

MARKS

Q.1 Question 1

- (i) Saturated refrigerant R-134a vapour at $P_1 = 400 \text{ kPa}$ is compressed by a piston to $P_2 = 16 \text{ bar}$ 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 $P_1 = 400 \text{ kPa} = 4 \text{ bar} \Rightarrow T_1 = T_{\text{sat}} = 8.93^\circ\text{C}$,
 $V_1 = V_g = 0.0509 \frac{\text{m}^3}{\text{kg}}$, $H_1 = 252.32 \frac{\text{kJ}}{\text{kg}}$, $S_1 = 0.9145 \frac{\text{kJ}}{\text{kg.K}}$ and

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$$U_1 = 231.97 \frac{\text{kJ}}{\text{kg}}.$$

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

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$$U_2 = 260.71 \frac{\text{kJ}}{\text{kg}}.$$

Notice that $P_2 \ll P_C$ and $V_2 \ll V_1$.

[2/8]

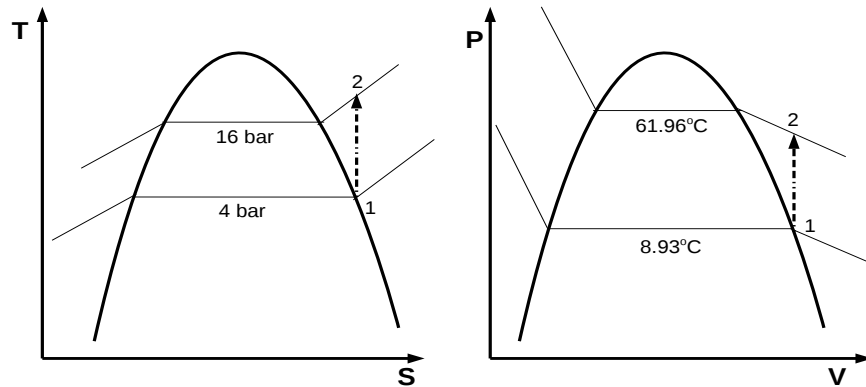
Now, from the First Law:

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

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

Solution:

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[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 $Q_H = 100 \text{ kJ}$, $T_H = 327^\circ \text{C}$ and $Q_C = 40 \text{ kJ}$. The efficiency is given by

$$\eta_T = \frac{W_{\text{cycle}}}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{40 \text{ kJ}}{100 \text{ kJ}} = 0.6 \implies 60\%$$

[4/4]

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

Solution:

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

$$0.6 = 1 - \frac{T_C}{T_H} = 1 - \frac{T_C}{600.15} \implies T_C = 240.06 \text{ K} = -33.09^\circ \text{C}$$

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Q.2 Question 2

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

$$\begin{aligned} \left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V; & \left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_P; \\ \left(\frac{\partial P}{\partial T}\right)_V &= \left(\frac{\partial S}{\partial V}\right)_T; & \left(\frac{\partial V}{\partial T}\right)_P &= -\left(\frac{\partial S}{\partial P}\right)_T \end{aligned}$$

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

$$d\mathbf{f} = \mathbf{M}d\mathbf{a} + \mathbf{N}d\mathbf{b} \quad (1)$$

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

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

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

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

[2/12] The fundamental thermodynamic relations,

$$dU = -PdV + TdS$$

$$dH = Tds + VdP$$

$$dA = -PdV - SdT$$

$$dG = -VdP - SdT$$

[2/12] have similar shape as Eqn. 1, where, for example, in the first relation: $U = f$, $M = -P$, $N = T$, $dV = da$ 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]

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

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- (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 m³.kg⁻¹ through the Redlich-Kwong equation of state,

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

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

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

[3/8]

Now substituting the variables by their values (and with $V=0.4646 \text{ m}^3.\text{kg}^{-1} = 2.5811 \times 10^{-2} \text{ m}^3.\text{kgmol}^{-1}$)

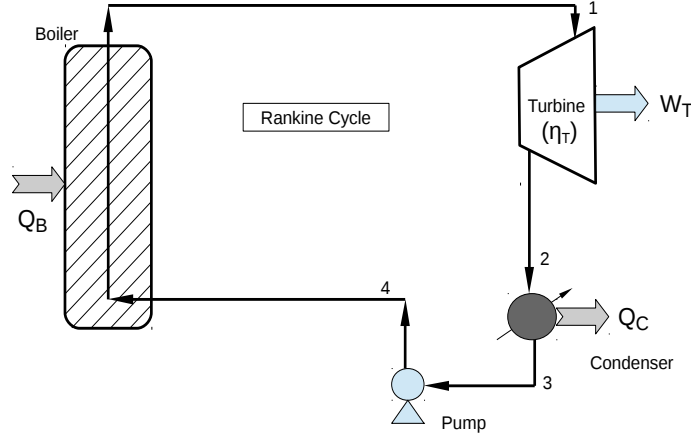
$$\begin{aligned} \left(\frac{\partial P}{\partial T}\right)_V &= \frac{8.314 \frac{\text{kJ}}{\text{kgmol.K}}}{(2.5811 \times 10^{-2} - 0.0211) \frac{\text{m}^3}{\text{kgmol}}} + \\ &\quad \frac{142.59 \text{ bar} \left(\frac{\text{m}^3}{\text{kgmol}}\right)^2 .\text{K}^{1/2}}{2 \times 2.5811 \times 10^{-2} \frac{\text{m}^3}{\text{kgmol}} (2.5811 \times 10^{-2} + 0.0211) \frac{\text{m}^3}{\text{kgmol}} (513.15\text{K})^{3/2}} \\ &= \left(\frac{\partial S}{\partial V}\right)_T = 2271.30 \frac{\text{kJ}}{\text{m}^3.\text{K}} \end{aligned}$$

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Q.3 Question 3

The steam generator of a nuclear power plant produces 25 kg.s^{-1} of water-steam at $P_1 = 140 \text{ bar}$ and $T_1 = 415^\circ\text{C}$. The fluid is used to drive a turbine (isentropic expansion) producing power (W_T) at $P_2 = 2.5 \text{ bar}$. 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 $P_1 = 140 \text{ bar}$, $T_{sat} = 336.75^\circ\text{C} > T_1 = 415^\circ\text{C}$, therefore the fluid is at superheated state. From the superheated steam table (via linear interpolation),

[2/10]

$H_1 = 3054.51 \text{ kJ.kg}^{-1}$ and

[2/10]

$S_1 = 6.0208 \text{ kJ.(kg.K)}^{-1}$.

