Q.1   **Question 1**

(a) Air contained in a piston-cylinder system undergoes three consecutive processes,

- Process 1–2: Isobaric cooling with P_1=69 kPa and V_1=0.11 m³;
- Process 2–3: Isochoric heating with P_3=345 kPa;
- Process 3–1: Polytropic expansion, with $PV = constant$.

(i) Calculate V_2 $\left(\text{in m}^3\right)$.   [4 marks]

Solution:

For Process 2–3: V_2=V_3. However the expansion 3–1 follows $PV = constant$,

$$P_1V_1 = P_3V_3 \Longrightarrow V_3 = \frac{P_1V_1}{P_3} = \mathbf{0.022} \; m^3 = \mathbf{V_2}$$

[4/4]

(ii) Calculate the work (in kJ) for each process.   [6 marks]

Solution:

Process 1–2:

$$\mathbf{W_{1-2}} = \int_{V_1}^{V_2} PdV = P\left(V_2 - V_1\right) = -6072J \Rightarrow \mathbf{-6.072kJ}$$

[2/6]   *Process 2–3: V_2=V_3 $\Longrightarrow$* $\mathbf{W_{2-3} = 0}$

[2/6]   *Process 3–1: $PV = C$*

$$\mathbf{W_{31}} = \int_{V_3}^{V_1} PdV = \int_{V_3}^{V_1} \frac{C}{V}dV = P_1V_1 \ln\frac{V_1}{V_3} = 12220J \Rightarrow \mathbf{12.22kJ}$$

[2/6]

(iii) Sketch the PV diagram for these processes.   [4 marks]

Solution:

[4/4]

(b) A closed system with 0.09 kg of air undergoes a polytropic process from $P_1 = 138$ kPa, $v_1 = 0.72$ m^3.kg^{-1} to a final state where $P_2 = 552$ kPa, $v_2 = 0.25$ m^3.kg^{-1}. Determine the work (in kJ) required for this compression. [6 marks]

Solution:

First stage is to calculate the polytropic coefficient,

$$P_1 v_1^n = P_2 v_2^n \implies \mathbf{n} = \frac{\ln P_2/P_1}{\ln v_1/v_2} = \mathbf{1.31}$$

[2/6] *Now, calculating the work with $V_i = v_i \times m$, thus $V_1 = 0.0648$ m^3 and $V_2 = 0.0225$ m^3:*

$$\mathbf{W} = \int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} \frac{C}{V^n} dV = C \frac{V^{1-n}}{1-n}\bigg|_{V_1}^{V_2} = \frac{P_2 V_2^n V_2^{1-n} - P_1 V_1^n V_1^{1-n}}{1-n} = \frac{P_2 V_2 - P_1 V_1}{1-n}$$

$$= \mathbf{-11.214kJ}$$

[4/6]

Q.2 **Question 2**

A geothermal power station (Rankine cycle) uses propane (n-C_3) as working fluid to produce power (W_T) in a turbine (isentropic expansion) with efficiency (η_T) of 90%. n-C_3 is vaporised by geothermal water (brine, $A - B$ in the diagram) at 90°C. After condensed, n-C_3 is driven to a heat exchanger (with thermal efficiency of 68%) and the cycle continues. The mass flow rate of n-C_3 ($\dot{m}_{C3}$) is 250 kg.s^{-1} and the heat capacity at constant pressure (C_p) of brine is 3565.5 J.(kg.K)$^{-1}$. Conditions for n-C_3 and brine flows are described in Table below.
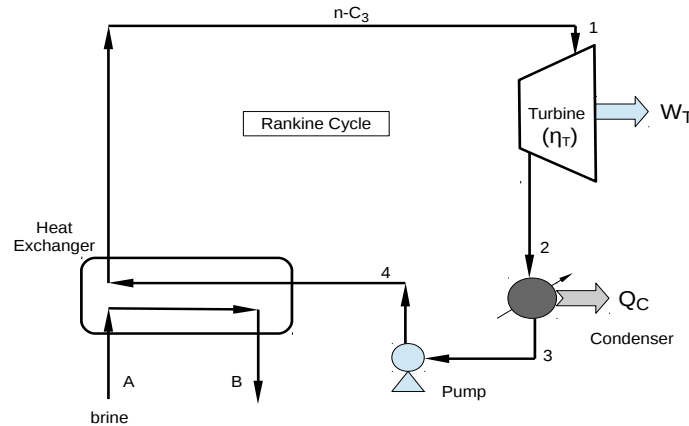
Stage	P (bar)	T (°C)	State	H (kJ.kg^{-1})	S (kJ.(kg.K)$^{-1}$)
1	16	50	**(a)**	**(b)**	**(c)**
2	6	–	wet vapour	**(d)**	–
3	6	–	sat. liquid	**(e)**	–
4	16	–	**(f)**	**(g)**	–
A	–	90	–	–	–
B	–	30	–	–	–

