

Q.1 Question 1

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

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

(i) Calculate V_2 (in m^3). [3 marks]

Solution:

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

$$P_1 V_1 = P_3 V_3 \implies V_3 = \frac{P_1 V_1}{P_3} = 0.022 \text{ m}^3 = V_2$$

[3/3]

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

Solution:

Process 1–2:

$$W_{1-2} = \int_{V_1}^{V_2} P dV = P (V_2 - V_1) = -6072 \text{ J} \Rightarrow -6.072 \text{ kJ}$$

[2/6]

Process 2–3: $V_2=V_3 \implies W_{2-3} = 0$

[2/6]

Process 3–1: $PV = C$

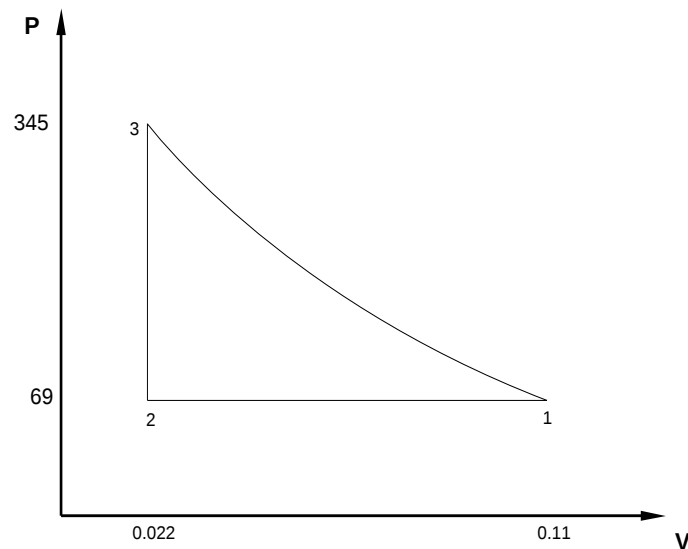
$$W_{31} = \int_{V_3}^{V_1} P dV = \int_{V_3}^{V_1} \frac{C}{V} dV = P_1 V_1 \ln \frac{V_1}{V_3} = 12220 \text{ J} \Rightarrow 12.22 \text{ kJ}$$

[2/6]

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

Solution:

[4/4]



- (b) Calculate the fugacity of steam at 300°C and 80 bar. For your calculations, you should use $h = 2785$ kJ/kg, $s = 5.791$ kJ/(kg.K) for steam at 300°C and 80 bar. Specific enthalpy and entropy of ideal gas at 300°C and 0.1 bar are $h^{IG} = 3077$ kJ/kg and $s^{IG} = 9.281$ kJ/(kg.K), respectively. Given,

$$d\mu = dG = RT d(\ln f).$$

Also, molar mass of water is 18 g/mol.

[7 marks]

Solution:

We can integrate this equation from low pressure so that fugacity is similar to pressure and the system can be considered an ideal gas,

[2/7]

$$\int_{G^{IG}}^G dG = RT \int_P^f d(\ln f) \Rightarrow f = P \exp\left(\frac{G - G^{IG}}{RT}\right)$$

[1/7]

The specific gibbs free energy of ideal gas (at low pressure, e.g., 0.1 bar)

$$g^{IG} = h^{IG} - Ts^{IG} = -2242.41 \text{ kJ/kg} \Rightarrow G^{IG} = -40.36 \text{ kJ/mol}$$

[1/7]

Now at 300°C and 80 bar,

$$g = h - Ts = -534.11 \text{ kJ/kg} \Rightarrow G = -9.61 \text{ kJ/mol}$$

[3/7]

Now calculating the fugacity,

$$f = P \exp\left(\frac{G - G^{IG}}{RT}\right) = 63.47 \text{ bar}$$

Total Question Marks:20

Q.2 Question 2

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

(i) ideal gas

[4 marks]

Solution:

Ideal gas: $V = \frac{RT}{P}$,

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

[2/4]

Now deriving β and κ ,

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

[2/4]

- (ii) $V = \frac{RT}{P} + b$

[4 marks]

Solution:

The derivatives are,

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

[2/4]

Now deriving β and κ ,

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

[2/4]

- (b) Calculate the compressibility factor (Z) and molar volume of sulphur dioxide (SO_2) vapour at 300 K and 4 bar using the Redlich-Kwong equation of state. Properties of SO_2 are: $T_c = 430$ K, $P_c = 78.7$ bar and $\omega = 0.251$ (acentric factor). In your iterative calculations, use $Z_0 = 1$ as initial guess of Z , and stop at the second iteration (Z_2). [12 marks]

Solution:

The generic form of Z is,

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

[2/12]

For SRK with $T_r = 0.8380$, $P_r = 0.3754$, $\beta = 3.88 \times 10^{-2}$ and $q = 6.7274$,

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

[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]

$$Z_2 = \mathbf{0.7160}$$

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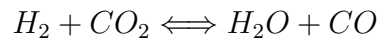
[8/12]

$$\text{or (using calculator) } Z_{22} = \mathbf{0.7088}$$

Total Question Marks:20

Q.3 Question 3

- (a) Assuming that all species and their mixtures are ideal gases, derive an equation for the Gibbs energy as a function of the reaction coordinate for the reaction below at 1000K.



