Thermodynamics: Classical to Statistical
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Lecture 21
Problems on classical thermodynamics - 1

Problem 1. calculate the final volume of one mole of an ideal gas initially at 273 K temperature and 1 atmospheric pressure if it absorbs 1000 calorie of heat during a reversible expansion. How to, how to solve at this problem?

This is reversible isothermal expansion if we consider, the problem is slightly modified now, to calculate the final volume of one mole of an ideal gas initially at 273 K temperature at 1 atmospheric pressure if it absorbs 1,000 calorie of heat during a reversible isothermal expansion. We have ideal gas, as well as isothermal process, and we know for ideal gas the internal energy depends only on temperature.

For isothermal process dU = 0 for an ideal gas and from first law of thermodynamics we know, if process is the reversible one

$$dU = \delta q_{rev} + \delta w_{rev}$$

. Since dU is 0, so we can write $\delta q_{rev} = - \delta w_{rev} = PdV$

and we need to calculate q reversible, if we integrate it we get,

$$\delta q_{rev} = nRT \ln V_2/V_1$$

and V_2 is the final volume and V1 is the initial volume. Initial volume $V_1 = \frac{nRT}{P}$, number of mole is 1 here, R is 0.082 in liter atmosphere unit and temperature is 273 and pressure is 1 atmospheric, V_1 is in liters. So we get the value of V_1 here and we need to calculate V_2. δq_{rev} again is 1,000 here, and n is 1, R is 2 in calorie unit, temperature is 273, we need to substitute the value here $V_1 = \frac{1\times 0.082\times 273}{1}$ lit

If we do it we get

$$1000 = 1\times 2 \times 273 \ln\frac{V_2}{V_1}$$

$$V_2 = 140 \text{ lit}$$

Problem 2. For a certain reaction at constant pressure ΔG is given as

$$\Delta G = -a + bT \ln T$$

where a and b are constants and T is absolute temperature and we need to calculate change in enthalpy or delta H.

Ans.

$$\Delta G = -a + bT\ln T$$

$$\Rightarrow \frac{\Delta G}{T} = \frac{a}{T} + b\ln T$$

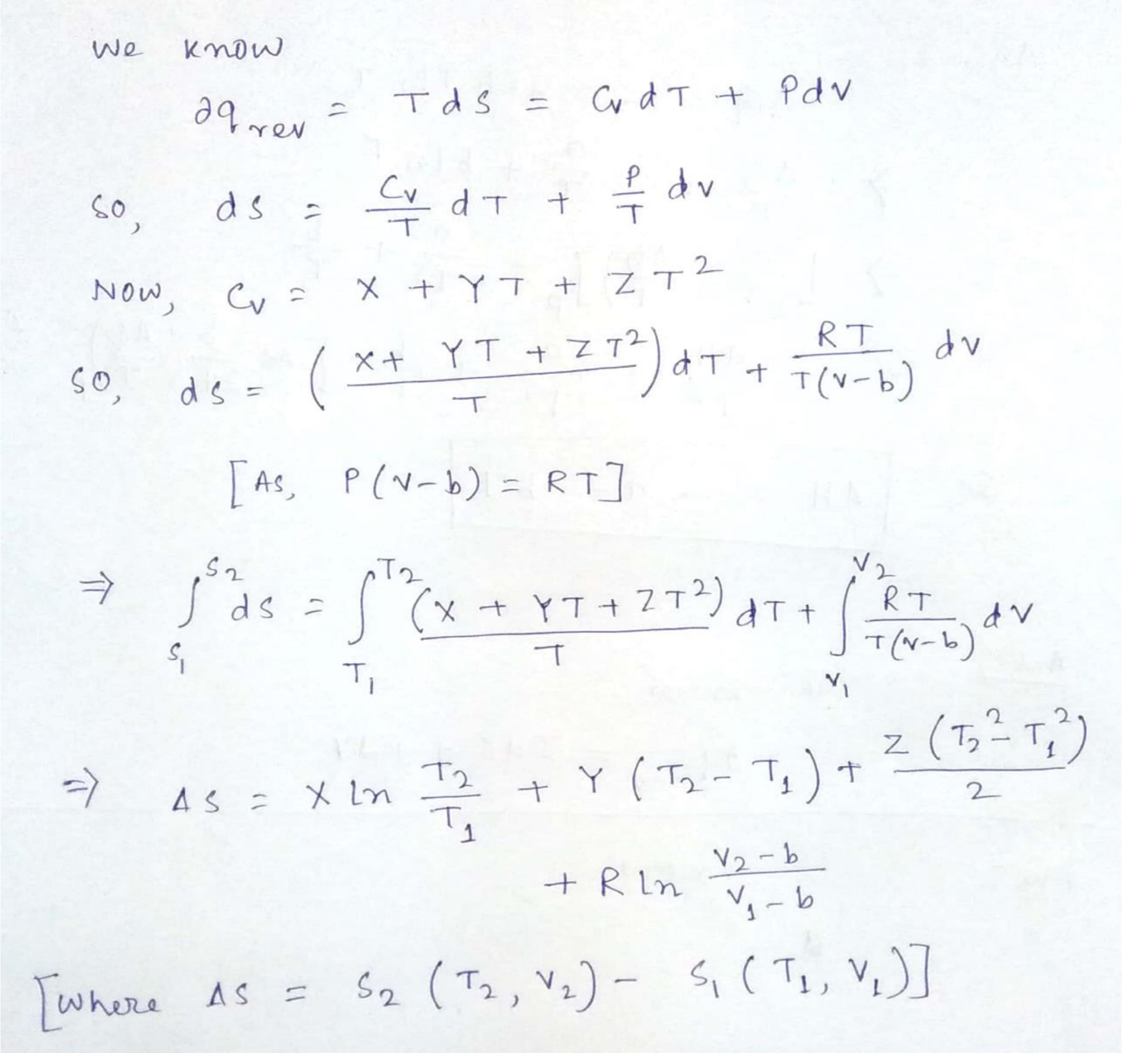
$$\Rightarrow \left[\frac{\partial}{\partial T}\left(\frac{\Delta n}{T}\right)\right]_P = \frac{a}{T^2} + \frac{b}{T}$$

