Thermodynamics HW #2

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1. The initial state of one mole of a monatomic ideal gas is P = 10 atm and T = 300 K. Calculate the change in the entropy of the gas for (a) an isothermal decrease in the pressure to 5 atm, (b) a reversible adiabatic expansion to a pressure of 5 atm, (c) a constant-volume decrease in the pressure to 5 atm.

initial condition : $P_0 = 10\,atm \,/\, T_0 = 300K \,/\, V_0 = \frac{nRT_0}{P_0} = 2.462\,L$

a) isothermal decrease : $\Delta U = 0 \rightarrow \therefore q = w$

$(P_1 = 5atm \,/\, V_1 = 4.924L)$ $P_0V_0 = nRT_0 = P_1V_1 \quad \therefore V_1 = \frac{P_0}{P_1}V_0 = \frac{10atm}{5atm}\cdot V_0 = 2V_0$

$q = w = \int_{V_0}^{V_1} PdV = \int_{V_0}^{V_1} \frac{nRT}{V}dV = nRT\cdot\ln\left(\frac{V_1}{V_0}\right) = nRT\cdot\ln 2$

$\therefore \Delta S = \frac{q}{T} = nR\cdot\ln 2 = 1mol\cdot 8.314\frac{J}{K\cdot mol}\cdot\ln 2 = 5.763\,J/K$

b) reversible adiabatic expansion : $q = 0 \quad \therefore \Delta S = \frac{q}{T} = 0$

$(P_2 = 5atm \,/\, V_2 = V_0\cdot(P_0/P_2)^{1/\gamma} = 3.732\,L)$

c) constant-volume decrease : $\Delta S = \int dS = \int\left(\frac{dU}{T} + \frac{P}{T}dV\right) = nC_v\int\frac{1}{T}dT = nC_v\ln\left(\frac{T_3}{T_0}\right)$

$(P_3 = 5atm \,/\, V_3 = V_0 \,/\, T_3 = \frac{1}{2}T_0 = 150K)$ $= 1mol\cdot\frac{3}{2}\times 8.314\frac{J}{K\,mol}\cdot\ln\frac{1}{2} = -8.644\,J/K$

2. One mole of monatomic ideal gas is subjected to the following sequence of steps:
   a. Starting at 300 K and 10 atm, the gas expands freely into a vacuum to triple its volume.
   b. The gas is next heated reversibly to 400 K at constant volume.
   c. The gas is reversibly expanded at constant temperature until its volume is again tripled.
   d. The gas is finally reversibly cooled to 300 K at constant pressure.

   Calculate the values of q and w and the changes in U, H and S.

a) expands freely into a vacuum

$(T_0 = 300K \,/\, P_0 = 10atm \,/\, V_0 = \frac{RT_0}{P_0} = 2.461L \rightarrow T_1 = 300K \,/\, P_1 = \frac{10}{3} atm \,/\, V_1 = 3V_0 = 7.385L)$

$: q = 0,\ w = 0, \Delta U = 0, \Delta H = 0,$

$\Delta S = \int dS = \int(\frac{dU}{T} + \frac{P}{T}dV) = \int \frac{nR}{V} dV = nR \cdot \ln\frac{V_1}{V_0} = 1mol \cdot 8.314 \frac{J}{K \cdot mol} \cdot \ln 3 = 9.134\ J/K$

b) heated at constant-volume.

$(T_1 = 300K \,/\, P_1 = \frac{10}{3} atm \,/\, V_1 = 7.385L \longrightarrow T_2 = 400K \,/\, P_2 = \frac{40}{9} atm \,/\, V_2 = V_1 = 7.385L)$

$: dV = 0 \rightarrow w = 0 \ \therefore \Delta U = q = nC_v\Delta T = 1 \times \frac{3}{2} \times 8.314 \frac{J}{K \cdot mol} \cdot 100K = 1.248\ kJ$

$\Delta H = nC_p\Delta T = 1 \times \frac{5}{2} \times 8.314 \times 100 = 2.078\ kJ$

$\Delta S = \int dS = \int(\frac{dU}{T} + \frac{P}{T}dV) = \int \frac{dU}{T} = \int \frac{nC_v}{T} dT = nC_v \cdot \ln\frac{T_2}{T_1}$

