Problem 6:

a) In an isolated system the entropy always increases through irreversible processes, in thermodynamic equilibrium it takes its maximum. \( \square \)

b) \( TS = U - XY - \sum p_i N_i \)

This equation relates all thermodynamic quantities with each other. \( \square \)

c) The equations of state are the first derivative of the fundamental equation (together with the first law). \( \square \)

For the internal energy they are

\[
\left( \frac{\partial U}{\partial S} \right)_{V,N} = T, \quad \left( \frac{\partial U}{\partial V} \right)_{S,N} = P, \quad \text{and} \quad \left( \frac{\partial U}{\partial N} \right)_{S,V} = \mu.
\]

\( \square \)

d) Maxwell relations are relations between thermodynamic quantities derived from the second derivative of thermodynamic potentials.

For a one-component system the \( \mu-Rs \) derived from the internal energy are

\[
\left( \frac{\partial T}{\partial x} \right)_{S,N} = \left( \frac{\partial \mu}{\partial S} \right)_{x,N}, \quad \left( \frac{\partial T}{\partial V} \right)_{S,N} = \left( \frac{\partial \mu}{\partial N} \right)_{S,V}, \quad \text{and} \quad \left( \frac{\partial \mu}{\partial \mu} \right)_{S,V} = \left( \frac{\partial \mu}{\partial S} \right)_{x,N}.
\]

\( \square \)

e) 2\rightarrow3

\[
\Delta U = - \int_{V_2}^{V_3} p \, dV = - \int_{V_2}^{V_3} P \, dV = - P(V_3 - V_2)
\]

\[
\Delta Q = \Delta U = \Delta q = \frac{3}{2} P, (V_3 - V_2)
\]
\[ \Delta Q_2 = \frac{5}{2} P_2 (V_4 - V_1) \]

\[ \gamma = 1 - \frac{\Delta Q_2}{\Delta Q_1} = 1 - \frac{P_2 (V_4 - V_1)}{P_1 (V_3 - V_2)} \tag{1} \]

\[ T^{3/2} V = \text{const} \]

\[ \downarrow \]

\[ P_2^{3/5} V_2^{5/2} = \text{const} \Rightarrow P_2^{3/5} V = \text{const} \]

\[ P_1^{3/5} V_2 = P_2^{3/5} V_1 \]

\[ P_1^{3/5} V_3 = P_2^{3/5} V_4 \]

\[ P_2^{3/5} (V_4 - V_1) = P_1^{3/5} (V_3 - V_2) \]

\[ \Rightarrow \gamma = 1 - \frac{P_2}{P_1} \frac{P_1^{3/5}}{P_2^{3/5}} = 1 - \frac{P_1^{2/5}}{P_2^{2/5}} \tag{1} \]

\[ f) \quad \gamma_{\text{ref}} = \frac{\text{what we want}}{\text{what we have to put in}} = \frac{\Delta Q_2}{\Delta V_4} = \frac{\Delta Q_2}{\Delta Q_1 - \Delta Q_2} \tag{1} \]

\[ g) \quad \gamma_{\text{ref}} = \frac{\Delta Q_2}{\Delta Q_1 - \Delta Q_2} = \frac{1}{\Delta Q_2 - 1} = \frac{1}{1 - \frac{\Delta Q_2}{\Delta Q_1}} - 1 = \frac{1 - \gamma}{\gamma} \]

\[ \text{if } \gamma \rightarrow 1 \quad \gamma_{\text{ref}} \rightarrow 0 \]

\[ \text{if } \gamma \rightarrow 0 \quad \gamma_{\text{ref}} \rightarrow \infty \]
Problem 7:

a) \[
\frac{\partial p}{\partial T} = \left( \frac{\partial V}{\partial P} \right)_T \left( \frac{\partial T}{\partial V} \right)_P = -1
\]

\[
\Rightarrow \left( \frac{\partial P}{\partial T} \right)_V = \frac{\left( \frac{\partial V}{\partial P} \right)_T}{\left( \frac{\partial V}{\partial P} \right)_T} = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = \frac{a_P}{k_T}
\]

Maxwell relation \[
(\frac{\partial S}{\partial V})_T = (\frac{\partial P}{\partial T})_V = \frac{a_P}{k_T}
\]

Section: \[
C_V = C_V + T \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial P} \right)_T = C_V + TV \frac{a_P}{k_T} \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = C_V + TV \frac{a_P^2}{k_T}
\]

\[
\Rightarrow k_T (C_P - C_V) = TV \frac{a_P^2}{k_T}
\]

b) \[
\left( \frac{\partial V}{\partial P} \right)_S = \left( \frac{\partial V}{\partial P} \right)_T + \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial T}{\partial P} \right)_S
\]

\[
\Rightarrow k_T - k_S = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T + \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_S = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial T}{\partial P} \right)_S = a_P \left( \frac{\partial T}{\partial P} \right)_S
\]

\[
\left( \frac{\partial S}{\partial P} \right)_T \left( \frac{\partial T}{\partial S} \right)_P \left( \frac{\partial P}{\partial S} \right)_T = -1
\]