$$\Rightarrow -\frac{\Delta H}{T^2} = \frac{a}{T^2} + \frac{b}{T} \quad \text{as} \left[\frac{\partial}{\partial T}\left(\frac{\Delta n}{T}\right)\right]_P = -\frac{\Delta H}{T^2}$$

So $$\Delta H = -a - bT$$

Problem 3. One mole of a gas obeying the equation of state P (V – b) = RT undergoes a change from the initial state T_1, V_1 to a final state T_2, V_2. What is the value of ΔS that we need to calculate? [Assume $C_V = X + YT + ZT^2$]

Ans.



We know

$$\partial q_{rev} = T\,dS = C_v\,dT + P\,dV$$

So, $$dS = \frac{C_v}{T}\,dT + \frac{P}{T}\,dV$$

Now, $$C_v = X + YT + ZT^2$$

So, $$dS = \left(\frac{X + YT + ZT^2}{T}\right)dT + \frac{RT}{T(V-b)}\,dV$$

[As, $P(V-b) = RT$]

$$\Rightarrow \int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} \frac{(X + YT + ZT^2)}{T}\,dT + \int_{V_1}^{V_2} \frac{RT}{T(V-b)}\,dV$$

$$\Rightarrow \Delta S = X \ln\frac{T_2}{T_1} + Y(T_2 - T_1) + \frac{Z(T_2^2 - T_1^2)}{2} + R\ln\frac{V_2 - b}{V_1 - b}$$

[Where $\Delta S = S_2(T_2, V_2) - S_1(T_1, V_1)$]

Problem 4. Show that $\left(\frac{\partial \mathrm{Cp}}{\partial \mathrm{p}}\right) = -\mathrm{T}\left(\frac{\partial^2 \mathrm{V}}{\partial \mathrm{T}^2}\right)_{\mathrm{P}}$

Ans. $$\mathrm{Cp} = \left(\frac{\partial \mathrm{q}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = \mathrm{T}\left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_{\mathrm{P}}$$

$$\Rightarrow \left(\frac{\partial \mathrm{Cp}}{\partial \mathrm{p}}\right) = \mathrm{T}\left(\frac{\partial^2 \mathrm{S}}{\partial \mathrm{T}\,\partial \mathrm{P}}\right)$$

From Maxwell's relation

$$\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = -\left(\frac{\partial \mathrm{S}}{\partial \mathrm{P}}\right)_{\mathrm{P}}$$

By differentiating with respect to T

$$\left(\frac{\partial^2 \mathrm{V}}{\partial \mathrm{T}^2}\right)_{\mathrm{P}} = -\left(\frac{\partial^2 \mathrm{S}}{\partial \mathrm{T}\,\partial \mathrm{P}}\right)$$

$$\Rightarrow \left(\frac{\partial \mathrm{Cp}}{\partial \mathrm{p}}\right) = -\mathrm{T}\left(\frac{\partial^2 \mathrm{V}}{\partial \mathrm{T}^2}\right)_{\mathrm{P}}$$

Problem 5. The volume of a system consisting of an ideal gas, decreases at constant pressure, as a result the temperature of 1.5 kg of water in the surroundings increases by 14.2℃. Calculate q_P for the system and it is given that C_P of water is 4.18 J g^{-1} K^{-1}.

