

2.3 THERMODYNAMICS

Thermal energy, or internal energy refers to the total energy of all the molecules in a body. **Heat** refers to the transfer of energy from one body to another due to a difference of temperature.

The first law of thermodynamics states that the heat Q absorbed by a system in some physical process is the sum of the work W done by the system on its external surroundings and the change ΔU in the total internal energy of the system:

$$Q = \Delta U + W.$$

Specific heat capacity or specific heat c is defined as the quantity of heat absorbed or emitted by 1 kg of mass of the system when its temperature changes by one degree. Since c depends on how the process of heating is carried out we introduce

- specific heat at constant pressure: $c_p = \frac{1}{m} \left(\frac{\partial Q}{\partial T} \right)_p$

- specific heat at constant volume: $c_v = \frac{1}{m} \left(\frac{\partial Q}{\partial T} \right)_v$

For liquids and solids we have $c \approx c_p \approx c_v = \frac{1}{m} \frac{Q}{\Delta T} = \frac{1}{m} \frac{\Delta U}{\Delta T}$.

For gases we introduce molar specific heats defined as the quantity of heat absorbed or emitted by 1 mole of mass of the system when its temperature changes by one degree. Thus we have:

- molar specific heat at constant pressure: $C_p = \frac{1}{n} \left(\frac{\partial Q}{\partial T} \right)_p$

- molar specific heat at constant volume: $C_v = \frac{1}{n} \left(\frac{\partial Q}{\partial T} \right)_v$,

where n expresses the amount of substance in moles.

For the ideal gas we have:

$$C_p = \frac{i+2}{2} R \quad C_v = \frac{i}{2} R.$$

The ratio of molar specific heats is called Poisson's constant: $\kappa = \frac{C_p}{C_v}$.

Molar specific heats are related by the following formula: $C_p - C_v = R$, where R is the universal gas constant.

A reversible process is a process in which a gas goes from one state to another through a succession of infinitesimally close equilibrium states in which pressure and temperature are defined at all instants.

A change in the internal energy of the system does not depend on the type of process but only on the temperature:

$$dU = n C_v dT.$$

The work done in taking a system from one state to another depends not only on the initial and final state of the system but also on the type of process:

$$\delta W = P(V).dV.$$

The total work done by the ideal gas when its volume changes from V_1 to V_2 is:

$$W = \int_{V_1}^{V_2} P(V) dV.$$

The first law of thermodynamics for a reversible process has the following form:

$$Q = n C_V (T_2 - T_1) + \int_{V_1}^{V_2} P(V) dV.$$

Summing up of reversible processes for ideal gases:

1. Isochoric process ($V = \text{constant}$):

- all the heat added to the gas is used to increase its internal energy or

$$Q = \Delta U = n C_V (T_2 - T_1)$$

2. Isobaric process ($P = \text{constant}$):

- the heat added to the gas is

$$Q = \Delta U + W = n C_P (T_2 - T_1).$$

3. Isothermal process ($T = \text{constant}$):

- the heat added to the gas is used for work done by the gas:

$$Q = W = nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{P_1}{P_2}$$

4. Adiabatic process ($\delta Q = 0$):

- the work of the gas is done on the account of its internal energy:

$$W = -\Delta U = n C_V (T_1 - T_2).$$

An adiabatic process can be described by the following equation:

$$P V^\kappa = \text{constant}.$$

Entropy S is a state variable which is defined as

$$dS = \frac{\delta Q}{T}.$$

Change in entropy of an ideal gas going from one state ($P_1; V_1; T_1$) to another state ($P_2; V_2; T_2$) is

$$\Delta S = n C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}.$$

The Carnot cycle consists of two isothermal and two adiabatic processes. We assume that the working substance is one mole of an ideal gas and the process takes place between the temperature of a hot reservoir T and the temperature of a cold reservoir T_0 . If we denote the amount of heat absorbed by the gas from the hot reservoir as Q and the amount of heat rejected to the cold reservoir as Q_0 the work done by the gas in one cycle is

$$W = Q - Q_0$$

The efficiency of the Carnot cycle is defined as the ratio of work done by the gas in one cycle and the amount of heat taken from the hot reservoir

$$\eta = \frac{W}{Q} = 1 - \frac{T_0}{T}.$$

If a Carnot cycle is operated in reverse, so that the external work W is done on the working gas, instead of by it, the result is a refrigerator. The working gas now absorbs heat Q_0 from a cold reservoir and will reject this heat increased by the amount of the external work W . For the **Carnot refrigerator cycle** the efficiency is defined as the ratio of heat Q_0 absorbed from a cold reservoir and external work W :

$$\eta_r = \frac{Q_0}{W}.$$

The second law of thermodynamics can be stated in many forms:

Clausius stated this law in following form:

- heat cannot, of itself, pass from a colder to a hotter body.

