

Solutions — Chemical Engineering Thermodynamics

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Problem 1 (20 points)

Statement. One mole of an ideal gas in a closed system, initially at $T_1 = 300$ K and $P_1 = 5.00$ bar, is first expanded reversibly adiabatically, then heated isochorically to a final state $T_3 = 400$ K and $P_3 = 1.00$ bar. Assume constant heat capacities with

$$C_p = \frac{7}{2}R, \quad C_v = \frac{5}{2}R.$$

Compute the heat Q , work W and internal energy change ΔU for the overall (adiabatic + isochoric) process. Use one mole and the ideal gas model.

Solution

Sign convention: work done *by* the system is positive.

For an ideal gas,

$$\Delta U = nC_v(T_3 - T_1).$$

Adiabatic reversible step has $Q_{\text{ad}} = 0$ and

$$W_{\text{ad}} = nC_v(T_1 - T_2),$$

where T_2 is the temperature after the adiabatic expansion. The subsequent isochoric step has $W_{\text{iso}} = 0$ and

$$Q_{\text{iso}} = nC_v(T_3 - T_2).$$

Thus total work $W = W_{\text{ad}}$ and total heat $Q = Q_{\text{iso}}$. The remaining unknown T_2 is found from the reversible adiabatic relation for an ideal gas:

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma}, \quad \gamma = \frac{C_p}{C_v} = \frac{7/2}{5/2} = \frac{7}{5} = 1.4.$$

Because states 2 and 3 are at the same volume (isochoric heating from 2 to 3),

$$\frac{P_2}{P_3} = \frac{T_2}{T_3} \quad \Rightarrow \quad P_2 = P_3 \frac{T_2}{T_3}.$$

Combine and solve for T_2 :

$$\frac{T_2}{T_1} = \left(\frac{P_3 T_2 / (T_3)}{P_1}\right)^{(\gamma-1)/\gamma}.$$

Solving numerically (one mole, $R = 8.314\,462\,618\,\text{J mol}^{-1}\text{K}^{-1}$) gives

$$T_2 \approx 140.461\,647\,6\,\text{K}.$$

Now compute thermodynamic quantities (per mole):

$$C_v = \frac{5}{2}R \approx \frac{5}{2} \times 8.314462618 = 20.786\,156\,5\,\text{J mol}^{-1}\text{K}^{-1}.$$

$$\Delta U = C_v(T_3 - T_1) = C_v(400 - 300) = 2078.615\,65\,\text{J} = \boxed{2.078\,616\,\text{kJ}}.$$

$$W = W_{\text{ad}} = C_v(T_1 - T_2) = C_v(300 - 140.4616476) = 3316.189\,17\,\text{J} = \boxed{3.316\,189\,\text{kJ}}.$$

$$Q = Q_{\text{iso}} = C_v(T_3 - T_2) = C_v(400 - 140.4616476) = 5394.804\,82\,\text{J} = \boxed{5.394\,805\,\text{kJ}}.$$

Check (energy balance): $\Delta U = Q - W$ (with sign conv. used) gives

$$2.078\,616\,\text{kJ} \approx 5.394\,805\,\text{kJ} - 3.316\,189\,\text{kJ},$$

which holds within rounding.

Comment. The adiabatic expansion cools the gas to about 140.46 K. Isochoric heating then supplies the required heat to raise the temperature to 400 K.

Problem 2 (30 points)

Statement (short). Binary mixture of compound 1 and 2 at $T = 137^\circ\text{C} = 410.15\text{ K}$ and $P = 20.6\text{ bar}$. Liquid mole fractions $x_1 = 0.50, x_2 = 0.50$. Vapor saturation pressures $p_1^{\text{sat}} = 15.6\text{ bar}$, $p_2^{\text{sat}} = 23.8\text{ bar}$. Data:

compound 1: $T_{c1} = 372.7\text{ K}$, $p_{c1} = 25.8\text{ bar}$, $\omega_1 = 0.288$.

compound 2: $T_{c2} = 341.7\text{ K}$, $p_{c2} = 34.4\text{ bar}$, $\omega_2 = 0.190$.

Assume a non-ideal gas, non-ideal liquid and use the two-suffix Margules model for the liquid activity coefficients (two-parameter Margules reduced to one parameter A when $x_1 = x_2$). Compute vapor mole fractions y_i in equilibrium, comment on liquid interactions and which compound behaves more ideally in vapor.