Calculate the reaction coordinate, ϵ , in the equilibrium. Given ΔG_f° (J.gmol⁻¹) at 1000K: (a) H₂O: -192420, (b) CO: -200240 and (c) CO₂: -395790. [13 marks]

Solution:

[1/13] *The Gibbs energy can be expressed as*

$$G = \sum y_i G_i + RT \sum y_i \ln y_i$$

$$G = \sum y_i \Delta G_{f,i}^\circ + RT \sum y_i \ln y_i$$

We can differentiate the total Gibbs energy as,

$$dG^t = d(nG) = n \frac{dG}{d\epsilon} + G \frac{dn}{d\epsilon}$$

[1/13] *Assuming the system is closed and in equilibrium: $dn = 0$ and $\frac{dG}{d\epsilon} = 0$. For 1 mole of H₂ and CO₂, the mole fraction of the gaseous species are*

$$y_{H_2} = \frac{1-\epsilon}{2} = y_{CO_2} \quad \text{and} \quad y_{H_2O} = \frac{\epsilon}{2} = y_{CO}$$

[5/13] *Thus,*

$$G = (y_{H_2} \Delta G_{f,H_2}^\circ + y_{CO_2} \Delta G_{f,CO_2}^\circ + y_{H_2O} \Delta G_{f,H_2O}^\circ + y_{CO} \Delta G_{f,CO}^\circ) +$$

$$RT (y_{H_2} \ln y_{H_2} + y_{CO_2} \ln y_{CO_2} + y_{H_2O} \ln y_{H_2O} + y_{CO} \ln y_{CO})$$

$$= \left[\frac{1-\epsilon}{2} \Delta G_{f,CO_2}^\circ + \frac{\epsilon}{2} (\Delta G_{f,H_2O}^\circ + \Delta G_{f,CO}^\circ) \right] + RT \left[(1-\epsilon) \ln \frac{1-\epsilon}{2} + \epsilon \ln \frac{\epsilon}{2} \right]$$

[1/13] *for $\Delta G_{f,H_2}^\circ = 0$. In the equilibrium $\frac{dG}{d\epsilon} = 0$, therefore*

[5/13]
$$\frac{dG}{d\epsilon} = B - A + RT \left[\ln \frac{\epsilon}{2} - \ln \frac{1-\epsilon}{2} \right] = 0 \implies \epsilon = 0.4531$$

with $A = \frac{-395790}{2}$ and $B = \frac{-192420 - 200240}{2}$.

- (b) Saturated ammonia (NH₃) vapour at $P_1 = 200$ kPa is compressed by a piston to $P_2 = 1.6$ MPa in a reversible adiabatic process. Calculate the work done per unit mass. [7 marks]

Solution:

[2/7] *At 200 kPa (2 bar), from the saturated tables:*

$$v_1 = 0.5946 \text{ m}^3/\text{kg} \quad T_1 = -18.86^\circ\text{C}$$

$$s_1 = 5.5969 \text{ kJ}/(\text{kg}\cdot\text{K}) \quad u_1 = 1300.39 \text{ kJ}/\text{kg}$$

Reversible and adiabatic compression implied in isentropic process, therefore $s_2 = s_1$. At $P_2 = 1.6 \text{ MPa} = 16 \text{ bar}$, the specific entropy of saturated ammonia vapour is $4.8542 \text{ kJ}/(\text{kg}\cdot\text{K})$, which is smaller than s_1 , indicating that the fluid is at superheated state. With P_2 and s_2 , in the superheated fluid table we can obtain (through linear interpolation),

[2/7]

$$v_2 = 0.1180 \text{ m}^3/\text{kg} \quad T_2 = 135.16^\circ\text{C}$$

$$s_2 = 5.5969 \text{ kJ}/(\text{kg}\cdot\text{K}) \quad u_2 = 1546.50 \text{ kJ}/\text{kg}$$

[3/7]

From the First Law,

$$\Delta u = q + w \text{ with } q = 0 \text{ because the process is adiabatic}$$

$$w = u_2 - u_1 = 246.11 \text{ kJ}/\text{kg} \text{ (positive because work is given to the system).}$$

Total Question Marks:20

Q.4 Question 4

Estimate the bubble and dew point temperatures of a 25 mol-% n-pentane (nC_5), 45 mol-% n-hexane (nC_6) and 30 mol-% n-heptane (nC_7) mixture at 1.013 bar. Also calculate the compositions at dew and bubble points. [20 marks]

Solution:

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For This problem, use

$$\ln P_i^{\text{sat}} = A_i - \frac{B_i}{RT}$$

with [P] = bar and [T] = K, and

$$\begin{array}{lll} A_{nC_5} = 10.422 & A_{nC_6} = 10.456 & A_{nC_7} = 11.431 \\ B_{nC_5} = 26799 & B_{nC_6} = 29676 & B_{nC_7} = 35200 \end{array}$$

If you are using an iterative method to solve this problem, do stop at the 5th iteration.

