Results of Midterm 2

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Problem 1 (heat engine)

Given 1 kg of water at 100°C and a very large block of ice at 0°C. A reversible heat engine absorbs heat from the water and expels heat to the ice until work can no longer be extracted from the system. The heat capacity of water is 4.2 J/g·K. At the completion of the process:

a) What is the temperature of the water?

b) How much heat has been absorbed by the block of ice in the process?

c) How much ice has been melted (the heat of fusion of ice is 333 J/g)?

d) How much work has been done by the engine?

(a) Because the block of ice is very large, we can assume its temperature to be constant. In the process the temperature of water gradually decreases. When work can no longer be extracted from the system, the efficiency of the cycle is zero:

\[ e = 1 - T_{ice}/T_{water} = 0 \quad \rightarrow \quad T_{water} = T_{ice} = 0^0 C \]

(b) The heat absorbed by the block of ice is

\[ Q_C = \int_{T_i}^{T_f} [1 - e(T)] m_{water}c_{water}dT = m_{water}c_{water} \int_{273}^{373} \frac{273}{T}dT = 1 \text{ kg} \times 4.2 \text{ kJ/kg} \times 273 \text{ K} \times \ln \left( \frac{373}{273} \right) = 357.9 \text{ kJ} \]

(c) The amount of melted ice:

\[ M_{ice} = \frac{Q_C}{L} = \frac{357.9 \text{ kJ}}{333 \text{ J/g}} = 1.07 \text{ kg} \]

(d) The work:

\[ W = Q_H - Q_C = 1 \text{ kg} \times 4.2 \text{ kJ/kg} \cdot \text{K} \times 100 \text{ K} - 357.9 \text{ kJ} = 62.1 \text{ kJ} \]
Problem 2 (vapor equation)

1. For Hydrogen (H₂) near its triple point \(T_{tr}=14\) K, the latent heat of vaporization \(L_{vap}=1.01\) kJ/mol. The liquid density is 71 kg·m⁻³, the solid density is 81 kg·m⁻³, and the melting temperature is given by \(T_{m}=13.99+P/3.3\), where \(T_{m}\) and \(P\) measured in K and MPa respectively. Compute the latent heat of sublimation.

2. The vapor pressure equation for H₂: \(P = P_0 \exp\left( -\frac{L_{vap}}{RT} \right)\) where \(P_0 = 90\) MPa.

Compute the slope of the vapor pressure curve \((dP/dT)\) for the solid H₂ near the triple point, assuming that the H₂ vapor can be treated as an ideal gas.

1. Near the triple point:

\[
L_{melt} = \frac{T_{tr}(V_L - V_S)}{dP} = \frac{14 \times \left( \left( \frac{2 \times 10^{-3}}{71} \right) - \left( \frac{2 \times 10^{-3}}{81} \right) \right)}{1/3.3 \times 10^6} \approx 162\ \text{J}
\]

\[
L_{vap} = T_{tr} \left( S_G - S_L \right) \quad L_{melt} = T_{tr} \left( S_L - S_S \right) \quad L_{sub} = T_{tr} \left( S_G - S_S \right)
\]

\[
L_{sub} = T_{tr} \left( S_G - S_S \right) = L_{vap} + L_{melt} = \left( 1010 + 162 \right) \text{J/mol} = 1172\ \text{J/mol}
\]
Problem 2 (cont.)

2. At the solid-gas phase boundary:

\[
\frac{dP}{dT} = \frac{L_{\text{sub}}}{T_{\text{tr}}(V_{G} - V_{L})} \approx \frac{L_{\text{sub}}}{T_{\text{tr}}V_{G}}
\]

Assuming that the H₂ vapor can be treated as an ideal gas

\[
P_{\text{tr}}V_{G} = RT_{\text{tr}}
\]

\[
V_{G} = \frac{RT_{\text{tr}}}{P_{\text{tr}}} = \frac{P_{0}\exp(-L_{\text{vap}}/RT_{\text{tr}})}{9 \times 10^{-7} \text{ Pa} \times \exp(-1010 J/(8.3 J/K \cdot \text{mol} \times 14 K)}
\]

\[
= 7.69 \times 10^{-3} \text{ m}^3 / \text{mol}
\]

\[
dP = \frac{L_{\text{sub}}}{T_{\text{tr}}V_{G}} = \frac{1172 J/\text{mol}}{14 K \times 7.69 \times 10^{-3} \text{ m}^3 / \text{mol}} = 1.09 \times 10^{4} \text{ Pa/K}
\]
One mole of Nitrogen ($N_2$) has been compressed at $T_0 = 273$ K to the volume $V_0 = 1$ liter in an adiabatically insulated container. The critical parameters for $N_2$ are: $V_C = 3Nb = 0.12$ liter/mol, $T_C = (8/27)(a/k_b)b = 126$ K. The gas goes through the free expansion process ($Q = 0$, $W = 0$, and, thus, $\Delta U = 0$), in which the pressure drops down to the atmospheric pressure $P_{atm} = 1$ bar. Assume that the gas obeys the van der Waals equation of state in the compressed state, and that it behaves as an ideal gas at the atmospheric pressure.