Statement using the concept of entropy and formulated for irreversible processes:

- the entropy of an isolated system must increase whenever it undergoes an irreversible process.

The third law of thermodynamics states:

- it is not possible to reach absolute zero temperature in any finite number of processes.

Problem 2-33. A wheel making $n=1200$ revolutions per minute is slowed by a break cooled by 8 cubic meters of water per hour. The temperature of the water is $t=10^\circ\text{C}$. The torque of the friction forces is $M=5000 \text{ N.m}$. Calculate the temperature of the water leaving the break, assuming that 75% of the work done by the friction forces is used to increase the internal energy of the cooling water. The specific heat of water is $c=4186 \text{ J.kg}^{-1}.\text{K}^{-1}$.

Solution: The work done by friction forces when the wheel is rotated by the angle φ is

$$W = M.\varphi$$

The work done by this force increases the internal energy of the water and surroundings. The part of this work, in our case 75%, increases the internal energy of the water that is used to cool the the break. This increase in the internal energy is accompanied by an increase in the temperature of the water. The same increase of temperature is obtained if we add to the water a certain amount of heat from an external source. To heat a mass of water m by the temperature Δt the amount of heat required is

$$Q = m.c.\Delta t.$$

From the first law of thermodynamics we have

$$0.75 W = m.c.\Delta t$$

or

$$0.75 M.\varphi = m.c.\Delta t \quad (1)$$

We assume a constant angular velocity $\omega = 2\pi n$. Suppose that in time t the wheel is rotated by the angle φ , where

$$\varphi = 2\pi n t$$

Substituting for φ into equation (1) we obtain for the increase in temperature:

$$\Delta t = 0.75 \frac{M \cdot 2\pi \cdot n \cdot t}{m \cdot c} = 0.75 \frac{5000 \times 2\pi \cdot \frac{1200}{60} \cdot 3600}{8 \times 10^3 \times 4186} = 50.6^\circ\text{C}.$$

Since the initial temperature of the water was 10°C , the final temperature of the water will be 60.6°C .

Problem 2-34. Calculate molar heat capacities C_V , C_P and Poisson's constant κ for a mixture of gases. The amounts of substance of the mixture components are n_1, n_2, \dots, n_k respectively and the molar heats of the components are $C_{1V}, C_{2V}, \dots, C_{kV}$ and $C_{1P}, C_{2P}, \dots, C_{kP}$.

Solution: One mole of the mixture is defined as the amount of substance containing N_A molecules. Thus the number of moles in the mixture is

$$n = n_1 + n_2 + \dots + n_k = \frac{m_1}{M_1} + \frac{m_2}{M_2} + \dots + \frac{m_k}{M_k}$$

where M_k is the molar mass of the k -component of the mixture.

To determine C_P we express the amount of heat that is required to increase the temperature of $(n_1 + n_2 + \dots + n_k)$ moles of the mixture by $1K$ at constant pressure using the following equation:

$$n_1 C_{1P} + n_2 C_{2P} + \dots + n_k C_{kP} = n C_P$$

From this equation we find

$$C_P = \frac{n_1 C_{1P} + n_2 C_{2P} + \dots + n_k C_{kP}}{n} = \frac{n_1 C_{1P} + n_2 C_{2P} + \dots + n_k C_{kP}}{n_1 + n_2 + \dots + n_k}$$

Similarly, to determine C_V we express the amount of heat that is required to increase the temperature of $(n_1 + n_2 + \dots + n_k)$ moles of the mixture by $1K$ at constant volume using the following equation:

$$n_1 C_{1V} + n_2 C_{2V} + \dots + n_k C_{kV} = n C_V$$

Thus we have

$$C_V = \frac{n_1 C_{1V} + n_2 C_{2V} + \dots + n_k C_{kV}}{n_1 + n_2 + \dots + n_k}.$$

Finally for Poisson's constant we obtain

$$\kappa = \frac{C_P}{C_V} = \frac{n_1 C_{1P} + n_2 C_{2P} + \dots + n_k C_{kP}}{n_1 C_{1V} + n_2 C_{2V} + \dots + n_k C_{kV}}.$$

Problem 2-35. Calculate the molar heat capacities C_V , C_P and Poisson's constant κ for a mixture of 3 kmoles of argon and 5 kmoles of oxygen O_2 .

