Department of Materials Science and Engineering
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AMSE205 Thermodynamics I

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Problem Set #2

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.

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.

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

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

Find the constrained maximum of this function corresponding to the condition

$$x + y = 1$$

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

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.

1. The initial state of one mole ($n=1$) of a monatomic ideal gas is P = 10 atm and T = 300 K. Calculate the change in the entropy (ΔS) 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.

$$P_1V_1 = nRT_1 \longrightarrow V_1 = \frac{0.08206 \times 300}{10} = 2.46\ l$$

a) Isothermal, $P_1 \longrightarrow P_2 = 5\ atm$

$$P_2V_2 = nRT_1 \longrightarrow V_2 = \frac{0.08206 \times 300}{5} = 4.92\ l \quad (V_2 = 2V_1)$$

$$\Delta S = \frac{q}{T} = \frac{R\cancel{T}\ln\left(\frac{V_2}{V_1}\right)}{\cancel{T}} = R\ln\left(\frac{V_2}{V_1}\right) = (8.314) \times \ln 2$$

$$= 5.76\ J/K$$

b) reversible adiabatic expansion, $P_1 \longrightarrow P_2 = 5\ atm$

$q = 0$ 이므로 $\Delta S = 0$

c) Constant volume, $P_1 \longrightarrow P_2 = 5\ atm$

$$P_2V_1 = nRT_2 \longrightarrow T_2 = \frac{2.46 \cdot 5}{0.08206} = 150\ K \quad \left(T_2 = \frac{1}{2}T_1\right)$$

$$\Delta S = \frac{q_v}{T} = \frac{\Delta U}{T} = \int C_v \frac{1}{T} dT = C_v \ln\left(\frac{T_2}{T_1}\right) = \frac{3}{2}R \times \ln\left(\frac{1}{2}\right)$$

$$= \frac{3}{2} \cdot 8.314 \cdot \ln\left(\frac{1}{2}\right)$$

$$= -8.64\ J/K$$

$n=1$

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.

$T_1 = 300K, \quad P_1 = 10 \text{ atm}, \quad V_1 = \frac{0.08206 \times 300}{10} = 2.46 \ell$

a) $1 \to 2, \quad V_2 = 3V_1 = 7.38 \ell, \quad P_2 = \frac{P_1}{3} = 3.33 \text{ atm}, \quad T_2 = 300K$

Because the gas expands freely in a vacuum,

$W = 0, \quad q = 0$

also $\Delta U = q - w = 0$

$\Delta H = \Delta U - \Delta PV = 0$

$\Delta S = R \ln\left(\frac{P_2}{P_1}\right) = (8.314) \cdot \ln 3 = 9.134 \text{ J/K}$

b) $2 \to 3, \quad T_3 = 400K, \quad V_3 = V_2 = 7.38 \ell$

$$P_3 = \frac{RT_3}{V_3} = \frac{0.08206 \cdot 400}{7.38} = 4.45 \text{ atm}$$

$W = 0 \quad (\Delta V = 0)$

$$\Delta U = q = \int C_v dT = C_v (T_3 - T_2) = \frac{3}{2} R (400 - 300)$$

$$= \frac{3}{2} \cdot 8.314 \cdot 100$$

$$= 1247 \text{ J}$$

$\Delta H = \Delta U + P\Delta V = \Delta U = 1247 \text{J}$

$$dS = \frac{\delta q}{T} = \frac{C_v dT}{T} = \frac{\frac{C_v dP \cancel{V}}{\cancel{R}}}{\frac{P\cancel{V}}{\cancel{R}}} = C_v \frac{dP}{P}$$

$$\sim \Delta S = \int_{P_2}^{P_3} \frac{C_v}{P} dP = C_v \ln\left(\frac{P_3}{P_2}\right) = \frac{3}{2} \cdot 8.314 \cdot \ln\left(\frac{4.45}{3.33}\right)$$

$$= 3.62 \text{ J/K}$$

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.

