Thermodynamics: Classical to Statistical

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Lecture - 33

Advance Problems - 1

Problems on Classical Thermodynamics

Problem 1:

One mole of a monoatomic ideal gas (γ = 5/3) at 27 ˚C is adiabatically compressed in a reversible process from an initial pressure of 1 atm to a final pressure of 50 atm. Calculate the resultant difference of temperature.

Solution:

We have,

P_1 = initial pressure = 1 atm.

P_2 = final pressure = 50 atm.

T_1 = initial temperature = 27°C = 300 K.

T_2 = the final temperature = ?

We know, for adiabatic process,

$$\left(\frac{P_2}{P_1}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right)^{\gamma}$$

Now, γ = 5/3. Substituing the values,

$$(50)^{\frac{5}{3}-1} = \left(\frac{T_2}{300}\right)^{\frac{5}{3}}$$

Or, $$\frac{2}{3}\ln 50 = \frac{5}{3}\ln T_2 - \frac{5}{3}\ln 300$$

Or, $$T_2 = 1434.5K$$

The resulting difference in temperature is,

$$T_2 - T_1 = (1434.5 - 300)\ K = 1134.5\ K = 861.5°C .$$

Problem 2:

An ideal gas expands reversibly according to the equation,

$$PV^n = A$$

where A is a constant. Show that the heat absorbed by the gas is w(γ-n)/(γ-1) where w is the work done by the gas during the process.

Solution:

For a reversible transformation we can write from first law of thermodynamics,

$$\delta q_{rev} = C_v\, dT + PdV \qquad (1)$$

or, $$q_{rev} = C_V \int_{T_1}^{T_2} dT + \int_{V_1}^{V_2} \frac{A}{V^n} dV$$

Considering,

C_v is the constant term or independent of temperature.

T_1 is the initial temperature.

T_2 is the final temperature.

V_1 is the initial volume.

V_2 is the final volume.

$$q_{rev} = C_V \left(T_2 - T_1\right) + A \frac{V_2^{-n+1} - V_1^{-n+1}}{-n+1}$$

Or, $$q_{rev} = C_V \left(T_2 - T_1\right) + \frac{P_2V_2 - P_1V_1}{1-n}$$

Or, $$q_{rev} = C_V \frac{P_2V_2 - P_1V_1}{R} + \frac{P_2V_2 - P_1V_1}{1-n}$$

Or, $$q_{rev} = \frac{P_2V_2 - P_1V_1}{1-n} \left[\frac{C_V (1-n)}{R} + 1 \right]$$

Here we consider one mole of an ideal gas.

But the work done by the gas w given by equation 1 is,

$$w = \frac{P_2V_2 - P_1V_1}{1-n}$$

$$q_{rev} = w\left[\frac{1-n}{\gamma-1}+1\right]$$

Or, $$q_{rev} = w\left[\frac{\gamma-n}{\gamma-1}\right]$$

Problem 3:

A reversible engine converts one sixth of the heat inputs into work. If the temperature of the sink is reduced by 62°C, its efficiency is doubled. Find the temperature of the source and the sink.

Solution:

To consider the efficiency of the engine we need to look at Carnot Cycle. The efficiency of the engine η is

$$\eta = \frac{1}{6} = 1 - \frac{T_2}{T_1}$$

Or, $$\frac{T_2}{T_1} = 1 - \eta = \frac{5}{6} \quad (1)$$

Where, T_1 is the temperature of the source and T_2 is the temperature of the sink.

If η′ is the efficiency of the engine when the temperature of the sink is reduced by 62°C, we can write,

$$\eta' = 2 \times \frac{1}{6} = 1 - \frac{T_2 - 62}{T_1}$$

Or, $$\frac{T_2 - 62}{T_1} = 1 - \frac{1}{3} = \frac{2}{3} \quad (2)$$

Dividing equation 2 by equation 1, we get,

$$\frac{T_2}{T_2 - 62} = \frac{5}{6} \times \frac{3}{2} = \frac{5}{4}$$

Or, $$\frac{T_2}{T_2 - 62} = \frac{5}{6} \times \frac{3}{2} = \frac{5}{4}$$

$$\text{Or,} \quad T_2 = 310$$

This is the temperature of the sink.