Solution: Since argon is a monatomic molecule we can write

$$C_{1V} = \frac{3}{2}R \quad \text{and} \quad C_{1P} = \frac{5}{2}R.$$

A molecule of oxygen O_2 is diatomic. Thus we have

$$C_{2V} = \frac{5}{2}R \quad \text{and} \quad C_{2P} = \frac{7}{2}R.$$

Following the results of problem 2-34 we can write

$$C_V = \frac{3 \frac{3}{2}R + 5 \frac{5}{2}R}{3 + 5} = \frac{17}{8} 8314 = 17667 \text{ J.K}^{-1} \text{ kmol}^{-1}$$

$$C_P = \frac{3 \frac{5}{2}R + 5 \frac{7}{2}R}{3 + 5} = \frac{25}{8} 8314 = 25981 \text{ J.K}^{-1} \text{ kmol}^{-1}$$

Finally for Poisson's constant we have

$$\kappa = \frac{C_P}{C_V} = \frac{25}{17} = 1.47.$$

Problem 2-36. The density of a gas at pressure $P = 10^5 \text{ Pa}$ and temperature $t = 20^\circ\text{C}$ is $\rho = 1.27 \text{ kg.m}^{-3}$. Calculate its specific heats c_V and c_P if Poisson's constant of the gas is $\kappa = 1.4$.

Solution: Poisson's constant is defined as $\kappa = \frac{C_P}{C_V}$.

We also know that $C_P = C_V + R$. Combining these two equations we obtain

$$C_V = \frac{R}{\kappa - 1}.$$

The relation between specific and molar heat is

$$c_V = \frac{C_V}{M} = \frac{R}{M(\kappa - 1)}.$$

Since we do not know the molar weight M of the gas we use the ideal gas law

$$P.V = \frac{m}{M} R.T \quad \Rightarrow \quad M = \frac{\rho R.T}{P}.$$

Substituting for M into the expression for c_V we obtain

$$c_V = \frac{P}{(\kappa - 1)\rho T} = \frac{10^5}{(1.4 - 1) \times 1.27 \times 293} = 671.8 \text{ J.kg}^{-1} \text{ K}^{-1}.$$

Similarly, for c_P we have

$$c_P = \kappa c_V = \kappa \frac{P}{(\kappa - 1)\rho T} = 940.6 \text{ J.kg}^{-1} \text{ K}^{-1}.$$

Problem 2-37. A quantity of CO at temperature $t_1 = 18^\circ\text{C}$ and pressure $P_1 = 294 \text{ kPa}$ is enclosed in a container of volume $V = 20 \text{ l}$. Calculate the temperature and pressure of the CO if it absorbs heat $Q = 21 \text{ kJ}$. The specific heat and the molar weight of CO are $c_V = 740 \text{ J.kg}^{-1} \text{ K}^{-1}$ and 28 kg/kmol .

Solution: $Q = mc_v(T_2 - T_1) \Rightarrow T_2 = \frac{Q}{m c_v} + T_1$ (1)

From the ideal gas law we have $m = \frac{P_1 V M}{R T_1}$ (2)

Substituting equation 2 into equation 1 we obtain

$$T_2 = \frac{Q R T_1}{P_1 V M c_v} + T_1$$
 (3)

Substituting equation 3 into Gay-Lussac's law we obtain for pressure

$$P_2 = P_1 \frac{T_2}{T_1} = \frac{Q R}{V M c_v} + P_1$$

Numerically we obtain

$$T_2 = \frac{21 \times 10^3 \times 8314 \times 291}{294 \times 10^3 \times 20 \times 10^{-3} \times 28 \times 740} + 291 = 708 K$$

$$P_2 = 294 \times 10^3 \frac{708}{291} = 715 \times 10^3 Pa$$

Problem 2-38. A certain amount of gas is enclosed in a volume $V=3$ l at pressure $P=2 \times 10^5 Pa$. The Poisson's constant of the gas is $\kappa=1.4$. Calculate the amount of heat that must be absorbed by the gas undergoing an isobaric process if its volume is allowed to increase three times.

Solution: From the first law of thermodynamics for an ideal gas we have

$$\delta Q = m c_v dT + P dV$$
 (1)

We can differentiate the ideal gas law $PV=nRT$

$$P dV + V dP = \frac{m}{M} R dT$$

Since the process is isobaric $dP=0$. Thus we have

$$m dT = \frac{M P dV}{R}$$
 (2)

Substituting equation (2) into equation (1) we obtain

$$\delta Q = c_v \frac{M P dV}{R} + P dV = \frac{C_v + R}{R} P dV = \frac{C_p}{R} P dV$$

After integration we have

$$Q = \frac{C_p}{R} P \int_{V_1}^{V_2} dV = \frac{C_p}{R} P (V_2 - V_1) = \frac{C_p}{R} P \cdot 2V$$

Combining equations $C_p - C_v = R$ and $\kappa = \frac{C_p}{C_v}$ we obtain

$$\frac{C_p}{R} = \frac{\kappa}{\kappa - 1}$$

Finally, for the heat that must be absorbed by the gas we have

$$Q = \frac{2\kappa}{\kappa - 1} PV = \frac{2 \times 1.4}{(1.4 - 1)} 2 \times 10^5 \times 3 \times 10^{-3} = 4.2 \times 10^3 J$$

Problem 2-39. Oxygen of mass of 3.2 g is enclosed in a cylinder fitted with a light frictionless piston at pressure $P_1 = 2 \times 10^5 \text{ Pa}$ at temperature $t_1 = 27^\circ\text{C}$. The oxygen is allowed to expand isothermally to double its volume. Calculate:

- the final temperature of the oxygen,
- the work done by the oxygen,
- the heat added to the oxygen in the process of expansion.
($M_{\text{O}_2} = 32 \text{ kg.kmol}^{-1}$).