c) $3 \to 4$, $T_4 = T_3 = 400K$, $V_4 = 3V_3 = 22.14\ \ell$

$$P_4 = \frac{0.08206 \times 400}{22.14} = 1.482\ atm$$

$\Delta U = 0$, $\Delta H = 0$ ($\because$ Isothermal)

$$W = -\int_{V_3}^{V_4} \frac{RT}{V} dV = RT \ln\left(\frac{V_3}{V_4}\right) = (8.314) \cdot 400 \cdot \ln\left(\frac{7.38}{22.14}\right)$$

$$= -3653\ J$$

$q = -w = 3653\ J$

$$dS = \frac{\delta q}{T} \Rightarrow \Delta S = R \ln\left(\frac{7.38}{22.14}\right) = (8.314) \cdot \ln\left(\frac{7.38}{22.14}\right)$$

$$= -9.13\ J/K$$

d) $4 \to 5$, $T_5 = 300K$, $P_5 = P_4 = 1.482\ atm$

$$V_5 = \frac{0.08206 \times 300}{1.482} = 16.6\ \ell$$

$$\Delta H = q_p = \int C_p dT = \frac{5}{2} R \cdot (T_5 - T_4) = \frac{5}{2} \cdot (8.314) \cdot (300 - 400)$$

$$= -2078\ J$$

$$W = P\Delta V = 1.482(16.6 - 22.14) = -821\ J$$

$$\Delta U = q_p - W = -2078 + 821 = -1257\ J$$

$$dS = C_p \frac{dV}{V} \Rightarrow \Delta S = \int_{V_4}^{V_5} C_p \frac{dV}{V} = C_p \ln\left(\frac{V_5}{V_4}\right) = \frac{5}{2} R \ln\left(\frac{16.6}{22.14}\right)$$

$$= -5.99\ J/K$$

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

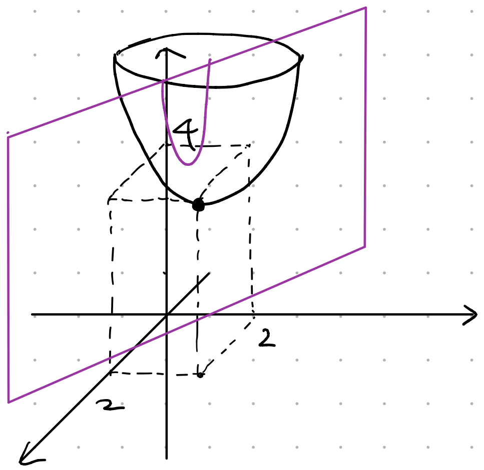
$$z = (x - 2)^2 + (y - 2)^2 + 4.$$

Find the constrained maximum 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)



Minimum value : $z=4$

b) $x+y=1 \longrightarrow y=-x+1$ 대입

$$\rightsquigarrow z = (x-2)^2 + (-x-1)^2 + 4$$
$$= (x^2-4x+4)+(x^2+2x+1)+4$$
$$= 2x^2-2x+9$$

$\rightsquigarrow \dfrac{dz}{dx} = 4x-2 \longrightarrow$ extreme value (Min) $(x,y,z) = \left(\frac{1}{2}, \frac{1}{2}, \frac{17}{2}\right)$

c) $\begin{cases} f(x,y) = (x-2)^2+(y-2)^2+4 \\ g(x,y) = 0 \iff x+y=1 \end{cases}$

$$\nabla f(x,y) = \lambda \nabla g(x,y)$$

$\begin{cases} \dfrac{\partial f}{\partial x} = 2(x-2) = \lambda \\ \dfrac{\partial f}{\partial y} = 2(y-2) = \lambda \end{cases} \Longrightarrow \lambda = 2(x-2) = 2(y-2)$

$\rightsquigarrow x=y \xrightarrow{\text{대입.}} x+y=1$

$\rightsquigarrow 2x=1$

$\rightsquigarrow x=\frac{1}{2}=y$

$\therefore (x,y)=\left(\frac{1}{2},\frac{1}{2}\right)$

$\longrightarrow z=\frac{17}{2}$

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.

a)

