beta = \frac{1}{\frac{T_1}{T_2} - 1}$$

$$\therefore \quad \beta = \frac{T_2}{T_1 - T_2}$$

$$\Rightarrow \beta = \frac{1-\eta}{\eta}.$$

131. **SECOND LAW OF THERMODYNAMICS :**

(a) **Classius statement :** It is impossible for a self acting machine. (The machine which does not require any external source of energy for working), unaided by any external agency to transfer heat from a body at lower temperature to another at a higher temperature. (or)
Heat cannot of itself flow from a colder body to a hotter body.

(b) **Kelvin statement :** It is impossible to construct a heat engine operating in a cycle to convert the heat energy completely into work without any change of working substance. (or)
No heat engine can convert whole of the heat energy supplied to it into useful work.

132. Absolute zero is the temperature at which reversible isothermal process takes place without any transfer of heat. i.e., at absolute zero isothermal and adiabatic processes are identical.