(a) In this Table, determine *(a)-(g)*. [7 marks]

Solution:

In order to fill the Table we need to calculate the thermodynamic properties for each stage of the cycle:

Stage 1: *At P_1 = 16 bar, T_1 = 50° C > T_{sat} (P_1) = 46.89° C. Therefore the fluid is*
[1/7] *at* **superheated state** *. From the superheated table for n-C_3 at P_1 and T_1, we can obtain:*
[1/7] **H_1 = 522.5 kJ.kg^{-1}** *and*
[1/7] **S_1 = 1.733 kJ.(kg.K)$^{-1}$** *.*

Stage 2: *At P_2 = 6 bar, the fluid is wet vapour after the isentropic expansion. We should first calculate the quality of the vapour in an ideal expansion (using values of entropy/enthapy obtained from the saturated n-C_3 table at P_2.*

$$x_{2s} = \frac{S_{2s} - S_f}{S_g - S_f} = \frac{1.733 - 0.446}{1.737 - 0.446} = 0.9969$$

now to calculate the ideal enthalpy,

$$x_{2s} = 0.9969 = \frac{H_{2s} - H_f}{H_g - H_f} = \frac{H_{2s} - 115.3}{478.3 - 115.3} \iff H_{2s} = 477.17\frac{kJ}{kg}$$

As the efficiency of the turbine is of 90%,

$$\eta_{Turbine} = 0.90 = \frac{H_2 - H_1}{H_{2s} - H_1} = \frac{H_2 - 522.5}{477.17 - 522.5} \iff \mathbf{H_2 = 481.70\frac{kJ}{kg}}$$

[1/7]

Stage 3: *At $P_3 = P_2 = 6$ bar, the fluid leaving the condenser towards the pump is saturated liquid, and the enthalpy and specific volume are the same of the liquid phase obtained from the saturated table:*

[1/7] $\mathbf{H_3} = H_f\,(P = 6\ bar) = \mathbf{115.3\ kJ.kg^{-1}}$
$V_3 = V_f\,(P = 6\ bar) = 1.931\times 10^{-3}\ m^3.kg^{-1}$

[1/7] **Stage 4:** *The fluid leaving the pump is* **sub-cooled liquid***. As there is no heat loss in the pump, we can assume $dH \approx VdP$, therefore*

$$\mathbf{H_4} = H_3 + V_3\,(P_4 - P_3) = 115.3\frac{kJ}{kg} + 1.931 \times 10^{-3}\frac{m^3}{kg}\,(16 - 6)\ bar = \mathbf{117.23\frac{kJ}{kg}}$$

[1/7]

Thus the Table becomes:

Stage	P (bar)	T (°C)	State	H (kJ.kg^{-1})	S (kJ.(kg.K)$^{-1}$)
1	*16*	*50*	**superheated vapour**	**522.5**	**1.733**
2	*6*	*–*	*wet vapour*	**481.70**	*–*
3	*6*		*sat. liquid*	**115.3**	*–*
4	*16*		**sub-cooled liquid**	**117.23**	*–*
A	*–*	*90*	*–*	*–*	*–*
B	*–*	*30*	*–*	*–*	*–*

(b) Calculate the power produced by the turbine (W_T) and the heat extracted in the condenser (Q_C) in *MW*.   [4 marks]
Solution:

$$\mathbf{W_T} = \dot{m}_{C3}\,(H_1 - H_2) = 250\frac{kg}{s} \times (522.5 - 481.70)\frac{kJ}{kg} = 10200\frac{kJ}{s} = \mathbf{10.2MW}$$

[2/4]

$$\mathbf{Q_C} = \dot{m}_{C3}\,(H_2 - H_3) = 250\frac{kg}{s} \times (481.70 - 115.30)\frac{kJ}{kg} = 91600\frac{kJ}{s} = \mathbf{91.6MW}$$