Again we have, $$\frac{T_2}{T_1} = \frac{5}{6}$$

$$\text{Or,} \quad T_1 = \frac{6T_2}{5} = \frac{6 \times 310}{5} = 372$$

The temperature of the source is 372 K and the temperature of the sink is 310 K.

Problem 4:

10 g of water at 60°C is mixed with 30 g of water at 20°C. Will the entropy of the resulting system increase or decrease? Calculate the change in entropy.

Solution:

Suppose the final temperature (after mixing of 10 g of water at 60°C and 30 g of water at 20°C) is t°C. We can write,

$$10 \times 1 \times (60 - t) = 30 \times 1 \times (t - 20)$$

$$\text{Or,} \quad 600 - 10t = 30t - 600$$

$$\text{Or,} \quad t = \frac{1200}{40} = 30$$

So the resulting temperature t is 30°C.

Now the change in entropy of 10 g of water due to change in temperature from 60 to 30°C is

$$\Delta S_1 = m_1 C \ln \frac{T_2}{T_1}$$

T_1 is 60 + 273 K = 333 K and T_2 = 30 + 273 K = 303 K.

$$\Delta S_1 = 10 \times 1 \times \ln \frac{333}{303}$$

$$\text{Or,} \quad \Delta S_1 = -0.944 calK^{-1}$$

Now the change in entropy of 30 g of water due to change in temperature from 20°C to 30°C is

$$\Delta S_2 = m_2 C \ln \frac{T_2}{T_1} = 30 \times 1 \times \ln \frac{333}{303}$$

$$\Delta S_2 = 1.007 cal K^{-1}$$

So total change in entropy due to mixing,

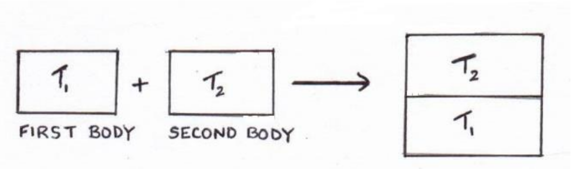
$$\Delta S_{mix} = \Delta S_1 + \Delta S_2 = 0.063 cal K^{-1}$$

Since ΔS_{mix} is positive, the entropy of the resulting system will increase. This problem was based on the concept of entropy of mixing.

Problem 5:

Two bodies of equal and constant thermal capacity 'C', at absolute temperatures T_1 and T_2 respectively (where $T_1 > T_2$) attain the same temperature on being placed in direct thermal contact. Calculate the loss of available energy.

Solution:



If T_c be the common final temperature of the two bodies then we can write,

$$C(T_1 - T_C) = C(T_C - T_2)$$

as $T_1 > T_2$ and both the bodies are considered to have equal masses, we get,

$$T_C = \frac{1}{2}(T_1 + T_2)$$

The entropy change of the first body,

$$\Delta S_1 = mC \ln \frac{T_C}{T_1}$$

The entropy change of the second body

$$\Delta S_2 = mC \ln \frac{T_C}{T_2}$$

The total entropy change for this process is,

$$\Delta S = \Delta S_1 + \Delta S_2$$

Or, $$\Delta S = mC \ln \frac{T_C}{T_1} + mC \ln \frac{T_C}{T_2}$$

Or, $$\Delta S = 2mC\ln T_C - mC\ln(T_1 \times T_2)$$

Or, $$\Delta S = mC\ln\frac{T_c^{\,2}}{T_1 \times T_2}$$

Now substituting the value of T_c, we get,

$$\Delta S = mC\ln\left[\frac{(T_1+T_2)^2}{4T_1T_2}\right]$$

If T_0 be the lowest available temperature, the amount of available energy is

$$= T_0 \times \Delta S = T_0 mC\, ln\left[\frac{(T_1+T_2)^2}{4T_1T_2}\right]$$

Problem 6:

The molar specific heat capacity at constant volume of diamond varies with temperature as

$$C_V = 3R \times \left(\frac{T}{\theta_D}\right)^3$$

where θ_D is the Debye temperature. Calculate the change in entropy in units of gas constant R of 1.2 g of diamond when it is heated at constant volume from 10 K to 350 K. Given atomic weight of carbon is 12 and θ_D is 2230 K.