(a) Find the change in the gas temperature.

(b) Find the change in the gas entropy (the entropy of one mole of the vdW gas is)

$$S_{vdW} = \frac{f}{2} R \ln T + R \ln(V - Nb) + f(N, m)$$

(a) The internal energy of the gas is conserved in this process ($Q = 0$ and $W = 0$). For 1 mole of the “vdW” Nitrogen (diatomic gas)

$$U_{vdW} = U_{ideal} - \frac{N^2a}{V} = \frac{5}{2} RT - \frac{N^2a}{V}$$

Thus,

$$\frac{5}{2} RT_0 - \frac{N^2a}{V_0} = \frac{5}{2} RT_f$$

$$T_f = T_0 - \frac{2 N^2a}{5 RV_0}$$

In terms of the critical parameters:

$$V_C = 3Nb \quad k_bT_C = \frac{8}{27} \frac{a}{b} \quad a = \frac{27}{8} k_bT_C \frac{V_C}{3N} \quad N^2a = \frac{9}{8} RT_C V_C$$

$$T_f = T_0 - \frac{9}{20} \frac{T_C V_C}{V_0} = 273 K - \frac{9}{20} \frac{126 \text{ K} \times 0.12 \text{ liter}}{1 \text{ liter}} = 266.2 \text{ K}$$
Problem 3 (vdW) (cont.)

(b) \[ S_{vdW} = \frac{f}{2} R \ln T + R \ln (V - Nb) + f(N, m) \]

\[ \Delta S = \frac{5}{2} R \ln \frac{T_f}{T_0} + R \ln \left( \frac{V_f}{V_0 -Nb} \right) = \frac{5}{2} R \ln \frac{T_f}{T_0} + R \ln \left( \frac{V_f}{V_0 -V_c/3} \right) \]

\[ T_f = T_0 - \frac{9}{20} \frac{T_c V_c}{V_0} = 266.2 \text{ K} \quad V_f = \frac{R T_f}{P_{atm}} = 2.2 \cdot 10^{-2} \text{ m}^3 \]

\[ \Delta S = \frac{5}{2} R \ln \frac{266.2}{273} + R \ln \left( \frac{2.2 \cdot 10^{-2}}{1 \cdot 10^{-3} - 0.04 \cdot 10^{-3}} \right) = -5.24 \cdot 10^{-1} + 26 \approx 25.5 \text{ J/K} \]
Problem 4 (phase transformations)

10 kg of water at 20\(^{0}\)C is converted to ice at -10\(^{0}\)C by being put in contact with a reservoir at -10\(^{0}\)C. This process takes place at constant pressure and the heat capacities at constant pressure of water and ice are 4180 and 2090 J/kg·K respectively. The heat of fusion of ice is 3.34·10\(^5\) J/kg.

(a) Calculate the heat absorbed by the cold reservoir.

(b) Calculate the change in entropy of the closed system “reservoir + water/ice”.

The conversion consists of three processes: (a) water at 20\(^{0}\)C → water at 0\(^{0}\)C; (b) water at 0\(^{0}\)C → ice at 0\(^{0}\)C; (c) ice at 0\(^{0}\)C → ice at -10\(^{0}\)C:

(a) the heat absorbed by the cold reservoir

\[ \Delta Q_{res} = 10 \text{ kg} \times (4180 \times 20 + 3.34 \cdot 10^5 + 2090 \times 10) \text{ J/kg} = 4.385 \cdot 10^6 \text{ J} \]

(b) the change in entropy of the sub-system “water/ice”:

cooling of water

\[ \Delta S_a = \int_{293K}^{273K} \frac{M_{C_p}^{water} dT}{T} = M_{C_p}^{water} \ln \left( \frac{273}{293} \right) = -2955 \text{ J/K} \]

forming ice

\[ \Delta S_b = - \frac{M_{L_{vap}}}{T_0} = - \frac{10 \text{ kg} \times 3.34 \cdot 10^5 \text{ J/kg}}{273K} = -12,234 \text{ J/K} \]

cooling of ice

\[ \Delta S_c = \int_{273K}^{263K} \frac{M_{C_p}^{ice} dT}{T} = M_{C_p}^{ice} \ln \left( \frac{263}{273} \right) = -780 \text{ J/K} \]

The increase of entropy of the reservoir:

\[ \Delta S_{res} = \frac{\Delta Q_{res}}{T_{res}} = \frac{4.385 \cdot 10^6 \text{ J}}{263 \text{ K}} = 16,673 \text{ J/K} \]

The total change of entropy of the whole system:

\[ \Delta S = \Delta S_a + \Delta S_b + \Delta S_c + \Delta S_{res} = 704 \text{ J/K} \]