Q.1 Question 1

(i) Saturated refrigerant R-134a vapour at $P_1 = 400\ kPa$ is compressed by a piston to $P_2 = 16$ bar in a reversible adiabatic process. Critical pressure and temperature of R-134a are 4.059 MPa and 101.06°C.

(a) Calculate the work done by the piston; [8 marks]

Solution:

In order to calculate the work executed by the piston we need to calculate the thermodynamic variables at states 1 and 2.

i. **State 1:** *Saturated vapour at* $P_1 = 400\ kPa = 4\ bar \Rightarrow T_1 = T_{sat} = 8.93^oC$, $V_1 = V_g = 0.0509\dfrac{m^3}{kg}$, $H_1 = 252.32\dfrac{kJ}{kg}$, $S_1 = 0.9145\dfrac{kJ}{kg.K}$ *and*

[3/8] $\mathbf{U_1 = 231.97\dfrac{kJ}{kg}}$.

ii. **State 2:** *Adiabatic (i.e., isentropic) compression to* $P_2 = 16\ bar \Rightarrow S_2 = S_1 = 0.9145\dfrac{kJ}{kg.K}$. *At this pressure, the saturated vapour entropy is smaller than the prescribed entropy, i.e.,* $S_g = 0.8982\dfrac{kJ}{kg.K} << S_2$. *Therefore, the fluid in 2 is at superheated state, thus (via linear interpolation):* $T_2 = 61.96^oC << T_C$, $V_2 = 0.01254\dfrac{m^3}{kg}$, $H_2 = 280.77\dfrac{kJ}{kg}$ *and*

[3/8] $\mathbf{U_2 = 260.71\dfrac{kJ}{kg}}$.

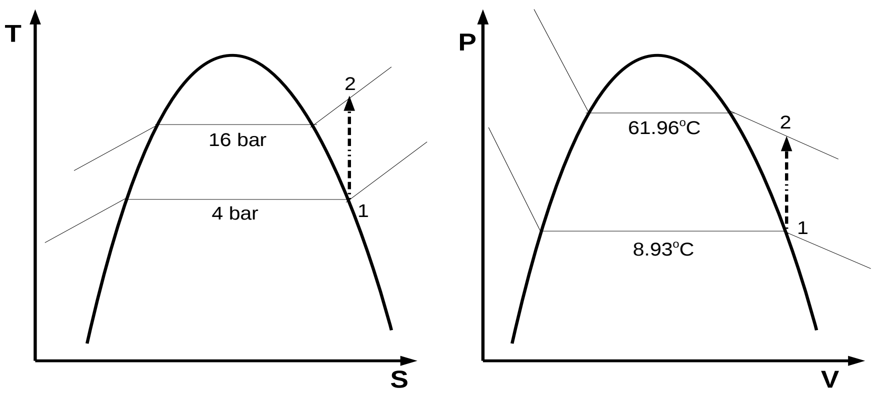
Notice that $P_2 << P_C$ *and* $V_2 << V_1$.

[2/8] *Now, from the First Law:*

$$dU = dQ + dW \Rightarrow U_2 - U_1 = 0 + \Delta W \Rightarrow \mathbf{\Delta W = 28.74\frac{kJ}{kg}}$$

(b) Sketch the TS and PV diagrams including the constant pressure and temperature lines. [4 marks]

Solution:



[4/4]

(ii) A reversible power cycle receives 100 kJ by heat transfer from a hot reservoir at 327°C and rejects 40 kJ by heat transfer to a cold reservoir at temperature T_C. Calculate:

(a) Thermal efficiency, $\eta_T \left(= \frac{W_{\text{cycle}}}{Q_H}\right)$, where W_{cycle} is the work produced by the cycle and Q_H is the heat associated to the hot reservoir. [4 marks]

Solution:

The problem supplies $Q_H = 100$ kJ, $T_H = 327°C$ and $Q_C = 40$ kJ. The efficiency is given by

$$\eta_{\mathbf{T}} = \frac{W_{cycle}}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{40kJ}{100kJ} = \mathbf{0.6} \implies \mathbf{60\%}$$

[4/4]

(b) Temperature of the cold reservoir (T_C) in °C. [4 marks]

Solution:

Since the cycle operates reversibly, $\eta_H = \eta_{max} = 1 - \frac{T_C}{T_H}$. Therefore with $T_H = 327°C = 600.15$ K,

$$0.6 = 1 - \frac{T_C}{T_H} = 1 - \frac{T_C}{600.15} \implies \mathbf{T_C = 240.06K = -33.09°C}$$