Ans. $$-(q_P)_{system} = +(q_P)_{surroundings} = m\ C_P\ \Delta T$$

Now, $m = 1500$ gm, $C_P = 4.18\ J\ g^{-1}\ K^{-1}$, $\Delta T = 14.2\ K$

$$(q_P)_{system} = 1500\ gm \times 4.18\ J\ g^{-1}\ K^{-1} \times 14.2\ K$$

$$\Rightarrow (q_P)_{system} = -89.034\ kJ$$

Problem 6. A typical resting person heats the surroundings at a rate of about 100 watt, where 1 watt is 1 J S^{-1}. Estimate the entropy the person generates in the surroundings in the course of a day at 300 K temperature.

Ans. So if we consider the heat transfer process is reversible one, we can write

$$(q_{rev})_{surr} = 100\ J\ S^{-1} \times 3600\ \times 24$$

1 day = 24 × 3600 S and temperature of the day is 300 K

So, $$(\Delta S)_{surr} = \frac{100 \times 3600 \times 24}{300}\ J\ K^{-1}$$

$$\Rightarrow (\Delta S)_{surr} = 28800\ J\ K^{-1}$$

Problem 7. Suppose 5 moles of an ideal monatomic gas at an initial temperature of 298 K and pressure of 10 atm is expanded adiabatically and reversibly until the pressure has decreased to 1 atmosphere. Calculate the final volume, final temperature, the internal energy change, the enthalpy change and the work done.

Ans. The information provided here are n is number of moles equals to 5, initial temperature T_1 is 298 Kelvin, initial pressure P_1 is 10 atm, final pressure P_2 is 1 atm, for monatomic gas C_V is $\frac{3}{2}$ R, for ideal monatomic gas C_P is $\frac{5}{2}$ R.

So, $$\frac{C_P}{C_V} = \gamma = \frac{5}{3}$$

We know for adiabatic reversible process

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

and if we substitute the value of V_1, here we get

$$P_1^{1-\gamma} T_1^{\gamma} = P_2^{1-\gamma} T_2^{\gamma}$$

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

if we substitute all this value we get final temperature T_2 is 118.76 K.

So once we got T_2, we know final pressure, we know number of moles, we can easily calculate final volume. So final temperature we obtained is 118.76 K and $V_2 = nR\frac{T_2}{P_2}$,

R = 0.082 lit atm , T_2 = 118.76 K and P_2 = 1 atm

if we calculate this we get V_2 = 48.69 litter.

Now for adiabatic process q = 0

So, $\Delta U = w$

Now $\Delta U = n C_V \Delta T = 5 \times \frac{3}{2} \times 8.314 \times (118.76 - 298)$

$\Delta U = - 11176.51$

Now, $\Delta H = n C_V \Delta T = 5 \times \frac{5}{2} \times 8.314 \times (118.76 - 298)$

$\Delta H = -18627.52$ J

Problem 8. A certain system is found to have Gibbs free energy given by G which is a function of pressure and temperature,

$$G(P, T) = RT \ln \left[\frac{aP}{(RT)^{5/2}}\right]$$

where a and R are constants. We need to find the value of C_P.

Ans. $G(P, T) = RT \ln (ap) - \frac{5}{2} RT \ln (RT)$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S = R\ln a + R\ln P - \frac{5}{2} R \ln R - \frac{5}{2} R \ln T - \frac{5}{2} RT \times \frac{1}{T}$$

$$\left(\frac{\partial G}{\partial T}\right)_P = R\ln (aP) - \frac{5}{2} R \ln RT - \frac{5}{2} R$$

So, $S = -R\ln (aP) + \frac{5}{2} R \ln RT + \frac{5}{2} R$

Now $C_P = \left(\frac{\partial q}{\partial T}\right)_P$

$dq = C_P \, dT$

$$\frac{dq}{T} = \frac{C_P \, dT}{T}$$

$$TdS = C_P\, dT$$

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

Now $S = -R\ln(aP) + \frac{5}{2} R \ln RT + \frac{5}{2} R$

Differentiating with respect to T at constant

$$\left(\frac{\partial s}{\partial T}\right)_P = \frac{5R}{2T}$$

Problem 9. Starting with H = U + PV, show that $\left(\frac{\partial U}{\partial T}\right)_P = C_P - P\left(\frac{\partial V}{\partial T}\right)_P$

Ans. $H = U + PV$

$$dH = dU + PdV + VdP$$

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P + 0$$

$$C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial U}{\partial T}\right)_P = C_P - P\left(\frac{\partial V}{\partial T}\right)_P$$