Thermodynamics: Classical to Statistical

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Lecture 22

Problems on classical thermodynamics - 2

Problem 10. Given that the molar Helmholtz free energy of a gas is defined as A_m,

$$A_m = -\frac{a}{V_m} - RT\ln\frac{V_m - b}{V_m^0} - f(T)$$

, where V_m is the molar volume of the gas, V_m^0 is the molar volume of the gas under standard conditions, 'R' is the gas constant, 'a' and 'b' empirical constants and f(T) is an arbitrary function of temperature. Find out the equation of state for the gas.

Ans. So we have $A_m = -\frac{a}{V_m} - RT\ln\frac{V_m - b}{V_m^0} - f(T)$

We know dA = - PdV – SdT

$$\Rightarrow \left(\frac{\partial A}{\partial V}\right)_T = -P$$

Now differentiating A_m with respect to V_m we get

$$\left(\frac{\partial A_m}{\partial V_m}\right)_T \equiv \frac{a}{V_m^2} - \frac{RT}{V_m - b}$$

$$P = -\frac{a}{V_m^2} + \frac{RT}{V_m - b}$$

So the equation of the state for the gas is

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

Problem 11. At 1 atm pressure, 1 mole of steam is condensed at 100°C, the wate is cooled to 0°C and then frozen to ice. What is the value of total entropy change ΔS for this process?

Given the heat of vaporization and fusion are 540 cal gm^{-1} and 80 cal gm^{-1} respectively and the average heat capacity of liquid water is 1 cal gm^{-1} deg^{-1} .

Ans. Total entropy change for this process,

$$\Delta S_{total} = \Delta S_{v\rightarrow l} + \Delta S_{l\rightarrow l} + \Delta S_{l\rightarrow s}$$

1 mole of water = 18 gm

$$\Delta S_{v\rightarrow l} = \frac{18\times540}{373} = -26.06 \text{ cal K}^{-1}$$

$$\Delta S_{l\rightarrow l} = mC_P \ln\frac{T_2}{T_1} = 18 \times 1 \times \ln\frac{273}{373} = -5.62 \text{ cal K}^{-1}$$

$$\Delta S_{l\rightarrow s} = -\frac{18 \times 80}{273} = -5.27 \text{ cal K}^{-1}$$

So $$\Delta S_{total} = (-26.06 - 5.62 - 5.27) = -36.95 \text{ cal K}^{-1}$$

Problem 12. A system undergoes a certain change in state by path 1 and the corresponding heat absorbed and work done by the system are 10 cal and 0 cal respectively. For the same change in state by another path, path 2 the above respective quantities are 15 cal and $0.5w_{max}$, where the w_{max} represents the work if the specified change is reversibly carried out, what is the value of w_{max}?

Ans. Basically here we are starting from the same initial state and we are going to the same final state where two different paths, one is path 1, another is path 2 and we get different amount of heat absorbed and work done for two different paths because work and heat both are path functions, whereas internal energy change is a state function, so the internal energy change for both the processes are the same.

Since internal energy is a state function, we can write

$$(10 - 0) \text{ cal} = (15 - 0.5w_{max}) \text{ cal}$$

$$0.5w_{max} = 10 \text{ cal}$$

Problem 13. In the vaporization of benzene at 1 bar pressure, ΔH = 7364 cal and ΔS = 20.85 cal, what is the normal boiling point of benzene?

Ans. Vaporization process is an equilibrium process, and during vaporization there is no change in the temperature, so

ΔG (T P) = 0, so it says $\Delta H = Tt_{rans}\, \Delta S$, T here is the transition temperature which is nothing but the normal boiling point of benzene

$$T_{trans} = \frac{\Delta H}{\Delta S} = \frac{7364}{20.85} = 353.19 \text{ K}$$

Problem 14. 2 moles of an ideal monatomic gas ($C_V = \frac{3}{2}R$) is mixed with 3 moles of an ideal diatomic gas, ($C_V = \frac{5}{2}R$) at room temperature. Calculate $(C_P)_{mix}$ for the mixture.