[2/4]

(c) Calculate the mass flow rate of brine in $kg.s^{-1}$.   [6 marks]

Solution:

The heat extracted by the n-C_3 $\left(\dot{Q}_{C3}\right)$ fluid in the heat exchanger can be easily calculated by

$$\dot{\mathbf{Q}}_{\mathbf{C3}} = \dot{m}_{C3}\left(H_1 - H_4\right) = \mathbf{101317.5}\frac{\mathbf{kJ}}{\mathbf{s}}$$

[2/6]   Assuming that the heat extracted from the geothermal fluid (brine), $\dot{Q}_{gf}$ is transferred to the n-C_3 stream with efficiency of 68%,

$$\eta_{HE} = 0.68 = \frac{\dot{Q}_{C3}}{\dot{Q}_{gf}} \iff \dot{\mathbf{Q}}_{\mathbf{gf}} = \mathbf{148996.32}\frac{\mathbf{kJ}}{\mathbf{s}}$$

[2/6]   With the heat generated by the geothermal fluid and the inlet/outlet fluid temperatures, we can now calculate the brine mass flow rate for the associated heat transferred,
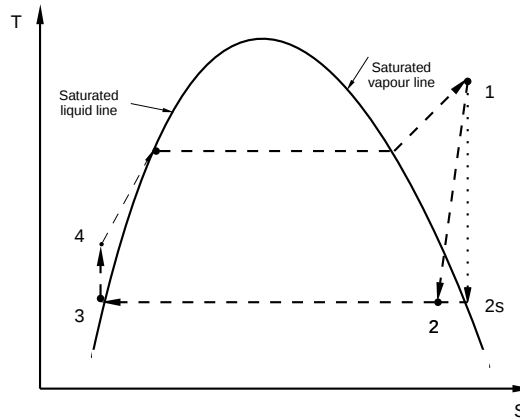
$$\dot{Q}_{gf} = 148996.32\frac{kJ}{s} = \dot{m}_{gf}C_p\left(T_A - T_B\right) \iff \dot{\mathbf{m}}_{\mathbf{gf}} = \mathbf{696.57}\frac{\mathbf{kg}}{\mathbf{s}}$$

[2/6]

(d) Sketch the temperature × entropy (TS) diagram for the process indicating the liquid and vapour saturated lines and each stage of the n-C_3 Rankine cycle.   [3 marks]

Solution:

[3/3]

To solve this problem, you should assume that the saturated liquid streams are incompressible, and therefore $dH = V dP$ (where H, V and P are enthalpy, volume and pressure, respectively). Quality of the vapour is expressed as

$$x_j = \frac{\Psi_j - \Psi_f}{\Psi_g - \Psi_f} \quad \text{with } \Psi = \{H, S\}$$

where S is the entropy. Efficiency of the turbine (η_{Turbine}) and the heat exchanger (η_{HE}) are given by,

$$\eta_{\text{Turbine}} = \frac{H_2 - H_1}{H_{2s} - H_1} \quad \text{and} \quad \eta_{\text{HE}} = \frac{\dot{Q}_{C3}}{\dot{Q}_{gf}}$$

where H_{2s} is the enthalpy of stream 2 assuming ideal turbine performance (i.e., reversible expansion). $\dot{Q}_{C3}$ and $\dot{Q}_{gf}$ are the heat associated with the n-C_3 and brine streams, respectively, at the heat exchanger.

Q.3   Question 3

(a) Develop expressions for the volume expansivity, $\beta = \dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_P$, and isothermal compressibility, $\kappa = -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial P}\right)_T$, for the following equations of state,

(i) ideal gas [4 marks]
Solution:
Ideal gas: $V = \dfrac{RT}{P}$,

$$\left(\dfrac{\partial V}{\partial T}\right)_P = \dfrac{R}{P} \quad \left(\dfrac{\partial V}{\partial P}\right)_T = -\dfrac{RT}{P^2}$$

[2/4] *Now deriving β and κ,*

$$\beta = \dfrac{1}{V}\dfrac{R}{P} = \dfrac{1}{\mathbf{T}} \quad and \quad \kappa = -\dfrac{1}{V}\left(-\dfrac{RT}{P^2}\right) = \dfrac{1}{\mathbf{P}}$$

[2/4]