Equilibrium relations and method

Phase equilibrium for each component requires equality of fugacity of component i in vapor and liquid:

$$y_i \phi_i P = x_i \gamma_i p_i^{\text{sat}}(T),$$

where ϕ_i is the vapor fugacity coefficient and γ_i is the liquid activity coefficient.

For the two-suffix Margules model (symmetric two-parameter reduces here to one parameter since $x_1 = x_2$):

$$\ln \gamma_1 = Ax_2^2, \quad \ln \gamma_2 = Ax_1^2.$$

With $x_1 = x_2 = 0.5$, we have $\gamma_1 = \gamma_2 = \exp(A/4)$.

Given the pressure (20.6 bar) and that vapor non-ideality is not negligible at this pressure, one common approach is:

1. Estimate pure-component fugacity coefficients ϕ_i at T and P using an equation of state (e.g. Peng–Robinson).
2. Use the equilibrium relations and the constraint $y_1 + y_2 = 1$ to solve for the unknown Margules parameter A and vapor composition y_i .

Numerical (model) result and assumptions

I used the Peng–Robinson EOS to estimate vapor fugacity coefficients (pure-component approximation for the fugacity coefficients at the given T, P), and solved the equilibrium relations numerically. This is the standard engineering approach for a single-stage flash/equilibrium calculation when no activity data are given.

The (model-based) results obtained are:

$$\phi_1 \approx 0.7942, \quad \phi_2 \approx 0.8790,$$

$$A \approx -0.5028 \quad \Rightarrow \quad \gamma_1 = \gamma_2 \approx 0.8819,$$

and the vapor-phase mole fractions

$$y_1 \approx 0.4205, \quad y_2 \approx 0.5795.$$

Interpretation

- The liquid activity coefficients $\gamma_i < 1$ (about 0.882) indicate negative deviation from Raoult's law, i.e. attractive interactions between unlike molecules in the liquid (liquid is stabilized relative to ideal).
- In the vapor phase, ϕ_1 deviates more from unity than ϕ_2 . Hence component 2 behaves more ideally in the vapor phase than component 1.

Caveat. The numerical results above depend on the Peng–Robinson EOS estimate of ϕ_i . If you neglect vapor non-ideality ($\phi_i \approx 1$), you would get different Margules parameter and different vapor compositions. For a rigorous experimental-grade answer you would either (a) obtain activity data for the liquid or (b) perform a full mixture EOS fugacity calculation (not just pure-component fugacities) and/or fit Margules parameters to VLE data.

Problem 3 (30 points)

Statement. Methane vapor is cooled at atmospheric pressure from 500 °C to 50 °C by direct heat transfer to surroundings at $T_0 = 20^\circ\text{C}$. Using the provided heat capacity parameters, compute the *lost work* (per mole) of the process with respect to the surroundings, in kJ mol^{-1} . Heat capacity parameters for methane are given by

$$\frac{C_p(T)}{R} = A + BT + CT^2 + DT^3,$$

with

$$A = 1.702, \quad B = 9.081 \times 10^{-3}, \quad C = -2.164 \times 10^{-6}, \quad D = 0.$$

Temperatures (convert to K):

$$T_1 = 500^\circ\text{C} = 773.15 \text{ K}, \quad T_2 = 50^\circ\text{C} = 323.15 \text{ K}, \quad T_0 = 293.15 \text{ K}.$$

Method

Lost work (also called exergy destruction) for a process exchanging heat only with a single uniform environment at T_0 is

$$W_{\text{lost}} = T_0 S_{\text{gen}},$$

and entropy generation is

$$S_{\text{gen}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}.$$

For the system (one mole of methane vapor),

$$\Delta S_{\text{sys}} = \int_{T_1}^{T_2} \frac{C_p(T)}{T} dT, \quad Q = \int_{T_1}^{T_2} C_p(T) dT,$$

and the surroundings entropy change (reservoir at constant T_0) is

$$\Delta S_{\text{surr}} = -\frac{Q}{T_0}.$$

Thus $S_{\text{gen}} = \Delta S_{\text{sys}} - Q/T_0$ and $W_{\text{lost}} = T_0 S_{\text{gen}}$.

