Assignment 4 : Solution.

Ans1. The change of state can be carried out reversibly as follows:

$$\begin{tikzcd}
\text{Ice } (0^\circ C, 1atm) \arrow[r, "\Delta S_1"] & \text{Water } (0^\circ C, 1atm) \arrow[r, "\Delta S_2"] & \text{Water } (100^\circ C, 1atm) \arrow[d, "\Delta S_3"] \\
& \text{Vapour} (273^\circ C, 2atm) & \text{Vapour} (100^\circ C, 1atm) \arrow[l, "\Delta S_4"']
\end{tikzcd}$$

$$\Delta S_1 = \frac{\Delta H_f}{T} = \frac{1000gm \times 80 cal.gm^{-1}}{273K} = 293.04\ cal.K^{-1}$$

$$\Delta S_2 = n\bar{C}_p \ln\frac{T_2}{T_1}$$

$$= \left(\frac{1000}{18} mol\right)\left(18\ cal\ K^{-1} mol^{-1}\right) \ln\frac{373}{273}$$

$$= 312.11\ cal.K^{-1}$$

$$\Delta S_3 = \frac{\Delta H_{vap}}{T} = \frac{1000 \times 540}{373}\ cal.K^{-1}$$

$$= 1447.72\ cal.K^{-1}$$

$$\Delta S_4 = n\bar{C}_p \ln\frac{T_2}{T_1} - nR\ln\frac{P_2}{P_1}$$

$$= \frac{1000}{18} mol \left[8 cal\ K^{-1}.\ \ln\frac{546}{373} - 1.987\ cal\ K^{-1} mol^{-1} \ln\frac{2}{1}\right]$$

$$= 92.84\ cal.K^{-1}$$

$$\text{Total } \Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4$$

$$= (293.04 + 312.11 + 1447.72 + 92.84)\ Cal\ K^{-1}$$

$$= 2145.71\ cal.K^{-1}$$

Ans ②.

As, $\Delta G = \Delta H - T\Delta S$

$$\Delta H_{263} = \Delta H_{273} + \int_{273}^{263} (\bar{C}_{P_S} - \bar{C}_{P_L})\, dT$$

$$\therefore \Delta H_{263} = -1440 \text{ cal}\cdot\text{mol}^{-1} + (9-18)(263-273) \text{ cal}\cdot\text{mol}^{-1}$$

$$= -1350 \text{ cal}\cdot\text{mol}^{-1}$$

To Calculate ΔS, the following reversible path is considered.

$$\begin{tikzcd}
H_2O\,(l, -10^\circ C) \arrow[r, "\Delta S_1"] & H_2O\,(l, 0^\circ C) \arrow[r, shift left, "\Delta S_2"] & H_2O\,(s, 0^\circ C) \arrow[l, shift left] \arrow[d, "\Delta S_3"] \\
 & & H_2O\,(s, -10^\circ C)
\end{tikzcd}$$

$$\Delta S_1 = n\bar{C}_{P_L} \ln \frac{T_f}{T_i} = (18 \text{ cal}\cdot K^{-1}) \ln \frac{273}{263}$$

$$= 0.672 \text{ cal} K^{-1}.$$

$$\Delta S_2 = \frac{\Delta H}{T} = -\frac{1440}{273} \text{ cal}\cdot K^{-1} = -5.275 \text{ cal}\cdot K^{-1}$$

$$\Delta S_3 = (9 \text{ cal}\cdot K^{-1}) \ln\left(\frac{273}{263}\right) = -0.336 \text{ cal} K^{-1}$$

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$= (0.672 - 5.275 - 0.336) \text{ cal } K^{-1}$$

$$= -4.94 \text{ cal } K^{-1}$$

$$\therefore \Delta G = \Delta H - T\Delta S$$

$$= (-1350 + 263 \times 4.94) \text{ cal}$$

$$= -51.043 \text{ cal}.$$

As, $\Delta G_{P,T}$ is negative, the process is a spontaneous Process.

Ans 3: Efficiency of engine = $\frac{T_2 - T_1}{T_2}$

$= \frac{400 - 300}{400} = 0.25$ [Engine]

Coefficient of performance (ψ) = $\frac{T_1}{T_2 - T_1}$ [For Ref.]

$= \frac{273}{300.3 - 273} = 10$

Work done by engine per sec = 2×10^3 J

Heat Extracted to prepare 3kg ice at 0°C = $3 \times 10^3 \times 334.72$ J

$= 1004.16 \times 10^3$ J

∴ Quantity of heat to be extracted per sec to prepare 3kg ice per min = $\frac{1004.16 \times 10^3 \, Js^{-1}}{60}$

$= 16.736 \times 10^3$ J. sec^{-1}

Quantity of heat actually extracted per sec. =

$= \psi \, |W|_{input} = 20 \times 10^3$ J sec^{-1}

Hence, rate of heat leakage to the refrigerator =

$= (20 - 16.736) \times 10^3$ J sec^{-1}

$= 3.264 \times 10^3$ J sec^{-1}

Amount of Heat needed for the engine per minute

$$= \frac{W}{\eta} = \frac{2 \times 60 \times 10^3\,J}{0.25} = 480 \times 10^3\,J.$$