(ii) $V = \dfrac{RT}{P} + b$ [4 marks]
Solution:
The derivatives are,

$$\left(\dfrac{\partial V}{\partial T}\right)_P = \dfrac{R}{P} \quad \left(\dfrac{\partial V}{\partial P}\right)_T = -\dfrac{RT}{P^2}$$

[2/4] *Now deriving β and κ,*

$$\beta = \dfrac{1}{V}\dfrac{R}{P} = \dfrac{R}{V}\dfrac{V-b}{RT} = = \dfrac{1}{\mathbf{T}}\dfrac{\mathbf{V}-\mathbf{b}}{\mathbf{V}} \quad and \quad \kappa = -\dfrac{1}{V}\left(-\dfrac{RT}{P^2}\right) = \dfrac{1}{\mathbf{P}}\left[\dfrac{\mathbf{V}-\mathbf{b}}{\mathbf{V}}\right]$$

[2/4]

(b) Calculate the compressibility factor (Z) of chloroform vapour at 450 K and 20 bar (molar volume of 1.35×10^{-3} m³.gmol⁻¹) using the Soave-Redlich-Kwong equation of state. Properties of chloroform are: T_c = 537 K, P_c = 5328.68 kPa and ω =0.218 (accentric factor). In your iterative calculations, use $PV = ZRT$ as an initial guess of Z, and stop at the second iteration (Z_2). [12 marks]
Solution:
The generic form of Z is,

$$Z = 1 + \beta - q\beta\dfrac{Z - \beta}{(Z + \epsilon\beta)(Z + \sigma\beta)} \quad with \ \beta = \Omega\dfrac{P_r}{T_r} \quad and \ q = \dfrac{\Psi\alpha}{\Omega T_r}$$

[2/12] *For SRK with $\mathbf{T}_r$=0.8380, $\mathbf{P}_r$=0.3754, β=3.88×10⁻² and q=6.7274 ,*

$$\mathbf{Z} = \mathbf{1} + \beta - \mathbf{q}\beta\dfrac{\mathbf{Z} - \beta}{\mathbf{Z^2} + \beta\mathbf{Z}}$$

[2/12] *The equation is non-linear and to find the root we can apply Newton-Raphson method*

$$Z_i = Z_{i-1} - \frac{\mathcal{F}(Z_{i-1})}{d\mathcal{F}/dZ(Z_{i-1})}$$

with,

$$\mathcal{F}(Z) = Z - \left[1 + \beta - q\beta\frac{Z-\beta}{Z^2+\beta Z}\right]$$

$$\frac{d\mathcal{F}}{dZ}(Z) = 1 + q\beta\frac{\beta^2 + 2\beta Z - Z^2}{(Z^2+\beta Z)^2}$$

[2/12]   *as initial guess, we can use the generic real gas EOS, $PV = Z_0 RT \implies Z_0 = 0.7217$.*
        Thus

[3/12] $Z_1 = \mathbf{0.7184}$
[3/12] $Z_2 = \mathbf{0.7160}$
                                   · · · · · · · · ·
[8/12]   *or (using calculator)* $Z_{22} = \mathbf{0.7088}$

Q.4 **Question 4**

The excess molar volume of a solution of ethanol (1) and methyl-buthyl ether (2) at 298.15 K is given by the following expression:

$$\overline{V}^{\mathrm{E}} = x_1 x_2 \left[-1.026 + 0.22 \left(x_1 - x_2\right)\right]$$

Given $\overline{V}_1 = 58.63$ cm³.mol⁻¹ and $\overline{V}_2 = 118.46$ cm³.mol⁻¹ ($\overline{V}_i$ is the molar volume of component i).

(a) What is the volume of the solution when 750 cm³ of pure ethanol is mixed with 1500 cm³ of methyl-buthyl ether at 298.15 K? [14 marks]

Solution:

First, we need to calculate the number of moles $n = \dfrac{V}{\overline{V}} \implies$ **n₁=12.79** *and* **n₂=12.66** *and the total number of moles* (n_T) *is 25.455. The molar fraction can now be cal-*

[4/14] *culated as* $x_i = n_i/n_T \implies$ **x₁=0.5025** *and* **x₂=0.4975** *. Substituting these values in,*

$$\overline{\mathbf{V}}^E = x_1 x_2 \left[-1.026 + 0.22 \left(x_1 - x_2\right)\right] = \mathbf{-0.2562}\frac{\mathbf{cm^3}}{\mathbf{mol}}$$