[4/4]

Q.2 Question 2

(i) Derive the Maxwell relations below from the fundamental thermodynamic equations. [12 marks]

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial s}\right)_V; \qquad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial s}\right)_P;$$
$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T; \qquad \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

Solution:
First, let's assume a functional $f = f(a,b)$ and rewrite it as a function of the variables a and b,

$$df = \left(\frac{\partial f}{\partial a}\right)_b da + \left(\frac{\partial f}{\partial b}\right)_a db$$

If we define $M = \left(\frac{\partial f}{\partial a}\right)_b$ and $N = \left(\frac{\partial f}{\partial b}\right)_a$, the equation above becomes

$$\mathbf{df = Mda + Ndb} \tag{1}$$

[2/12] *Now, if we differentiate M and N with respect to b and a, respectively,*

$$\left(\frac{\partial M}{\partial b}\right)_a = \frac{\partial^2 f}{\partial a \partial b} \quad \textit{and} \quad \left(\frac{\partial N}{\partial a}\right)_b = \frac{\partial^2 f}{\partial b \partial a}$$

If the functional f is continuous and differentiable over all domain,

$$\frac{\partial^2 f}{\partial a \partial b} = \frac{\partial^2 f}{\partial b \partial a} \Longrightarrow \left(\frac{\partial \mathbf{M}}{\partial \mathbf{b}}\right)_{\mathbf{a}} = \left(\frac{\partial \mathbf{N}}{\partial \mathbf{a}}\right)_{\mathbf{b}} \tag{2}$$

[2/12] *The fundamental thermodynamic relations,*

$$dU = -PdV + TdS$$
$$dH = Tds + VdP$$
$$dA = -PdV - SdT$$
$$dG = -VdP - SdT$$

have similar shape as Eqn. 1, where, for example, in the first relation: $U = f$,
[2/12] *$M = -P$, $N = T$, $dV = da$ and $dS = db$. Using relation 2, $-\left(\frac{\partial \mathbf{P}}{\partial \mathbf{S}}\right)_{\mathbf{V}} = \left(\frac{\partial \mathbf{T}}{\partial \mathbf{V}}\right)_{\mathbf{S}}$.*
Applying the same to the remaining relations we obtain:

$$\left(\frac{\partial \mathbf{T}}{\partial \mathbf{P}}\right)_{\mathbf{S}} = \left(\frac{\partial \mathbf{V}}{\partial \mathbf{s}}\right)_{\mathbf{P}}$$

[2/12]

$$\left(\frac{\partial \mathbf{P}}{\partial \mathbf{T}}\right)_{\mathbf{V}} = \left(\frac{\partial \mathbf{S}}{\partial \mathbf{V}}\right)_{\mathbf{T}}$$

[2/12]

$$\left(\frac{\partial \mathbf{V}}{\partial \mathbf{T}}\right)_{\mathbf{P}} = -\left(\frac{\partial \mathbf{S}}{\partial \mathbf{P}}\right)_{\mathbf{T}}$$

[2/12]

(ii) Using the Maxwell relations above, evaluate $\left(\frac{\partial S}{\partial V}\right)_T$ for water vapour at 240°C and specific volume of 0.4646 $m^3.kg^{-1}$ through the Redlich-Kwong equation of state,

$$P = \frac{RT}{V-b} - \frac{a}{V\,(V+b)\,T^{1/2}}$$

with $a = 142.59$ bar$\left(\frac{m^3}{kgmol}\right)^2 (K)^{\frac{1}{2}}$ and $b = 0.0211\frac{m^3}{kgmol}$. [8 marks]

Solution:

The Maxwell relation $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$ *allows to determine* $\left(\frac{\partial S}{\partial V}\right)_T$ *from the PVT relationship in the RK EOS. Thus,*

$$\left(\frac{\partial \mathbf{P}}{\partial \mathbf{T}}\right)_{\mathbf{V}} = \frac{\mathbf{R}}{\mathbf{V}-\mathbf{b}} + \frac{\mathbf{a}}{\mathbf{2V}\,(\mathbf{V}+\mathbf{b})\,\mathbf{T}^{\frac{3}{2}}}$$