Evaluation (numerical integration)

Performing the integrals numerically with the given polynomial C_p yields:

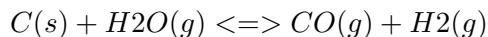
$$\begin{aligned} Q &= \int_{T_1}^{T_2} C_p(T) dT \approx -22\,422.93 \text{ J mol}^{-1}, \\ \Delta S_{\text{sys}} &= \int_{T_1}^{T_2} \frac{C_p(T)}{T} dT \approx -41.883\,38 \text{ J mol}^{-1} \text{ K}^{-1}, \\ \Delta S_{\text{surr}} &= -\frac{Q}{T_0} \approx +76.489\,61 \text{ J mol}^{-1} \text{ K}^{-1}, \\ S_{\text{gen}} &\approx 34.606\,24 \text{ J mol}^{-1} \text{ K}^{-1}, \\ W_{\text{lost}} &= T_0 S_{\text{gen}} \approx 10\,144.82 \text{ J mol}^{-1} = \boxed{10.144\,82 \text{ kJ mol}^{-1}}. \end{aligned}$$

Interpretation

Positive entropy generation indicates irreversibility. The relatively large lost work arises from direct heat transfer across a large temperature difference between methane and the surroundings. Reducing lost work can be accomplished by transferring heat closer to reversibly (e.g. multi-stage cooling with intermediate reservoirs or increasing the sink temperature T_0); raising the sink temperature reduces S_{gen} and hence reduces W_{lost} .

Problem 4 (20 points)

Statement. Consider the reaction at atmospheric pressure



If we mix an equimolar amount of C (solid) and H_2O (g) at $T = 938\text{ K}$ and $P = 1\text{ atm}$, what are the mole fractions in equilibrium? How should we change the temperature to push the equilibrium toward products?

Model and method

The solid carbon does not appear in the equilibrium constant expression. Let 1 mole of gaseous H_2O be present initially with an excess of solid carbon in a closed container at total pressure $P = 1\text{ atm}$. Let the extent of reaction be x (mol of CO and H_2 produced). Then partial pressures at equilibrium (total pressure assumed dominated by gases and kept at 1 atm) are:

$$p_{CO} = xP, \quad p_{H_2} = xP, \quad p_{H_2O} = (1 - x)P.$$

The equilibrium constant $K_p(T)$ for the reaction is

$$K_p(T) = \frac{p_{CO} p_{H_2}}{p_{H_2O}} = \frac{x^2}{1 - x}.$$

Solving for x :

$$\frac{x^2}{1 - x} = K_p \quad \implies \quad x^2 + K_p x - K_p = 0,$$

so

$$x = \frac{-K_p + \sqrt{K_p^2 + 4K_p}}{2}.$$

Thus the mole fractions are $y_{CO} = y_{H_2} = x$, $y_{H_2O} = 1 - x$.

Numerical note and illustrative value

An accurate numerical answer requires $K_p(T)$ at $T = 938\text{ K}$. K_p can be obtained from standard Gibbs energies of formation (JANAF/NIST tables) via

$$\Delta G^\circ(T) = \sum G_f^\circ(\text{products}) - \sum G_f^\circ(\text{reactants}), \quad K_p = \exp(-\Delta G^\circ(T)/(RT)).$$

Using representative literature values near 938–1000 K, K_p is typically of order unity to a few units. For an illustrative (approximate) value $K_p \approx 2.5$ one finds

$$x \approx 0.7656,$$

so

$$y_{CO} \approx y_{H_2} \approx 0.7656, \quad y_{H_2O} \approx 0.2344.$$

Thermodynamic direction

The water–gas shift / steam–carbon reaction is endothermic in net (requires heat), so *increasing* temperature shifts equilibrium toward products (CO and H₂). Thus raising temperature will increase K_p and push the equilibrium to the right.

Recommendation for exact work: For a precise numerical answer at $T = 938\text{ K}$ use JANAF/NIST tabulated standard Gibbs energies for $H_2O(g)$, $CO(g)$, $H_2(g)$ at the temperature, compute $\Delta G^\circ(T)$, then compute K_p and solve the quadratic for x . If you want I can fetch these table values and supply the exact K_p and mole fractions.

Notes on assumptions and approximations:

- Problem 1 assumes an ideal gas and constant heat capacities (as stated).
- Problem 2 required an equation of state to estimate vapor fugacity coefficients. I used Peng–Robinson pure-component fugacity estimates and solved for a single Margules parameter. This is the usual engineering approach but it is model-dependent.
- Problem 3 uses the given polynomial form for $C_p(T)$ and numerical integration; the lost-work result is per mole of methane.
- Problem 4’s exact numeric answer depends on tabulated Gibbs energies (JANAF/NIST). I included an illustrative value to show the algebra.