Chemical Engineering Thermodynamics
Quiz 9
March 14, 2019

In Homework Problem 8.14 an isolated chamber was considered with rigid walls that is divided into two compartments of equal volume with one compartment under a perfect vacuum. Consider a nonideal gas at **10 MPa and 300 K** fills the second compartment. After the partition is ruptured and a long time passes the temperature and pressure are uniform in the two chambers. **Find the final T_f and P_f using an ideal gas at 10 MPa and 300 K as the reference state.**

Equation of State: $Z = 1 - aP/(RT^2)$
a = 20,000 cm^{3}K/mole
Ideal Gas Heat Capacity: $C_p^{ig} = 15R$ (for i.g. $C_v^{ig} = C_p^{ig} - R$)
R = 8.31 J/(K mole)

$$\left(\frac{H-H^{ig}}{RT}\right) = -\int_0^P T\left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \qquad \left(\frac{S-S^{ig}}{R}\right) = -\int_0^P \left[(Z-1) + T\left(\frac{\partial Z}{\partial T}\right)_P\right]\frac{dP}{P}$$

a) Give an energy balance for this problem. (Circle your answer)
b) Derive a formula for the necessary departure function. (Circle your answer)
c) Write an expression for $U^f - U^i$ that can be used in an excel sheet. (Circle your answer)
d) Determine T_f **and** P_f. **(List the steps used in Excel to solve for these values and obtain the values. Give the equations used to determine the two unknowns.)** (Circle the final values.)
e) Explain the need for the departure function. That is, why do we need the departure function to solve this problem?

ANSWERS:
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a) Give an energy balance for this problem.

$\Delta U = 0$ or $U^f = U^i$

b) Derive a formula for the necessary departure function.

U = H – PV (from the thermodynamic square)

$(U\text{-}U^{ig})/(RT) = (H\text{-}H^{ig})/(RT) - Z + 1$

$$\frac{\left(U-U^{ig}\right)}{RT} = -\int_0^P T\left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - Z + 1$$

$$\left(\frac{\partial Z}{\partial T}\right)_P = \frac{2aP}{RT^3}$$

$$\frac{\left(U-U^{ig}\right)}{RT} = -\frac{2aP}{RT^2} - 1 + \frac{aP}{RT^2} + 1 = -\frac{aP}{RT^2}$$

$$\left(U-U^{ig}\right) = -\frac{aP}{T}$$

c) $$U^{T,P} = \int_{300K}^{T} C_V^{ig}\, dT + \left(U-U^{ig}\right)^{T,P}$$

$$U^i = -\frac{aP^i}{T^i} = -667\frac{\text{J}}{\text{mole}}$$

$$U^f = C_V\left(T_f - 300\text{K}\right) - \frac{aP^f}{T^f} = 116\frac{\text{J}}{\text{mole K}}\left(T_f - 300K\right) - \frac{20{,}000\frac{\text{cm}^3\text{ K}}{\text{mole}}P^f}{T^f}$$

$$\left(U^f - U^i\right) = 116\frac{\text{J}}{\text{mole K}}\left(T_f - 300\text{K}\right) - \frac{20{,}000\frac{\text{cm}^3\text{ K}}{\text{mole}}P^f}{T^f} + 667\frac{\text{J}}{\text{mole}} = 0 \quad (1)$$

d) Determine $\boldsymbol{T_f}$ **and** $\boldsymbol{P_f}$

Make 4 cells in Excel, T^f, P^f, Equation (1) and the EOS (2), below

$$V^i = \frac{RT^i}{P^i} - \frac{a}{T^i} = \frac{8.31\frac{\text{cm}^3\text{MPa}}{\text{mole K}}300\text{K}}{10\text{MPa}} - \frac{20{,}000\frac{\text{cm}^3\text{ K}}{\text{mole}}}{300\text{K}} = 182\frac{\text{cm}^3}{\text{mole}}$$

$$V^f = 2V^i = 365\frac{\text{cm}^3}{\text{mole}}$$

$$0 = RT^f - \frac{aP^f}{T^f} - P^f V^f$$

$$0 = 8.31\frac{\text{cm}^3\text{MPa}}{\text{mole K}}T^f - \frac{20{,}000\frac{\text{cm}^3\text{ K}}{\text{mole}}P^f}{T^f} - P^f 365\frac{\text{cm}^3}{\text{mole}} \qquad (2)$$

Use solver varying T^f and P^f to obtain 0 for the two equations.

T^f = 297 K and P^f = 5.72 MPa

e) Explain the need for the departure function. That is, why do we need the departure function to solve this problem?

C_p is only available for the ideal gas state and C_v can only be easily calculated from C_p in the ideal gas state, $C_v^{ig} = C_p^{ig} - R$. So we need to do temperature and pressure changes in the ideal gas state.