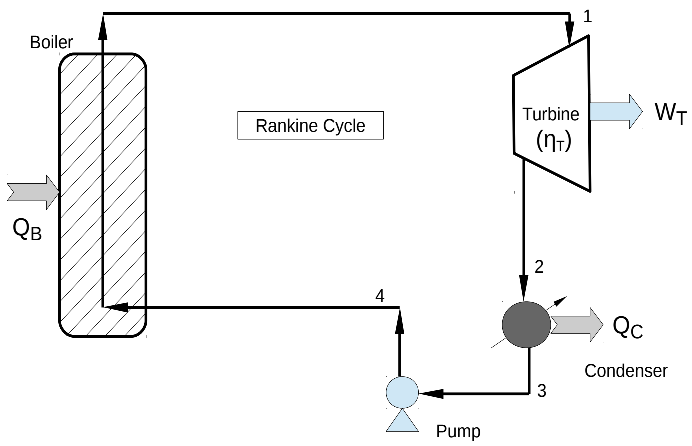
[3/8] *Now substituting the variables by their values*

$$\left(\frac{\partial \mathbf{P}}{\partial \mathbf{T}}\right)_{\mathbf{V}} = \left(\frac{\partial \mathbf{S}}{\partial \mathbf{V}}\right)_{\mathbf{T}} = \mathbf{1.0043}\frac{\mathbf{kJ}}{\mathbf{m^3.K}}$$

[5/8]

Q.3 **Question 3**

The steam generator of a nuclear power plant produces 25 kg.s^{-1} of water-steam at P_1 = 140 bar and T_1= 415°C. The fluid is used to drive a turbine (isentropic expansion) producing power (W_T) at P_2 = 2.5 bar. Before the vaporisation in the boiler, the fluid needs to be condensed into liquid water (stage 3) producing Q_C of heat.



(a) Calculate H_1, H_2, H_4, S_1 and x_2 (quality of the steam). [10 marks]

Solution:

State 1: *At P_1 = 140 bar, T_{sat} = 336.75°C > T_1= 415°C, therefore the fluid is at superheated state. From the superheated steam table (via linear interpolation),*

[2/10] $\mathbf{H_1 = 3054.51\ kJ.kg^{-1}}$ *and*

[2/10] $\mathbf{S_1 = 6.0208\ kJ.(kg.K)^{-1}}$.

State 2: *Isentropic expansion at P_2 = 2.5 bar $\longrightarrow$ S_2=S_1. We can calculate the quality of the water-steam at 2.5 bar,*

$$\mathbf{x_2} = \frac{S_2 - S_f}{S_g - S_f} = \mathbf{0.8105}$$

[2/10] *With the quality we can then calculate the H_2,*

$$x_2 = \frac{H_2 - H_f}{H_g - H_f} \implies \mathbf{H_2 = 2303.50 \frac{kJ}{kg}}$$

[2/10]

State 3: *After the condenser, water is at liquid state at P_3=P_2 (no pressure drop) with $H_3 = H_f$ = 535.37 kJ.kg^{-1}, $S_3 = S_f$ = 1.6072 kJ.(kg.K)$^{-1}$ and $V_3 = V_f$ = 1.0672×10^{-3} m^3.kg^{-1}.*

State 4: *Assuming the liquid water is incompressible $dH \equiv VdP$ with $P_4 = P_1$*

$$\mathbf{H_4} = H_3 + V_3\,(P_4 - P_3) = \mathbf{550.04 \frac{kJ}{kg}}$$

[2/10]

(b) Determine the power produced in the turbine (W_T) in MW. [2 marks]
Solution:
For $\dot{m}_w = 25\ kg.s^{-1}$,

$$\mathbf{W_T} = \dot{m}_w \left(H_1 - H_2\right) = \mathbf{18775.25 \frac{kJ}{s}} = \mathbf{18.8MW}$$

[2/2]

(c) Determine the heat extracted from the steam (Q_C) in MW. [2 marks]
Solution:

$$\mathbf{Q_C} = \dot{m}_w \left(H_2 - H_3\right) = \mathbf{44203.25 \frac{kJ}{s}} = \mathbf{44.2MW}$$

[2/2]

(d) Determine the heat supplied by the boiler (Q_B) in MW. [2 marks]
Solution:

$$\mathbf{Q_B} = \dot{m}_w \left(H_1 - H_4\right) = \mathbf{62611.75 \frac{kJ}{s}} = \mathbf{62.6MW}$$

[2/2]

(e) Calculate the efficiency of the cycle $\left(\eta_{\text{cycle}} = \frac{W_T}{Q_B}\right)$. [2 marks]
Solution:

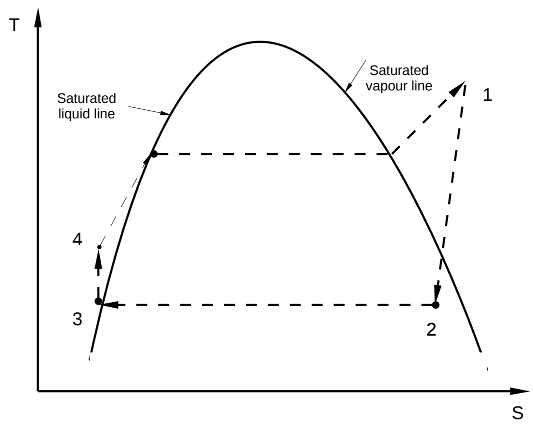
$$\eta_{cycle} = \frac{W_T}{Q_B} = \mathbf{0.30} \Longrightarrow \mathbf{30\%}$$

[2/2]

(f) Sketch the temperature × entropy (TS) diagram for the process indicating the liquid and vapour saturated lines and each stage of the water-steam Rankine cycle. [2 marks]

Solution:

[2/2]



To solve this problem, you should assume that the saturated liquid streams are incompressible, and therefore $dH = VdP$ (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.

Q.4 Question 4

Two chemical species, 1 and 2 are mixed in a solution at 25°C and atmospheric pressure. The volume change is given by the following equation,

$$\Delta V = x_1 x_2 \left(45 x_1 + 25 x_2\right)$$

where ΔV is expressed in $cm^3.gmol^{-1}$. At these temperature and pressure conditions, $V_1 = 110$ and $V_2 = 90$ $cm^3.gmol^{-1}$. Determine the partial molar volumes of the chemical species in a solution containing 40%-mol of species 1. [20 marks]

Solution:

$x_1 = 0.4$ and $x_2 = 1 - x_1 = 0.6$. The volume change is the excess volume,

$$\Delta V = x_1 x_2 \left(45 x_1 + 25 x_2\right) = \mathbf{V}^E = \mathbf{7.92} \frac{\mathbf{cm^3}}{\mathbf{gmol}}$$

[5/20] *The volume of the binary solution is given by*

$$\mathbf{V} = V^E + x_1 V_1 + x_2 V_2 = \mathbf{105.92} \frac{\mathbf{cm^3}}{\mathbf{gmol}}$$

[5/20] *The partial molar properties in binary mixtures can be obtained by $\overline{M}_1 = M + x_2 \frac{dM}{dx_1}$ and $\overline{M}_2 = M - x_1 \frac{dM}{dx_1}$, thus for partial molar volumes*

$$\overline{\mathbf{V}}_\mathbf{1} = V + x_2 \frac{dV}{dx_1} = \mathbf{171.92} \frac{\mathbf{cm^3}}{\mathbf{gmol}}$$

[5/20] *and*

$$\overline{\mathbf{V}}_\mathbf{2} = V - x_1 \frac{dV}{dx_1} = \mathbf{61.92} \frac{\mathbf{cm^3}}{\mathbf{gmol}}$$

[5/20]

Q.5 Question 5

(i) A concentrated binary solution containing mainly species 2 (though $x_2 \neq 1$) is in equilibrium with a vapour phase containing both species 1 and 2. Pressure and temperature of this two-phase system are 1 bar and 298.15 K. Given $\mathcal{H}_1 = 200$ bar (Henry constant) and $P_2^{sat} = 0.10$ bar, calculate x_1 and y_1. [10/10 marks]

Solution:

Assuming that at 1 bar the vapour phase behaves as an ideal gas. The vapour phases fugacities are then equal to the partial pressures. Assume the Lewis/Randall rule applies to concentrated species 2 and that Henry's law applies to dilute species 1, therefore,

$$y_1 P = \mathcal{H}_1 x_1; \quad \textit{and} \quad y_2 P = x_2 P_2^{sat}$$

[5/10] *with $x_1 + x_2 = 1$. Thus $P = y_1 P + y_2 P$ becomes,*

$$P = \mathcal{H}_1 x_1 + (1 - x_1) P_2^{sat} \implies \mathbf{x_1 = 4.502 \times 10^{-3}}$$

[5/10] *and* $\mathbf{y_1} = \dfrac{\boldsymbol{\mathcal{H}_1 x_1}}{\mathbf{P}} = \mathbf{0.9}$.