$= 1mol \times \frac{3}{2} \times 8.314 \frac{J}{Kmol} \times \ln(\frac{4}{3}) = 3.588\ J/K$

c) reversibly expanded at constant-temperature

$(T_2 = 400K \,/\, P_2 = \frac{40}{9} atm \,/\, V_2 = 7.385L \rightarrow T_3 = 400K \,/\, P_3 = \frac{P_2}{3} = \frac{40}{27} atm \,/\, V_3 = 3V_2 = 22.155L)$

$: dT = 0 \rightarrow \Delta U = 0, \Delta H = 0 \ \therefore q = w = \int PdV = nRT\int\frac{1}{V}dV = nRT \cdot \ln\frac{V_3}{V_2}$

$= 1mol \cdot 8.314 \frac{J}{K \cdot mol} \cdot 400K \cdot \ln 3 = 3.654\ kJ$

$\Delta S = \int dS = \int(\frac{dU}{T} + \frac{P}{T}dV) = \int \frac{nR}{V} dV = nR \cdot \ln\frac{V_3}{V_2}$

$= 1 \times 8.314 \times \ln 3 = 9.134\ J/K$

d) reversibly cooled at constant-pressure

$(T_3 = 400K \,/\, P_3 = \frac{40}{27} atm \,/\, V_3 = 22.155L \longrightarrow T_4 = 300K, P_4 = \frac{40}{27} atm, V_4 = 16.616\ L)$

$: W = P \cdot \Delta V = \frac{40}{27} \times (16.616 - 22.155) \times 101.325 = -0.831\ kJ$

$q = nC_p\Delta T = 1mol \times \frac{5}{2} \times 8.314 \frac{J}{K \cdot mol} \times (-100K) = -2.078\ kJ$

$\Delta U = q - w = -1.248\ kJ \ / \ \Delta H = \Delta U + \Delta(PV) = -2.078\ kJ$

$\Delta S = \int dS = \int(\frac{dU}{T} + \frac{P}{T}dV) = nC_v\int\frac{1}{T}dT + nR\int\frac{1}{V}dV = nC_v \ln(\frac{T_4}{T_3}) + nR \cdot \ln(\frac{V_4}{V_3}) = -5.980\ J/K$

$\therefore$ Total : $q = 2.823kJ,\ w = 2.823kJ,\ \Delta U = 0kJ,\ \Delta H = 0kJ,\ \Delta S = 15.876J/K$

3.(a) Find the extreme value of the function,

$$z = (x - 2)^2 + (y - 2)^2 + 4.$$

Find the constrained ~~maximum~~ minimum(?) of this function corresponding to the condition

$$x + y = 1$$

(b) by eliminating one variable and (c) by using a Lagrange undetermined multiplier method.

a) $z = (x-2)^2 + (y-2)^2 + 4 = f(x,y)$

$f_x = 2(x-2) = 2x-4$, $f_{xx} = 2$, $f_{xy} = 0$

$f_y = 2(y-2) = 2y-4$, $f_{yy} = 2$

$\rightarrow$ at $x=2, y=2$, $z=4$ $\rightarrow D = f_{xx} \cdot f_{yy} - (f_{xy})^2 = 4 > 0$ $\therefore$ minimum value

i.e. $f(2,2) = 4$ is extreme minimum value.

b) $z = (x-2)^2 + (y-2)^2 + 4$, $x + y = 1 \rightarrow y = 1 - x$

$\rightarrow z = (x-2)^2 + (-x-1)^2 + 4$

$= (x^2 - 4x + 4) + (x^2 + 2x + 1) + 4$

$= 2x^2 - 2x + 9$

$\rightarrow dz/dx = 4x - 2 = 0 \rightarrow \therefore x = \frac{1}{2}$, $d^2z/dx^2 = 4 \Rightarrow$ The function has minimum value.

i.e. minimum value is

$\Rightarrow 2 \cdot (\frac{1}{2})^2 - 2(\frac{1}{2}) + 9 = \frac{1}{2} - 1 + 9 = \frac{17}{2}$ at $x = \frac{1}{2}, y = \frac{1}{2}$.