Solution:

(a) $T_2 = 300.15 \text{ K}$.

(b) From the first law of thermodynamics

$$\delta Q = n C_V dT + P dV$$

and bearing in mind the fact that the process is isothermal ($dT=0$), we see that all the heat added to the gas is used on work done by the gas.

From the ideal gas law we can determine the pressure

$$P = \frac{n.R.T}{V}$$

Now we can determine $P.dV$:

$$P.dV = n.R.T.\frac{dV}{V}$$

Thus the work done by the gas is

$$W = n.R.T \int_{V_1}^{V_2} \frac{dV}{V} = n.R.T \ln \frac{2V_1}{V_1} = \frac{3.2 \times 10^{-3}}{32} 8.314 \times 10^3 \times 300 \times \ln 2 = 172.8 \text{ J}$$

(c) The heat added to gas during expansion is

$$Q = 172.8 \text{ J}$$

Problem 2-40. The compression ratio of a Diesel engine is $\frac{V_1}{V_2} = 15$. A mass of gas in a cylinder of this engine occupies an initial volume $V_1 = 1 \text{ l}$ at pressure $P_1 = 10^5 \text{ Pa}$ and temperature $t_1 = 16^\circ\text{C}$. If the gas is compressed adiabatically, determine the temperature and pressure after compression. Assuming that the gas behaves like an ideal gas for which $\kappa = 1.4$ calculate the work done by external forces during compression.

Solution: An adiabatic process is described by the equation:

$$P_1.V_1^\kappa = P_2.V_2^\kappa \quad (1)$$

where subscripts 1 and 2 denote the initial and final state respectively. The behaviour of a gas is also described by the ideal gas law

$$P.V = n.R.T$$

The ratio of initial and final temperature is

$$\frac{T_2}{T_1} = \frac{P_2.V_2}{P_1.V_1} \quad (2)$$

Substituting equation 2 into equation 1 we obtain

$$T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\kappa - 1} = 289 (15)^{1.4 - 1} = 846 \text{ K}.$$

From equation 1 we have

$$P_2 = P_1 \left(\frac{V_1}{V_2} \right)^{\kappa} = 10^5 \times (15)^{1.4} = 4.4 \times 10^6 \text{ Pa}.$$

From the first law of thermodynamics we have for an adiabatic process:

$$dW = -dU$$

which means that the work done by the gas is done on the account of its internal energy or

$$W = -\Delta U = n C_V (T_1 - T_2). \quad (3)$$

The molar heat can be found from: $C_P - C_V = R$ and $\kappa = \frac{C_P}{C_V}$.

Thus we have:
$$C_V = \frac{R}{\kappa - 1} \quad (4)$$

Substituting equation 4 into equation 3 we obtain:

$$W = n \frac{R}{\kappa - 1} (T_1 - T_2) \quad (5)$$

The product (nR) is found from the ideal gas law for the first state

$$n \cdot R = \frac{P_1 \cdot V_1}{T_1}$$

Finally, for the work we have:

$$W = \frac{P_1 \cdot V_1}{T_1} \frac{1}{\kappa - 1} (T_1 - T_2) = \frac{10^5 \times 10^{-3}}{289} \frac{1}{1.4 - 1} (289 - 846) = -496 \text{ J}$$

Note that the work is negative, which means that during compression the work is done by some external agent.

Problem 2-41. A certain amount of gas at pressure $P_0 = 1 \times 10^5 \text{ Pa}$ is enclosed in a volume $V_0 = 1 \text{ l}$. The gas undergoes the following processes successively:

- (I) it is isobarically heated so that its volume is doubled,
- (II) it is isochorically heated so that its pressure is doubled,
- (III) it is allowed to expand adiabatically, so that its temperature is equal to the initial temperature.

Calculate:

- the total amount of heat added to the gas during these processes,
- the total work done by the gas,
- the total change of its internal energy.

Draw a graph of all three processes in a $P - V$ diagram. Poisson's constant $\kappa = 1.4$.