Solution:

The change in entropy is given by,

$$\Delta S = \int nC_V\frac{dT}{T}$$

where n = 1.2 / 12 = 0.1.

$$\Delta S = 0.1\int_{10}^{350}\frac{12\pi^4}{5}R\left(\frac{T}{\theta_D}\right)^3\frac{dT}{T}$$

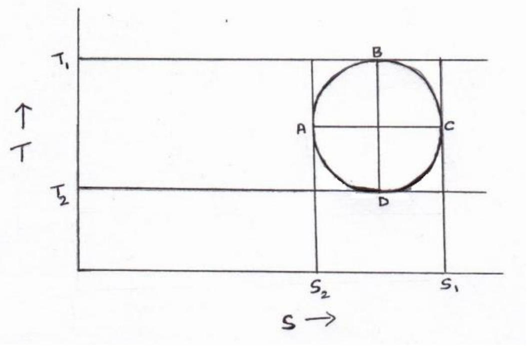
or, $$\Delta S = 0.1 \times \frac{3R\times 4\pi^4}{5{\theta_D}^3}\int_{10}^{350}T^2\,dT$$

or, $$\Delta S = \frac{0.1\times 3\times R\times 4\times 3.14^4}{5\times 2230^3}\times\frac{1}{3}(350^3 - 10^3)$$

or, $$\Delta S = 0.30\,R$$

Problem 7:

Calculate the efficiency of the cycle ABCDA as depicted in the T-S diagram given below in terms of T_1 and T_2. Given AC = BD.



Solution:

In the T-S diagram the heat absorbed is given by

q = area of ABC S_1S_2A = area of semicircle ABCA + area of rectangle ACS_1S_2

$$\text{or,} \quad q = \frac{1}{2} \times \pi \times \frac{BD^2}{2} + AS_1 \times AC$$

$$\text{or,} \quad q = \frac{1}{8} \times \pi \times (T_1 - T_2)^2 + \left(\frac{T_1 - T_2}{2} + T_2\right)(T_1 - T_2)$$

$$q = \frac{1}{8} \times \pi \times (T_1 - T_2)^2 + \frac{1}{2}(T_1 + T_2)(T_1 - T_2)$$

Work done, w, is given by,

w = area of the circle ABCD

$$\text{or,} \quad w = \pi \times \frac{BD^2}{2} = \frac{\pi}{4}(T_1 - T_2)^2$$

So the efficiency of the cycle ABCDA is given by

$$\eta = \frac{Work\ output}{Heat\ input}$$

$$\eta = \frac{\frac{\pi}{4}(T_1 - T_2)^2}{\frac{1}{8} \times \pi \times (T_1 - T_2)^2 + \frac{1}{2}(T_1 + T_2)(T_1 - T_2)}$$

$$\text{Or,} \quad \eta = \frac{2(T_1 - T_2)}{(T_1 - T_2) + 4(T_1 + T_2)}$$

$$\text{Or,} \quad \eta = \frac{2(T_1 - T_2)}{5T_1 + 3T_2}$$

Problem 8:

Determine the values of C_v, C_p and γ for SO_3 gas.

Solution:

SO_3 molecule is non-linear.

The internal energy per mole

$$U = U_{trans} + E_{rot}$$

Or, $$U = 3\times\frac{1}{2}RT + 3\times\frac{1}{2}RT$$

or, $$U = 3RT$$

The specific heat capacity is,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3R$$

$$C_P = C_V + R = 3R + R = 4R$$

$$\gamma = \frac{C_P}{C_V} = \frac{4R}{3R} = \frac{4}{3}$$

Problem 9:

For the reaction,

$$2\ NO\ (g) + O_2\ (g) = 2\ NO_2\ (g)$$

the value of ΔH = 113.1 kJ. If 6 moles of NO reacts with 3 moles of O_2 at 1 atm pressure and 298 K temperature to form NO_2, calculate the work done in kJ unit against a pressure of 1 atm. What is the internal energy change, ΔU, for the reaction?

Solution:

At constant pressure,

$$w = -P(V_2 - V_1) = -(n_2RT - n_1RT)$$

Or, $$w = -(n_2 - n_1)RT = -\{6-(6+3)\}RT$$

Or, $$w = 3RT = 3\times 8.314\times 298 = 7.432kJ$$

Now Δn for the reaction = 2 – (2 + 1) = -1.

$$\Delta U = \Delta \text{H} - \Delta nRT$$

Or, $$\Delta U = (-113.1) \times (-1) \times \frac{8.314 \times 298}{1000}$$

Or, $$\Delta U = -110.62 kJ$$