Ans. The total internal energy $U = U_1 + U_2$,

so we can write, $$\left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U_1}{\partial T}\right)_V + \left(\frac{\partial U_2}{\partial T}\right)_V$$

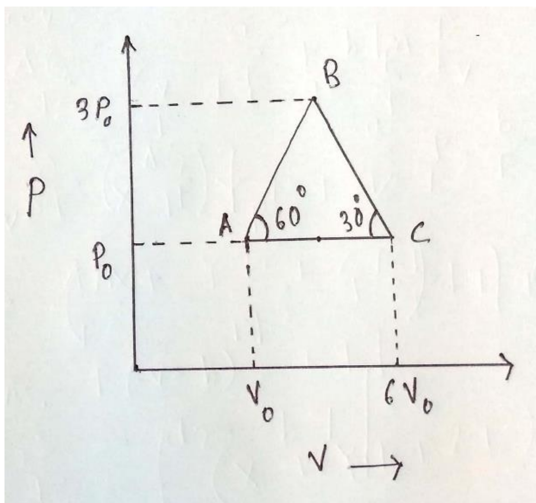
$$n(C_v)_{mix} = n(C_v)_1 + n(C_v)_2$$

$$\Rightarrow \quad 5\,(C_v)_{mix} = 2\times\frac{3}{2}R + 3\times\frac{5}{2}R$$

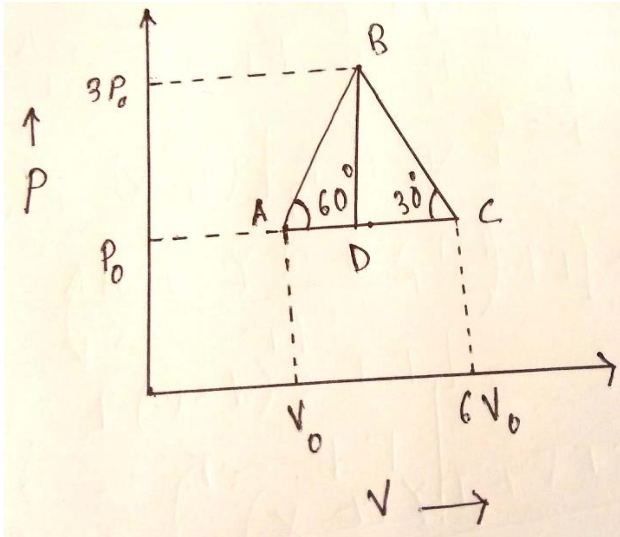
$$\Rightarrow \quad (C_v)_{mix} = \frac{21}{10}R$$

So $$(C_P)_{mix} = R + \frac{21}{10}R = \frac{31}{10}R$$

Problem 15. 2 moles of an ideal monatomic gas undergoes a cyclic process ABCA as shown in the figure below, and we need to calculate the ratio of temperature at B and A.



Ans. So here you can see that at point A and C both pressure and volume are given, whereas at point B only pressure is given, volume is not given. So we need to calculate first what is the volume at point B. We draw one perpendicular line starting from B which meets at point D on line AC.



So number of moles n is 2 here, at point A.

At point A temperature $T_A = \frac{P_0V_0}{2R}$, at point B, $P = 3P_0$

$$\text{Now } AD = BD \cot 60°$$

$$DC = BD \cot 30°$$

$$\frac{AD}{DC} = \frac{1}{3} \text{ or, } \quad 3AD = DC$$

$$AC = AD + DC = 4AD$$

$$AC = (6V_0 - V_0) = 4AD$$

$$AD = \frac{5}{4} V_0$$

$$\text{So volume at point B} = V_0 + \frac{5}{4} V_0 = \frac{9}{4} V_0$$

We know $PV = nRT$.

So, $\quad P_BV_B = 2RT_B$

$$\Rightarrow \quad T_B = \frac{P_B V_B}{2R} = \frac{27 P_0 V_0}{8R}$$

$$P_B = 3P_0, \; V_B = \frac{9}{4} V_0$$

$$T_A = \frac{P_0 V_0}{2R}$$

$$T_A : T_B = 27 : 4$$

Problem 16. Helium of mass 1.6 gram is expanded adiabatically 3 times and then compressed isobarically to the initial volume, find ΔS for the process.

Ans. For adiabatic process, $q = 0, \Delta S_1 = 0$

Total entropy change, $\Delta S = \Delta S_1 + \Delta S_2 = 0 + nC_P \ln \frac{T_2}{T_1}$

$$n = 1.6 / 4 = 0.4, \quad C_P = \frac{5}{2} R$$

$$\Delta S = \Delta S_2 = 0.4 \times \frac{5}{2} R \ln \frac{T_2}{T_1}$$

$$\Delta S = -2.2 \text{ cal K}^{-1}$$