(ii) Chemical species A and B are in vapour-liquid equilibrium at 298.15 K. The following conditions are applied to this system:

$$\begin{array}{ll} \ln \gamma_A = 1.8 x_B^2 & \ln \gamma_B = 1.8 x_A^2 \\ P_A^{sat} = 1.24 \text{ bar} & P_B^{sat} = 0.89 \text{ bar} \end{array}$$

Assuming that $y_i P = x_i \gamma_i P_i^{sat}$ (where γ_i is the activity coefficient of species i) is valid,

(a) Calculate the pressure P and the vapour mole fraction y_A for a liquid mole fraction $x_A = 0.65$. [6 marks]

Solution:

With x_A =0.65 and x_B=0.35, we can calculate the activity coefficients, γ_A γ_B
[3/6] *and apply in $P = x_A \gamma_A P_A^{sat} + x_B \gamma_B P_B^{sat}$ leading to* **P=1.671 bar** *. The vapour*
[3/6] *mole fraction is obtained from $y_A = \dfrac{x_A \gamma_A P_A^{sat}}{P}$, leading to* $\mathbf{y_A = 0.6013}$.

(b) Calculate the range of overall mole fraction z_A in which this system may exist. [4 marks]

Solution:

[1/4] *From mass balance for species A*

$$z_A = V y_A + L x_A \implies z_A = V y_A + (1 - V) x_A \implies \mathbf{V} = \frac{\mathbf{z_A - x_A}}{\mathbf{y_A - x_A}}$$

[1/4] *The overall vapour mole fraction V, varies from 0 to 1,* $\mathbf{0 \leq V \leq 1}$ *, therefore*
[2/4] *(replacing in the equation above)* $\mathbf{0.6013 \leq z_A \leq 0.65}$.

- Generic cubic equation of state:

$$Z = 1 + \beta - q\beta \frac{Z-\beta}{(Z+\varepsilon\beta)(Z+\sigma\beta)} \quad \text{(vapour and vapour-like roots)}$$

$$Z = 1 + \beta + (Z+\epsilon\beta)(Z+\sigma\beta)\left(\frac{1+\beta-Z}{q\beta}\right) \quad \text{(liquid and liquid-like roots)}$$

$$\text{with} \quad \beta = \Omega\frac{P_r}{T_r} \quad \text{and} \quad q = \frac{\Psi\alpha(T_r)}{\Omega T_r}$$

$$\alpha_{\text{SRK}} = \left[1 + \left(0.480 + 1.574\omega - 0.176\omega^2\right)\left(1-\sqrt{T_r}\right)\right]^2$$

$$\alpha_{\text{PR}} = \left[1 + \left(0.37464 + 1.54226\omega - 0.26992\omega^2\right)\left(1-\sqrt{T_r}\right)\right]^2$$

EOS	α	σ	ε	Ω	Ψ
vdW	1	0	0	1/8	27/64
RK	$T_r^{-1/2}$	1	0	0.08664	0.42748
SRK	α_{SRK}	1	0	0.08664	0.42748
PR	α_{PR}	$1+\sqrt{2}$	$1-\sqrt{2}$	0.07780	0.45724

- Newton-Raphson (root-finder) method: $X_i = X_{i-1} - \dfrac{\mathcal{F}(X_{i-1})}{d\mathcal{F}/dX\,(X_{i-1})}$

- Fundamental thermodynamic equations:

$$dU = dQ + dW; \quad dH = dU + d(PV); \quad dA = dU - d(TS); \quad dG = dH - d(TS)$$

$$dU = TdS - PdV; \quad dH = TdS + VdP; \quad dA = -SdT - PdV; \quad dG = -SdT + VdP$$

$$dH = C_pdT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]dP; \quad dS = C_p\frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$dU = C_vdT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV; \quad dS = C_v\frac{dT}{T} - \left(\frac{\partial P}{\partial T}\right)_V dV$$

- Polytropic Relations:

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \quad ; TV^{\gamma-1} = \text{ const}; \; TP^{\frac{1-\gamma}{\gamma}} = \text{ const}; \; PV^{\gamma} = \text{ const}$$

- Raoult's Law:

$$y_iP = x_iP_i^{\text{sat}} \quad \text{and} \quad y_iP = x_i\gamma_iP_i^{\text{sat}} \quad \text{with } i = 1, 2, \cdots N$$

- Henry's Law:

$$x_i\mathcal{H}_i = y_iP \quad \text{with } i = 1, 2, \cdots N$$

- Antoine Equation:

$$\log_{10} P^\star = A - \frac{B}{T+C} \quad \text{with P}^\star \text{ in mm-Hg and T in °C}$$

- Solutions:

$$M^{\text{E}} = M - \sum_{i=1}^{N} x_iM_i; \; \overline{M}_1 = M + x_2\frac{dM}{dx_1}; \; \overline{M}_2 = M - x_1\frac{dM}{dx_1}$$