Ans 4: As, $\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V$

$[V_m = \bar{V}]$

(a) for a van der Waals gas

$$P = \frac{nRT}{V-nb} - \frac{n^2 a}{V^2} = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V = \left(\frac{R}{V_m - b}\right)$$

(b) for a Dieterici gas:

$$P = \frac{RT e^{-a/RTV_m}}{V_m - b}$$

$$\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V = \frac{R\left(1 + \frac{a}{RV_mT}\right) e^{-a/RV_mT}}{V_m - b}$$

For an Isothermal $\overset{\text{Expansion}}{\downarrow}$ process,

$$\Delta S = \int_{V_i}^{V_f} dS = \int_{V_i}^{V_f} \left(\frac{\delta S}{\delta V}\right)_T dV$$

So we can simply compare $\left(\frac{\delta S}{\delta V}\right)_T$ expressions for the three gases.

For a perfect gas,

$$p = \frac{nRT}{V} = \frac{RT}{V_m} \quad \text{so} \quad \left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V = \frac{R}{V_m}$$

$\left(\frac{\delta S}{\delta V}\right)_T$ is certainly greater for a van der waals gas than for a perfect gas, for the denominator is smaller for the Van der waals gas. To compare the vander waals gas to the Dieterici gas, we assume that both have the same Parameter b. (That is reasonable, for b is an excluded volume in both equation of state). In that case,

$$\left(\frac{\delta S}{\delta V}\right)_{T,\,Die.} = \frac{R\left(1+\frac{a}{RV_mT}\right)e^{-a/RV_mT}}{V_m-b}$$

$$= \left(\frac{\delta S}{\delta V}\right)_{T,\,vdw}\left(1+\frac{a}{RV_mT}\right)e^{-a/RV_mT}$$

Now, notice that the additional factor in $\left(\frac{\delta S}{\delta V}\right)_{T,\,Die.}$ has the form $(1+x)e^{-x}$, where $x>0$. This factor is always less than 1. Clearly, $(1+x)e^{-x}<1$ for large x, for then the exponential dominates. But $(1+x)e^{-x}<1$ even for small x, as can be seen by using the power series expansion for the exponential: $(1+x)(1-x+x^2/2+\dots\dots)$ $= 1-\frac{x^2}{2}+\dots\dots$ So $\left(\frac{\delta S}{\delta V}\right)_{T,\,Die} < \left(\frac{\delta S}{\delta V}\right)_{T,\,vdw}$.

To Summerize, for isothermal expansion:

$$\boxed{\Delta S_{vdW} > \Delta S_{Die}} \quad \text{and} \quad \boxed{\Delta S_{vdW} > \Delta S_{perfect}}.$$

The comparison between a perfect gas and a Dieterici gas depends on particular values of constants a and b and on the physical conditions.

Ans 5. As, $S = S(T, P)$

$$dS = \left(\frac{\delta S}{\delta T}\right)_P dT + \left(\frac{\delta S}{\delta P}\right)_T dP$$

$$\text{As, } \left(\frac{\delta S}{\delta T}\right)_P = \frac{C_P}{T}$$

$$\text{Also, } \left(\frac{\delta S}{\delta P}\right)_T = -\left(\frac{\delta V}{\delta T}\right)_P \quad \& \quad \alpha = \frac{1}{V}\left(\frac{\delta V}{\delta T}\right)_P$$

$$\Rightarrow dq_{rev} = TdS = C_P\, dT - T\left(\frac{\delta V}{\delta T}\right)_P dP$$

$$C_S = \left(\frac{\delta q}{\delta T}\right)_S = C_P - TV\alpha\left(\frac{\delta P}{\delta T}\right)_S$$

~~Also~~ $\Rightarrow$

$$\boxed{C_S = C_P - \alpha V \times \frac{\Delta_{trs} H}{\Delta_{trs} V}.}$$

Ans 6. (i) According to Trouton's rule

$$\Delta_{vap}H \approx 85\,\mathrm{J\,K^{-1}\,mol^{-1}} \times T_b$$
$$= 85\,\mathrm{J\,K^{-1}\,mol^{-1}} \times 342.2\,\mathrm{K}$$
$$= 29.1\,\mathrm{kJ\,mol^{-1}}$$

(ii) Use the integrated form of the Clausius - Clapeyron eq^n rearranged to

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta_{vap}H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

At $T_1 = 342.2\,K$, $P_1 = 1.0$ atm [Normal Boiling Point]; thus at 25°C.

$$\ln\left(\frac{P_2}{1.0\,atm}\right) = \left(\frac{2.91 \times 10^4\,J\,mol^{-1}}{8.314\,J\,K^{-1}\,mol^{-1}}\right) \times \left(\frac{1}{342.2\,K} - \frac{1}{298.2\,K}\right)$$

$$\ln P_2 = -1.51$$

$$P_2 = e^{-1.51} = 0.22\,atm.$$

At 60°C, $\ln\left(\frac{P_2}{1\,atm}\right) = \left(\frac{2.91 \times 10^4\,J\,mol^{-1}}{8.3145\,J\,K^{-1}\,mol^{-1}}\right) \times \left(\frac{1}{342.2\,K} - \frac{1}{333.2\,K}\right)$

$$P_2 = 0.76\,atm.$$