c) $f(x,y) = (x-2)^2 + (y-2)^2 + 4 \longrightarrow \nabla f = (\frac{\partial f}{\partial x}, \frac{\partial f}{\partial y}) = (2x-4, 2y-4)$

$g(x,y) = x + y - 1 \longrightarrow \nabla g = (\frac{\partial g}{\partial x}, \frac{\partial g}{\partial y}) = (1, 1)$

Let (a,b) satisfies $\begin{cases} \nabla f = \lambda \cdot \nabla g \\ x + y = 1 \end{cases}$ $\rightarrow$ Then, $\begin{cases} 2a - 4 = \lambda \\ 2b - 4 = \lambda \\ a + b = 1 \end{cases}$

$\Rightarrow \therefore \lambda = -3, a = \frac{1}{2}, b = \frac{1}{2}$

i.e. minimum value is $f(\frac{1}{2}, \frac{1}{2}) = (-\frac{3}{2})^2 + (-\frac{3}{2})^2 = \frac{17}{2}$

4. A rigid container is divided into two compartments of equal volume by a partition. One compartment contains 1 mole of ideal gas A at 1 atm, and the other compartment contains 1 mole of ideal gas B at 1 atm.
   (a) Calculate the entropy increase in the container if the partition between the two compartments is removed.
   (b) If the first compartment had contained 2 moles of ideal gas A, what would have been the entropy increase due to gas mixing when the partition was removed?
   (c) Calculate the corresponding entropy changes in each of the above two situations if both compartments had contained ideal gas A.

Initial : $\begin{cases} A : 1mol,\ 1atm,\ V_0 \\ B : 1mol,\ 1atm,\ V_0 \end{cases}$

a) partition removed $\Rightarrow$ "$V_0 \rightarrow 2V_0$"

$$\Delta S_A = \int dS_A = \int \frac{nR}{V} dV = nR \cdot \ln \frac{V_A}{V_{A,0}} = 1mol \cdot 8.314 \frac{J}{K \cdot mol} \cdot \ln 2 = 5.763 J/K$$

$$\Delta S_B = \int dS_B = \int \frac{nR}{V} dV = nR \cdot \ln \frac{V_B}{V_{B,0}} = 1mol \cdot 8.314 \frac{J}{K \cdot mol} \cdot \ln 2 = 5.763 J/K$$

$$\therefore \Delta S = \Delta S_A + \Delta S_B = 11.526 J/K$$

b) $\Delta S_A = \int dS_A = \int \frac{nR}{V} dV = nR \cdot \ln \frac{V_A}{V_{A,0}} = 2mol \cdot 8.314 \frac{J}{K \cdot mol} \cdot \ln 2 = 11.526 J/K$

$$\Delta S_B = \int dS_B = \int \frac{nR}{V} dV = nR \cdot \ln \frac{V_B}{V_{B,0}} = 1mol \cdot 8.314 \frac{J}{K \cdot mol} \cdot \ln 2 = 5.763 J/K$$

$$\therefore \Delta S = \Delta S_A + \Delta S_B = 17.289 J/K$$

C-1) 같은 Gas → partition 제거해도 indistinguishable하므로 $\therefore \Delta S = 0$

C-2) $\begin{cases} A_1 : 2mol,\ 2atm,\ V_0 \\ A_2 : 1mol,\ 1atm,\ V_0 \end{cases} \longrightarrow \begin{cases} A_1 : 2mol,\ \frac{3}{2}atm,\ \frac{4}{3}V_0 = V_1 \\ A_2 : 1mol,\ \frac{3}{2}atm,\ \frac{2}{3}V_0 = V_2 \end{cases}$

$$\Delta S_1 = nR \cdot \ln \frac{V_1}{V_0} = 2 \times 8.314 \times \ln \frac{4}{3} = 4.784 J/K$$

$$\Delta S_2 = nR \cdot \ln \frac{V_2}{V_0} = 1 \times 8.314 \times \ln \frac{2}{3} = -3.371 J/K$$

$$\therefore \Delta S = \Delta S_1 + \Delta S_2 = 1.413 J/K$$