Maxwell relation \[
(\frac{\partial S}{\partial P})_T (\frac{\partial T}{\partial P})_S = \frac{a_P}{k_T} \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T
\]

\[
\Rightarrow k_T - k_S = -a_P \frac{T}{(\frac{\partial S}{\partial P} / \frac{\partial P}{\partial S})_T} = - \frac{T a_P}{C_P} \left( \frac{\partial S}{\partial P} \right)_T = \frac{T a_P}{C_P} \left( \frac{\partial S}{\partial P} \right)_T = \frac{TV a_P^2}{C_P}
\]

\[
\Rightarrow (P (k_T - k_S)) = TV a_P^2
\]
\( 3 \text{a)} \quad \left( \frac{\partial u}{\partial x} \right)_T = \left( \frac{\partial u}{\partial s} \right)_s + \left( \frac{\partial u}{\partial x} \right)_x \left( \frac{\partial s}{\partial x} \right)_T = \gamma + T \left( \frac{\partial s}{\partial x} \right)_T = \gamma - T \left( \frac{\partial y}{\partial T} \right)_x \)

\( 3 \text{b)} \quad du = \left( \frac{\partial u}{\partial t} \right)_x \{\gamma \}, dt + \left( \frac{\partial u}{\partial x} \right)_x \{\gamma \}, dx + \frac{s}{T} \left( \frac{\partial u}{\partial v} \right)_T \{\gamma \}, dv \}

\[ du = \left( \frac{2}{3} \left( \frac{\partial u}{\partial t} \right)_x \{\gamma \} \right)_T, \left( \frac{\partial u}{\partial x} \right)_x \{\gamma \} \right)_T = \left( \frac{\partial}{\partial T} \left[ \gamma - T \left( \frac{\partial y}{\partial T} \right)_x \} \right)_x \}

\[ \text{def. } C_x \]

\[ \frac{\partial C_x}{\partial t} = \alpha \]

\( 3 \text{c)} \quad \text{Use all } \quad \frac{\partial (C_v)}{\partial v} = 0 \)

\[ (P + \frac{n^2a}{V^2})(V-nb) = nRT \implies P = \frac{nRT}{V-nb} - \frac{n^2a}{V^2} \]

\[ \frac{\partial P}{\partial T} \text{ in } V-nb \implies (-\theta + T \left( \frac{\partial P}{\partial T} \right)_V = - \frac{nRT}{V-nb} + \frac{n^2a}{V^2} + T \frac{n^R}{V-nb} \]

\[ \left( \frac{\partial C_v}{\partial V} \right)_T = \left( \frac{\partial}{\partial V} \frac{n^2a}{V^2} \right)_V = 0 \]

\( 3 \text{d)} \quad du = C_v dT + \left( \frac{\partial u}{\partial v} \right)_T dv \]

\[ = C_v dT + \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dv = C_v dT + \frac{n^2a}{V^2} dv \]

\[ \Rightarrow U(V, T) - U(V_0, T_0) = C_v (T - T_0) - n^2a \left( \frac{1}{V} - \frac{1}{V_0} \right) \]
2) The internal energy of a van der Waals gas contains kinetic and potential energy. While a change in temperature changes the kinetic part of the internal energy, a change in volume, even at constant temperature changes the average distance between the molecules and therefore the potential energy contribution to the internal energy. The smaller the volume, the closer the particles and the more negative the potential energy since the particles attract each other.
Problem 9:

4) a) \[ \left( \frac{\partial V}{\partial P} \right)_T = -V \chi_T = -n T \hat{f}(P) \]

\[ \left( \frac{\partial V}{\partial T} \right)_P = V \chi_P = n \frac{R}{p} + \frac{n A}{T^2} \]

\[ dV \text{ is exact} \]

\[ \Rightarrow \left( \frac{\partial}{\partial T} \left( \frac{\partial V}{\partial p} \right)_T \right)_P = \left( \frac{\partial}{\partial p} \left( \frac{\partial V}{\partial T} \right)_P \right)_T \]

\[ \Rightarrow \hat{f}(P) = -n \frac{R}{p^2} \]

\[ \Rightarrow \hat{f}(P) = \frac{R}{p^2} \]

b) 2) \[
\int dV = \left( \frac{\partial V}{\partial P} \right)_T dP + \left( \frac{\partial V}{\partial T} \right)_P dT = -n T \frac{R}{p^2} dP + \left[ \frac{n R}{p} + \frac{n A}{T^2} \right] dT
\]

Explore \( V = V_0 \) at \( T = T_0 \) and \( P = \infty \)

\[
V(P, T) = -n \int_{T_0}^{T} \frac{R}{P^2} dP' + \int_{T_0}^{T} \left[ \frac{n R}{P} + \frac{n A}{T^2} \right] dT' + V_0
\]

\[ = n \frac{RT_0}{P} + \frac{n R}{P} (T - T_0) = n A \left( \frac{T}{T} - \frac{T}{T_0} \right) + V_0 \]

\[ = n \frac{R T_0}{P} - n A \left( \frac{T}{T} - \frac{T}{T_0} \right) + V_0 \]