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

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

[2/10]

With the quality we can then calculate the H_2 ,

$$x_2 = \frac{H_2 - H_f}{H_g - H_f} \Rightarrow H_2 = 2303.50 \frac{\text{kJ}}{\text{kg}}$$

[2/10]

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

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

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

[2/10]

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- (b) Determine the power produced in the turbine (
- W_T
-) in MW.

[2 marks]

Solution:For $\dot{m}_w = 25 \text{ kg.s}^{-1}$,

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

[2/2]

- (c) Determine the heat extracted from the steam (
- Q_C
-) in MW.

[2 marks]

Solution:

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

[2/2]

- (d) Determine the heat supplied by the boiler (
- Q_B
-) in MW.

[2 marks]

Solution:

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

[2/2]

- (e) Calculate the efficiency of the cycle (
- $\eta_{\text{cycle}} = \frac{W_T}{Q_B}$
-).

[2 marks]

Solution:

$$\eta_{\text{cycle}} = \frac{W_T}{Q_B} = 0.30 \implies 30\%$$

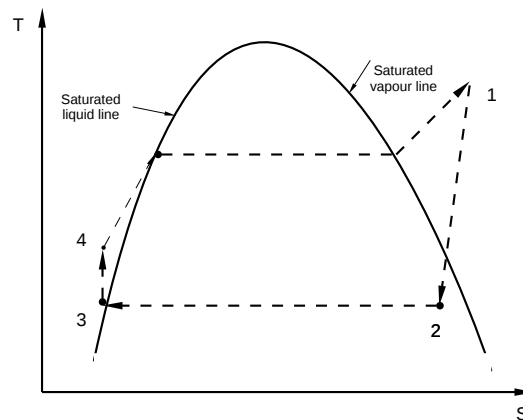
[2/2]

- (f) Sketch the temperature
- \times
- 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,

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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.

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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,

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

where ΔV is expressed in $\text{cm}^3 \cdot \text{gmol}^{-1}$. At these temperature and pressure conditions, $V_1 = 110$ and $V_2 = 90 \text{ cm}^3 \cdot \text{gmol}^{-1}$. 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,

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

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

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

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

$$\bar{V}_1 = V + x_2 \frac{dV}{dx_1} = 124.76 \frac{\text{cm}^3}{\text{gmol}}$$

[3/20] and

$$\bar{V}_2 = V - x_1 \frac{dV}{dx_1} = 93.36 \frac{\text{cm}^3}{\text{gmol}}$$

[3/20] where

$$\begin{aligned} V &= V^E + \sum_{i=1}^n x_i V_i = x_1 x_2 (45x_1 + 25x_2) + x_1 V_1 + x_2 V_2 \\ &= x_1 (1 - x_1) [45x_1 + 25(1 - x_1)] + x_1 V_1 + (1 - x_1) V_2 \end{aligned}$$

and

$$\frac{dV}{dx_1} = 25 - 10x_1 - 60x_1^2 + (V_1 - V_2)$$

[4/20]

We can verify the solution through

$$V = x_1 \bar{V}_1 + x_2 \bar{V}_2 = 105.92 \frac{\text{cm}^3}{\text{gmol}}$$

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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 $P_2^{\text{sat}} = 0.10$ 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,

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

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

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

[5/10] and $y_1 = \frac{\mathcal{H}_1 x_1}{P} = 0.9$.

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

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

Assuming that $y_i P = x_i \gamma_i P_i^{\text{sat}}$ (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:

[3/6] With $x_A = 0.65$ and $x_B = 0.35$, we can calculate the activity coefficients, γ_A γ_B and apply in $P = x_A \gamma_A P_A^{\text{sat}} + x_B \gamma_B P_B^{\text{sat}}$ leading to $P = 1.671$ bar. The vapour

[3/6] mole fraction is obtained from $y_A = \frac{x_A \gamma_A P_A^{\text{sat}}}{P}$, leading to $y_A = 0.6013$.

- (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

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

[1/4] The overall vapour mole fraction V , varies from 0 to 1, $0 \leq V \leq 1$, therefore

[2/4] (replacing in the equation above) $0.6013 \leq z_A \leq 0.65$.

- Generic cubic equation of state:

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

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

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

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

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

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: $X_i = X_{i-1} - \frac{\mathcal{F}(X_{i-1})}{d\mathcal{F}/dX(X_{i-1})}$
- Fundamental thermodynamic equations:

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

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

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

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

- Polytropic Relations:

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

- Raoult's Law:

$$y_i P = x_i P_i^{\text{sat}} \quad \text{and} \quad y_i P = x_i \gamma_i P_i^{\text{sat}} \quad \text{with } i = 1, 2, \dots, N$$

- Henry's Law:

$$x_i \mathcal{H}_i = y_i P \quad \text{with } i = 1, 2, \dots, N$$

- Antoine Equation:

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

- Solutions:

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