Solution: For each of the three processes we determine the work done by the gas, the heat added and the change of its internal energy following the first law of thermodynamics:

$$\delta Q = dU + \delta W$$

where

$$dU = \frac{m}{M} C_V dT = \frac{m}{M} \frac{R}{\kappa - 1} dT.$$

(I) Isobaric process:

After this process the gas will have the pressure $P_1 = P_0$, the volume $V_1 = 2V_0$ and the temperature T_1 can be found from the ideal gas law:

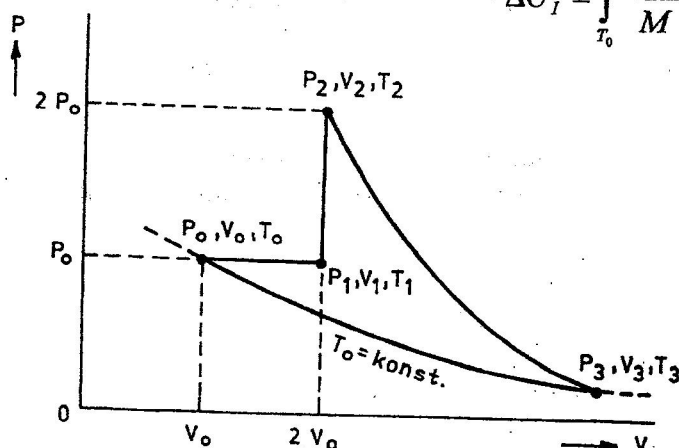
$$\frac{P_0 V_0}{T_0} = \frac{P_0 2V_0}{T_1} \Rightarrow T_1 = 2T_0.$$

The work done by the gas:

$$W_I = \int_{V_0}^{2V_0} P dV = P_0 V_0$$

The change in the internal energy is:

$$\Delta U_I = \int_{T_0}^{2T_0} \frac{m}{M} \frac{R}{\kappa - 1} dT = \frac{m}{M} \frac{R}{\kappa - 1} T_0.$$



From the ideal gas law we have:

$$T_0 = \frac{P_0 V_0}{R} \frac{M}{m}.$$

Thus for the change in internal energy we obtain:

$$\Delta U_I = \frac{m}{M} \frac{R}{\kappa - 1} \cdot \frac{P_0 V_0}{R} \frac{M}{m} = \frac{P_0 V_0}{\kappa - 1}.$$

The heat added to the gas in this process is therefore:

$$Q_I = \Delta U_I + W_I = \frac{P_0 V_0}{\kappa - 1} + P_0 V_0 = P_0 V_0 \frac{\kappa}{\kappa - 1}.$$

(II) Isochoric process:

The parameters of the gas at the beginning of this process are:

$$P_1 = P_0 \quad V_1 = 2V_0 \quad T_1 = 2T_0$$

After this isochoric process the gas will have the following parameters:

$$V_2 = V_1 = 2V_0 \quad P_2 = 2P_1 = 2P_0,$$

and the temperature can be found from the ideal gas law:

$$P_1 V_1 = nR T_1 = nR 2T_0$$

$$\Rightarrow T_2 = 4T_0$$

$$2P_1 V_1 = nR T_2.$$

Since the work done by the gas in an isochoric process equals zero ($W_{II} = 0$), from the first law of thermodynamics we see that $Q_{II} = \Delta U_{II}$. Thus for the change in the internal energy of the gas we obtain:

$$\Delta U_{II} = \int_{T_1}^{T_2} \frac{m}{M} \frac{R}{\kappa - 1} dT = \frac{m}{M} \frac{R}{\kappa - 1} \int_{2T_0}^{4T_0} dT = \frac{m}{M} \frac{R}{\kappa - 1} 2T_0 = \frac{2P_0 V_0}{\kappa - 1}.$$

The amount of heat added to the gas in this process is therefore:

$$Q_{II} = \frac{2P_0 V_0}{\kappa - 1}.$$

(III) Adiabatic process:

The parameters of the gas at the beginning of this process are:

$$P_2 = 2P_0 \quad V_2 = 2V_0 \quad T_2 = 4T_0$$

After this adiabatic process the gas will have parameters P_3 , V_3 and temperature $T_3 = T_0$. Volume V_3 can be found by combining the equation for the adiabatic process and the ideal gas law:

$$P_3 V_3^\kappa = P_2 V_2^\kappa \quad P_3 V_3 = nRT_3 \quad P_2 V_2 = nRT_2$$

$$V_3 = \left(\frac{T_2}{T_3} \right)^{\frac{1}{\kappa-1}} V_2 = \left(\frac{4T_0}{T_0} \right)^{\frac{1}{\kappa-1}} 2V_0 = 2^{\frac{1+\kappa}{\kappa-1}} V_0$$

Similarly we determine the pressure of the gas:

$$P_3 = \left(\frac{V_2}{V_3} \right)^\kappa P_2 = \left(\frac{2V_0}{V_0 \cdot 2^{\frac{1+\kappa}{\kappa-1}}} \right)^\kappa 2P_0 = P_0 2^{\frac{\kappa+1}{\kappa-1}}.$$