[2/14] *The molar volume of the solution is given by*

$$\overline{V}^E = \overline{V} - \sum_{i=1}^{2} x_i \overline{V}_i \implies \overline{\mathbf{V}} = \mathbf{88}.\mathbf{1392}\frac{\mathbf{cm^3}}{\mathbf{mol}}$$

[2/14] *The total volume can then be calculated as*

$$\mathbf{V^T} = \overline{\mathbf{V}}.\mathbf{n_T} = \mathbf{2243}.\mathbf{5835}\ \mathbf{cm^3}$$

[6/14]

(b) What would be the volume if the solution was ideal? [6 marks]

Solution:

The volume of the ideal solution is

$$\mathbf{V_T^{ideal}} = n_T \sum_{i=1}^{2} x_i \overline{V}_i = \mathbf{2250}.\mathbf{1055}\ \mathbf{cm^3}$$

[6/6]

Q.5 **Question 5**

A mixture of 2 kg of H_2 and 4 kg of N_2 was compressed in a piston-cylinder in a polytropic process with $n = 1.2$. During the compression, the temperature increased from 22 to 150°C. Determine the heat transfer (in kJ) and the entropy change (in kJ/K) of the process. The entropy change is expressed as,

$$\Delta S = m_T \left[\overline{C}_v \ln \frac{T_2}{T_1} + \frac{R}{\overline{MW}} \ln \frac{V_2}{V_1} \right]$$

where m_T is the total mass of the gaseous mixture, $\overline{MW}$ and $\overline{C}_v$ are the averaged molar mass and heat capacity at constant volume of the mixture. For this range of temperature, you should assume constant heat capacity at constant volume (C_v) of 0.745 and 10.32 kJ.(kg.K)$^{-1}$, for N_2 and H_2, respectively. Molar mass of H_2: 2.016 g.mol^{-1}, N_2: 28.01 g.mol^{-1}. [20 marks]

Solution:

For H_2 (1) and N_2 (2), $n_1 = 0.9921$, $n_2=0.1428$ and $n_T = 1.1349$ (also $m_T = 6kg$) $\Longrightarrow$

[2/20] $\mathbf{y_1 = 0.8742}$ *and* $\mathbf{y_2 = 0.1258}$ *. Now we can calculate the averaged molecular weight* $\overline{MW}$,

$$\mathbf{\overline{MW}} = \sum_{i=1}^{2} y_i MW_i = \mathbf{5.2860} \frac{\mathbf{kg}}{\mathbf{kgmol}}$$

[2/20] *and*

$$\overline{C}_v = \sum_{i=1}^{2} y_i C_{v,i} = 9.1155 \frac{kJ}{kg.K}$$

From the first law, $dU = dQ - dW$, for the polytropic compression ($PV^n = C$) we need work to be executed,

$$dW = PdV \Longrightarrow \mathbf{W} = \int_1^2 PdV = \int_1^2 \frac{C}{V^n}dV = \frac{CV^{1-n}}{1-n}\bigg|_1^2 = \frac{PV}{1-n}\bigg|_1^2 = \frac{n_T RT}{1-n}\bigg|_1^2$$

$$= \frac{m_T}{\overline{MW}} \frac{R(T_2-T_1)}{1-n} = \mathbf{-6038.98kJ}$$

[4/20] *The variation in internal energy can be calculated as,*

$$\mathbf{\Delta U} = \sum_{i=1}^{2} m_1 C_{v,i} \Delta T = \mathbf{3023.36kJ}$$

[4/20] *Thus, the heat is*

$$\mathbf{Q} = \Delta U + W = \mathbf{-3016.62kJ}$$

[4/20] *Now to calculate the variation in entropy,*

$$\mathbf{\Delta S} = m_T \left[\overline{C}_v \ln \frac{T_2}{T_1} + \frac{R}{\overline{MW}} \ln \frac{V_2}{V_1} \right] = m_T \left[\overline{C}_v \ln \frac{T_2}{T_1} + \frac{R}{\overline{MW}} \ln \left(\frac{T_1}{T_2} \right)^{\frac{1}{n-1}} \right]$$

$$= m_T \left[\overline{C}_v - \frac{\frac{R}{\overline{MW}}}{n-1} \right] \ln \frac{T_2}{T_1} = \mathbf{2.7042} \frac{\mathbf{kJ}}{\mathbf{K}}$$

[4/20]