Solution:

[2/20] *For the bubble point, we need to solve*

$$\sum_{i=1}^3 y_i = 1 = \frac{x_{C5} P_{C5}^{\text{sat}}}{P} + \frac{x_{C6} P_{C6}^{\text{sat}}}{P} + \frac{x_{C7} P_{C7}^{\text{sat}}}{P}$$

for T, with

$$\ln P_i^{\text{sat}} = A_i - \frac{B_i}{RT}.$$

[5/20] *Leading to $T = 334.94 \text{ K}$ (at the 5th iteration) with composition $y = [0.5483 \ 0.0883 \ 0.3634]$*
 [3/20] *for n-pentane, n-hexane and n-heptane, respectively. .*

[2/20] *For the dew point, we need to solve*

$$\sum_{i=1}^3 x_i = 1 = \frac{y_{C5} P}{P_{C5}^{\text{sat}}} + \frac{y_{C6} P}{P_{C6}^{\text{sat}}} + \frac{y_{C7} P}{P_{C7}^{\text{sat}}}$$

[5/20] *for T, leading to $T = 350.58 \text{ K}$ (at the 5th iteration) with composition $x = [0.0742 \ 0.3463 \ 0.5795]$.*

[3/20]

Total Question Marks:20

Q.5 Question 5

- (a) What is the change in entropy when 700 litres of CO₂ and 300 litres of N₂, each at 1 bar and 25°C blend to form a gas mixture at the same conditions? Assume ideal gases, and given

$$\Delta S = -nR \sum_{i=1}^n y_i \ln y_i,$$

where S , n and y are entropy, number of moles and mole fraction, respectively.
[10 marks]

Solution:**[2/10]**

For CO₂ (1) and N₂ (2) at 1 bar and 25°C with ideal gas behaviour, mole fraction (x_i) = volume fraction (y_i) as,

$$x_i = \frac{n_i}{n}, \text{ and } y_i = \frac{V_i}{V}$$

$$x_i = \frac{n_i}{n} = \frac{PV_i/(RT)}{PV/(RT)} = \frac{V_i}{V}$$

[2/10]

Therefore,

$$y_1 = 0.7 \implies V_1^t = 0.7 \text{ cm}^3$$

$$y_2 = 0.3 \implies V_2^t = 0.3 \text{ cm}^3$$

[2/10]

At $P = 1 \text{ bar}$ and $T = 298.15 \text{ K}$, the number of moles, n , is

$$n = \frac{P}{RT} \sum V_i^t = 40.34 \text{ moles}$$

[4/10]

The entropy change is

$$\Delta S = -nR \sum_{i=1}^n y_i \ln y_i = 204.88 \text{ J/K}$$

- (b) Calculate the bubble point pressure and vapour composition for a liquid mixture of 41.2 mol-% of ethanol (1) and n-hexane (2) at 331 K. Given,

$$\ln \gamma_1 = \frac{A}{\left(1 + \frac{Ax_1}{Bx_2}\right)^2}, \quad \ln \gamma_2 = \frac{A}{\left(1 + \frac{Bx_2}{Ax_1}\right)^2}$$

$$\ln P_1^{\text{sat}} = C_1 + \frac{D_1}{T + E_1}, \quad \ln P_2^{\text{sat}} = C_2 + \frac{D_2}{T + E_2}$$

where $A = 2.409$, $B = 1.970$, $C_1 = 16.1952$, $C_2 = 14.0568$, $D_1 = -3423.53$, $D_2 = -2825.42$, $E_1 = -55.7152$, $E_2 = -42.7089$. $[P] = \text{kPa}$ and $[T] = \text{K}$.
[10 marks]

Solution:

[2/10] *At 331 K, the saturation pressures are $P_1^{sat} = 42.90 \text{ kPa}$ and $P_2^{sat} = 7054 \text{ kPa}$.*

[2/10] *The liquid solution with $x_1 = 0.412$ and $x_2 = 0.588$ results in the following activity coefficient $\gamma_1 = 2.011$ and $\gamma_2 = 1.521$.*

[2/10] *The partial pressure of ethanol and n-hexane are,*

$$P_1 = x_1 \gamma_1 P_1^{sat} = 35.55 \text{ kPa}$$

$$P_2 = x_2 \gamma_2 P_2^{sat} = 63.09 \text{ kPa}$$

[2/10] *The bubble pressure is*

$$P = P_1 + P_2 = 98.64 \text{ kPa}$$

[2/10] *And the composition of the vapour phase is*

$$y_1 = \frac{P_1}{P} = 0.360 \quad \text{and} \quad y_2 = 0.640$$

Total Question Marks:20