In an adiabatic process the work of the gas is done on the account of its internal energy:

$$W_{III} = -\Delta U_{III} = -\int_{T_2}^{T_3} \frac{m}{M} C_V dT = -\frac{m}{M} \frac{R}{\kappa - 1} \int_{4T_0}^{T_0} dT = \frac{m}{M} \frac{R}{\kappa - 1} 3T_0 = \frac{3P_0 V_0}{\kappa - 1}.$$

Thus for the change in internal energy of the gas we obtain:

$$\Delta U_{III} = -\frac{3P_0 V_0}{\kappa - 1}.$$

The total work done in all three processes is:

$$W = W_I + W_{II} + W_{III} = P_0 V_0 + \frac{3P_0 V_0}{\kappa - 1} = P_0 V_0 \frac{\kappa + 2}{\kappa - 1} = 850 J.$$

The total heat added to the gas is:

$$Q = Q_I + Q_{II} + Q_{III} = P_0 V_0 \frac{\kappa}{\kappa - 1} + \frac{2P_0 V_0}{\kappa - 1} = P_0 V_0 \frac{\kappa + 2}{\kappa - 1} = 850 J.$$

Finally, the total change in the internal energy of the gas is:

$$\Delta U = \Delta U_I + \Delta U_{II} + \Delta U_{III} = \frac{P_0 V_0}{\kappa - 1} + \frac{2 P_0 V_0}{\kappa - 1} - \frac{3 P_0 V_0}{\kappa - 1} = 0.$$

Problem 2-42. Compute the entropy change of $m=5 \text{ g}$ of air which is cooled from temperature $t_1 = 50^\circ\text{C}$ to $t_2 = 0^\circ\text{C}$ when the process is carried out:

- (a) at constant volume,
- (b) at constant pressure.

($M=28.5 \text{ kg.kmol}^{-1}$, $\kappa=1.4$).

Solution: We assume that air behaves like an ideal gas. Thus we can write:

$$\delta Q = TdS = dU + \delta W$$

or

$$dS = \frac{dU}{T} + \frac{\delta W}{T} \quad (1)$$

$$\text{where } dU = nC_v dT \quad \text{and} \quad \delta W = P.dV \quad (2)$$

(a) Isochoric process $V=\text{constant}$:

Substituting equation 2 into equation 1 we have:

$$dS = nC_v \frac{dT}{T} + \frac{PdV}{T} = nC_v \frac{dT}{T}.$$

After integration we obtain

$$\Delta S = nC_v \int_{T_1}^{T_2} \frac{dT}{T} = \frac{m}{M} \frac{5}{2} R \ln \frac{T_2}{T_1}$$

Substituting numerical values we obtain

$$\Delta S = \frac{5 \times 10^{-3}}{28.5} \frac{5}{2} \times 8314 \times \ln \frac{273.15}{323.15} = -0.6 \text{ J.K}^{-1}.$$

(b) Isobaric process $P=\text{constant}$:

The product $P.dV$ is obtained by differentiation of the ideal gas law for case of $P=\text{constant}$:

$$P.dV = n.R.dT$$

$$dS = nC_v \frac{dT}{T} + \frac{PdV}{T} = nC_v \frac{dT}{T} + nR \frac{dT}{T} = n(R + C_v) \frac{dT}{T}.$$

After integration we substitute numerical values:

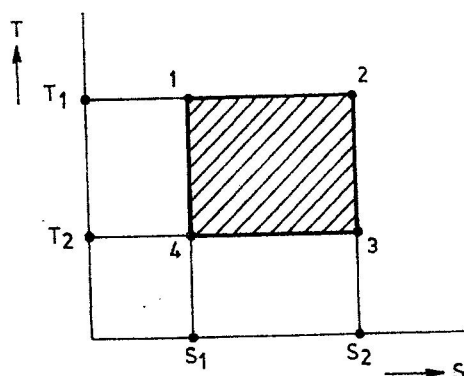
$$\Delta S = \frac{m}{M} R \left(1 + \frac{5}{2}\right) \ln \frac{T_2}{T_1} = \frac{5 \times 10^{-3}}{28.5} 8314 \left(1 + \frac{5}{2}\right) \ln \frac{273.15}{323.15} = -0.85 \text{ J.K}^{-1}.$$

Problem 2-43. An ideal gas heat engine operates in a Carnot cycle between temperatures $t_1 = 327^\circ\text{C}$ and $t_2 = 127^\circ\text{C}$. The amount of heat $Q_1 = 12560 \text{ J}$ per cycle is added to the heat engine. Determine the heat Q_2 rejected to the low temperature reservoir and the work W that is done.

Solution: We can draw a Carnot cycle in a $T - S$ diagram.