A	B
$n = 1$ mol	$n = 1$ mol
$P = 1$ atm	$P = 1$ atm

$\Longrightarrow$

A	B
$n = 1$ mol	$n = 1$ mol
$P = 0.5$ atm	$P = 0.5$ atm

<u>Isothermal</u>

$T_1 = T_2$

$$\Delta S_A = \frac{q}{T} = \frac{R\cancel{T}\ln\left(\frac{V_{A2}}{V_{A1}}\right)}{\cancel{T}} = R\ln\left(\frac{P_{A1}}{P_{A2}}\right) \qquad (\because P_1V_1 = P_2V_2)$$

$$= R\ln\left(\frac{1}{0.5}\right)$$

$$= R\ln 2$$

$$\Delta S_B = \frac{q}{T} = \frac{R\cancel{T}\ln\left(\frac{V_{B2}}{V_{B1}}\right)}{\cancel{T}} = R\ln\left(\frac{P_{B1}}{P_{B2}}\right)$$

$$= R\ln\left(\frac{1}{0.5}\right)$$

$$= R\ln 2$$

$$\therefore \Delta S_{system} = \Delta S_A + \Delta S_B = 2R\ln 2 = 11.526 \text{ J/K}$$

b)

A	B
$n = 2$ mol	$n = 1$ mol
$P = 2$ atm	$P = 1$ atm

$\Longrightarrow$

A	B
$n = 2$ mol	$n = 1$ mol
$P = 1$ atm	$P = 0.5$ atm

$$\Delta S_A = \frac{q}{T} = \frac{n_A R\cancel{T}\ln\left(\frac{P_{A1}}{P_{A2}}\right)}{\cancel{T}} = 2R\ln\left(\frac{P_{A1}}{P_{A2}}\right)$$

$$= 2R\ln 2$$

$$\Delta S_B = \frac{q}{T} = \frac{n_B R\cancel{T}\ln\left(\frac{P_{B1}}{P_{B2}}\right)}{\cancel{T}} = R\ln\left(\frac{P_{B1}}{P_{B2}}\right)$$

$$= R\ln 2$$

$$\therefore S_{sys} = \Delta S_A + \Delta S_B = 3R\ln 2 = 17.289 \text{ J/K}$$

c) In a),

	A	A′	⇒	A
V_1	$n=1$ $P=1$	$n=1$ $P'=1$		$n=2$ mol

$$\begin{cases} P_{A1} = \dfrac{RT}{V_1} & P_{A2} = \dfrac{2RT}{2V_1} = \dfrac{RT}{V_1} \\ P_{A'1} = \dfrac{RT}{V_1} & P_{A'2} = \dfrac{2RT}{2V_1} = \dfrac{RT}{V_1} \end{cases}$$

$$\Delta S_A = \frac{q}{T} = n_A R \ln\left(\frac{P_{A1}}{P_{A2}}\right) = 0$$

$\Delta S_{A'}$ 역시 동일하게 $\Delta S_{A'} = 0$

$\therefore \Delta S_{sys} = 0$

In b).

A	A′	⇒	A
$n_A=2$ V_1	$n_{A'}=1$ V_1		$n=3$ mol $V_2=2V_1$

$$\begin{cases} P_{A1} = \dfrac{2RT}{V_1} , & P_{A2} = \dfrac{3RT}{2V_1} \\ P_{A'1} = \dfrac{RT}{V_1} , & P_{A'2} = \dfrac{3RT}{2V_1} \end{cases}$$

$$\Delta S_A = n_A R \ln\left(\frac{P_{A1}}{P_{A2}}\right) = 2R\ln\left(\frac{4}{3}\right)$$

$$\Delta S_{A'} = n_{A'} R \ln\left(\frac{P_{A'1}}{P_{A'2}}\right) = R\ln\left(\frac{2}{3}\right)$$

$$\therefore \Delta S_{sys} = \Delta S_A + \Delta S_{A'} = 2R\ln\left(\frac{4}{3}\right) + R\ln\left(\frac{2}{3}\right)$$

$$= R\ln\left(\frac{32}{27}\right)$$

$$= 1.413 \text{ J/K}$$