Heat added $= Q_1 = \text{area: } S_1, 1, 2, S_2.$

Rejected heat $= Q_2 = \text{area: } S_1, 4, 3, S_2.$



Work done = $W = Q_1 - Q_2 = \text{area: } 1, 2, 3, 4.$

Change in entropy:

$$dS = \frac{Q_1}{T_1} = \frac{12560}{600} = 20.9 \text{ J.K}^{-1}$$

The work done is:

$$W = (T_1 - T_2)dS = (600 - 400) \times 20.9 = 4180 \text{ J.}$$

The heat rejected is:

$$Q_2 = 8380 \text{ J.}$$

Problem 2-44. A Carnot engine operates with efficiency $\eta_1 = 40\%$. To increase the efficiency to $\eta_2 = 50\%$ what must be the increase of the temperature of the heat source? The temperature of the cold reservoir remains unchanged at $t_2 = 9^\circ\text{C}$.

Solution: The efficiency of the Carnot cycle is

$$\eta = \frac{W}{Q} = \frac{T_1 - T_2}{T_1} \Rightarrow T_1 = \frac{T_2}{1 - \eta}.$$

Thus for the first case we have:

$$T_1 = \frac{T_2}{1 - \eta_1}.$$

For the second case we have:

$$T_1' = \frac{T_2}{1 - \eta_2}.$$

Finally

$$\Delta T = T_1' - T_1 = \frac{T_2(\eta_2 - \eta_1)}{(1 - \eta_1)(1 - \eta_2)} = \frac{282 \times (0.5 - 0.4)}{(1 - 0.4)(1 - 0.5)} = 94 \text{ K}$$

Temperature of the heat source must be increased by 94°C .

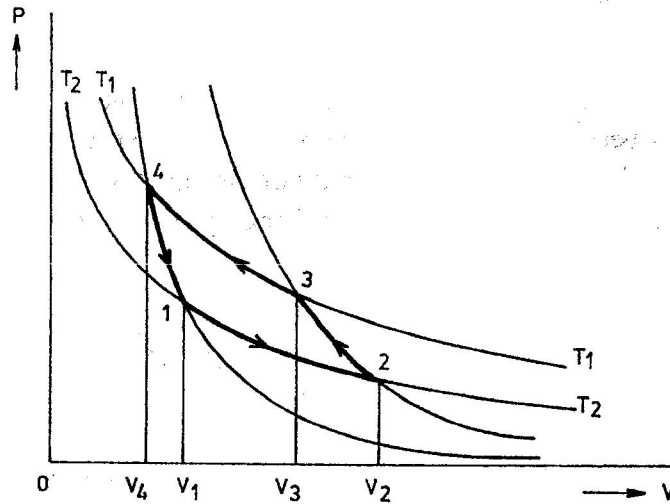
Problem 2-45. For the Carnot refrigerator cycle the efficiency is defined as the ratio of the heat $Q_{1,2}$ absorbed from a cold reservoir and the external work W . Calculate this efficiency in terms of temperatures of cold and hot temperature reservoirs.

Solution: The gas absorbs heat from the freezer compartment at temperature T_2 and exhausts it into the room at temperature T_1 . The heat absorbed during isothermal expansion (1→2) from the freezer compartment is

$$Q_{1,2} = nRT_2 \ln \frac{V_2}{V_1}$$

The work that must be done by external forces is denoted as W' and the work that must be done by the gas is denoted as W . It is obvious that $W' = -W$.

The Carnot refrigerator cycle is shown in the following P - V diagram.



The work done by gas in different processes of the cycle is:

(a) isothermal processes:

$$W_{1,2} = nRT_2 \ln \frac{V_2}{V_1}$$

and

$$W_{3,4} = nRT_1 \ln \frac{V_4}{V_3}$$

(b) adiabatic processes:

$$W_{2,3} = -W_{4,1}$$

To determine the efficiency of the cycle we have to find the relation between ratios $\frac{V_2}{V_1}$ and $\frac{V_4}{V_3}$. To do this we use the fact that change of entropy in a reversible process along a closed path is equal to zero, $dS = 0$. Thus in our case we have:

$$\Delta S_{1,2} = n.R. \ln \frac{V_2}{V_1}$$

$$\Delta S_{3,4} = n.R. \ln \frac{V_4}{V_3}$$

$$\Delta S_{2,3} = 0$$

$$\Delta S_{4,1} = 0.$$

For a closed path we therefore have

$$\Delta S = \Delta S_{1,2} + \Delta S_{2,3} + \Delta S_{3,4} + \Delta S_{4,1} = 0.$$

From this equation after substitution we obtain $\frac{V_2}{V_1} = \frac{V_3}{V_4}$

The work done by the gas in process 3→4 is

$$W_{3,4} = -nRT_1 \ln \frac{V_2}{V_1}$$

The total work done by the gas is

$$W = W_{1,2} + W_{2,3} + W_{3,4} + W_{4,1} = nR(T_2 - T_1) \ln \frac{V_2}{V_1}$$

The work done by external forces is

$$W' = nR(T_1 - T_2) \ln \frac{V_2}{V_1}$$

Finally for the efficiency of the Carnot refrigerator we obtain

$$\eta_r = \frac{Q_{1,2}}{W'} = \frac{T_2}{(T_1 - T_2)}.$$

Problem 2-46. A steel bullet falls from height $h=20\text{ m}$ with initial velocity $v_0 = 4\text{ m.s}^{-1}$. After being reflected from the ground the bullet reaches height $h_0 = 4\text{ m}$. Calculate the increase of temperature of the bullet if 60 % of the deformation work is used to increase its internal energy. The specific heat of steel is $c = 418.6\text{ J/(kg.K)}$.

$$\left[\Delta t = 0.6 \frac{2g(h - h_0) + v_0^2}{2c} = 0.23^\circ\text{C} \right]$$

Problem 2-47. A certain amount of air of mass $m=1\text{ kg}$, pressure $P_1 = 10^5\text{ Pa}$ and temperature $t=20^\circ\text{C}$ is compressed to pressure $P_2 = 10^6\text{ Pa}$. Calculate the work that must be done if the process is carried out:

(a) isothermally

(b) adiabatically.

($M_{\text{air}}=28.5\text{ kg/kmol}$, $C_V = \frac{5}{2}R$ and $\kappa=1.4$).

$$\left[(a) \quad W' = \frac{m}{M} RT_1 \ln \frac{P_2}{P_1} = 196 \times 10^3\text{ J} \right]$$

$$\left[(b) \quad W' = \frac{m}{M} C_V T_1 \left[\left(\frac{P_2}{P_1} \right)^{\frac{\kappa-1}{\kappa}} - 1 \right] = 198 \times 10^3\text{ J} \right]$$

Problem 2-48. Calculate the change in entropy when $m_1 = 4\text{ kg}$ of water of temperature $t_1 = 80^\circ\text{C}$ is mixed with $m_2 = 6\text{ kg}$ of water of temperature $t_2 = 20^\circ\text{C}$. The specific heat of water is $c = 4186\text{ J/(kg.K)}$.

$$\left[\Delta S = c \left(m_1 \ln \frac{T}{T_1} + m_2 \ln \frac{T}{T_2} \right) = 176\text{ J.K}^{-1} \right]$$

Problem 2-49. Prove that the total change in entropy of an ideal gas undergoing a Carnot cycle is zero.

$$\left[\oint dS = 0 \right]$$

Problem 2-50. A steam engine utilizes a heat source at temperature $t_1 = 210^\circ\text{C}$, the exhaust temperature is $t_2 = 40^\circ\text{C}$. Calculate the theoretical work which can be obtained if the amount of heat added to the engine is $Q=4.2\text{ KJ}$.

$$\left[W = Q \frac{T_1 - T_2}{T_1} = 1.48 \times 10^3 J \right]$$

Problem 2-51. A Carnot refrigerator absorbs heat from the freezer compartment so that it changes water of temperature $t_1 = 20^\circ C$ and mass $m = 3.6 \text{ kg}$ into ice of temperature $t_2 = 0^\circ C$ in time $\tau = 1 \text{ hour}$. If the compressor output is 100 W calculate the heat which must be exhausted into the room. The specific heat of water is $c = 4186 \text{ J/(kg.K)}$, the heat of fusion is $l = 334 \text{ kJ/kg}$.

$$\left[Q_1' = P'\tau + m(c \Delta t + l) = 1.87 \times 10^6 J \right]$$

2.4 CHANGES OF PHASE, REAL GASES

When a material changes phase from a solid to a liquid, or from a liquid to a gas, a certain amount of energy is involved in this **change of phase**.

The heat required to change one kilogram of a substance from the solid to the liquid state is called **heat of fusion** l_F .

The heat required to change one kilogram of a substance from the liquid to the vapour is called **heat of vaporisation** l_v .

Heats of fusion and vaporisation are also called **latent heats**.

Heats of vaporisation and fusion also refer to the amount of heat released by a substance when it changes from a gas to a liquid, or from a liquid to a solid.

Clausius-Clapeyron's equation expresses the dependence of the latent heat of the substance on the change in its temperature and pressure:

$$l = \frac{T(V_2 - V_1)}{m} \frac{dP}{dT}$$

where V_2 and V_1 are the volume of the substance in the higher and lower phase and m is the mass of the substance.

The behaviour of real gases at high pressures and near their liquefaction point deviates from the ideal gas law. These deviations are due to the finite size of molecules and to the attractive forces between molecules which become greater in these situations. An equation which describes the behaviour of real gases is **van der Waal's equation of state**:

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = n R T$$

where constants a and b are experimental constants that are different for different gases.