all numbers are off by 1 or not 3

Problem 6:

a) In an isolated system the entropy always increases through irreversible processes. In thermodynamic equilibrium it takes its maximum. (1)

b) $TS = U - XY - \sum_j \mu_j N_j$

This equation relates all thermodynamic quantities with each other. (1)

c) The equations of state are the first derivatives of the fundamental equation (together with the first law.) (1)

For the internal energy they are

$\left(\frac{\partial U}{\partial S}\right)_{X,\{N_j\}} = T$, $\left(\frac{\partial U}{\partial X}\right)_{S,\{N_j\}} = Y$, and $\left(\frac{\partial U}{\partial N_j}\right)_{S,X,\{N_{i\neq j}\}} = \mu_j$ (1)

d) Maxwell relations are relations between thermodynamic quantities derived from the second derivatives of thermodynamic potentials. (1)

For a one-component system the M-R's derived from the internal energy are

$\left(\frac{\partial T}{\partial X}\right)_{S,N} = \left(\frac{\partial Y}{\partial S}\right)_{X,N}$, $\left(\frac{\partial T}{\partial N}\right)_{S,X} = \left(\frac{\partial \mu}{\partial S}\right)_{X,N}$, and $\left(\frac{\partial Y}{\partial N}\right)_{S,X} = \left(\frac{\partial \mu}{\partial X}\right)_{S,N}$

(1)

e) $2 \to 3$

$$\Delta W = -\int P\,dV = -\int_{V_2}^{V_3} P_1\,dV = -P_1(V_3 - V_2)$$

$$\Delta U = \int dU = \int \tfrac{3}{2} nR\,dT = \tfrac{3}{2}\int V\,dP + P\,dV$$

$$= \tfrac{3}{2} P_1 \int dV = \tfrac{3}{2} P_1 (V_3 - V_2)$$

$$\Delta Q_1 = \Delta U \cancel{-} \Delta W = \tfrac{5}{2} P_1 (V_3 - V_2)$$

$4 \to 1 \qquad \Delta Q_2 = \frac{5}{2} P_2 (V_4 - V_1)$

$$\eta = 1 - \frac{\Delta Q_2}{\Delta Q_1} = 1 - \frac{P_2 \, (V_4 - V_1)}{P_1 \, (V_3 - V_2)} \qquad 1$$

adiabats: $\quad T^{3/2} V = \text{const}$

$$\Downarrow$$

$$P^{3/2} V^{5/2} = \text{const} \quad \Rightarrow \quad P^{3/5} V = \text{const}$$

$$P_1^{3/5} V_2 = P_2^{3/5} V_1$$

$$P_1^{3/5} V_3 = P_2^{3/5} V_4$$

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

$$\Rightarrow \quad \eta = 1 - \frac{P_2}{P_1} \frac{P_1^{3/5}}{P_2^{3/5}} = 1 - \frac{P_2^{2/5}}{P_1^{2/5}} \qquad 1$$

f) $\quad \eta_{ref} = \dfrac{\text{what we want}}{\text{what we have to put in}} = \dfrac{\Delta Q_2}{\Delta W_{tot}} = \dfrac{\Delta Q_2}{\Delta Q_1 - \Delta Q_2} \qquad 1$

g) $\quad \eta_{ref} = \dfrac{\Delta Q_2}{\Delta Q_1 - \Delta Q_2} = \dfrac{1}{\frac{\Delta Q_1}{\Delta Q_2} - 1} = \dfrac{1}{\frac{1}{1-\eta} - 1} = \dfrac{1-\eta}{\eta}$

if $\eta \to 1 \qquad \eta_{ref} \to 0$

if $\eta \to 0 \qquad \eta_{ref} \to \infty$

Problem 7:

a) (4)
$$\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial T}{\partial V}\right)_p = -1$$

$$\Rightarrow \left(\frac{\partial p}{\partial T}\right)_V = \frac{\left(\frac{\partial V}{\partial T}\right)_p}{-\left(\frac{\partial V}{\partial p}\right)_T} = \frac{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p}{-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T} = \frac{\alpha_p}{\kappa_T}$$

Maxwell-relation $\Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha_p}{\kappa_T}$

lecture: $C_p = C_V + T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p = C_V + TV\frac{\alpha_p}{\kappa_T}\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = C_V + TV\frac{\alpha_p^2}{\kappa_T}$

$$\Rightarrow \kappa_T (C_p - C_V) = TV\alpha_p^2$$

b) (4)
$$\left(\frac{\partial V}{\partial p}\right)_S = \left(\frac{\partial V}{\partial p}\right)_T + \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_S$$

$$\Rightarrow \kappa_T - \kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T + \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_S = \alpha_p \left(\frac{\partial T}{\partial p}\right)_S$$

$$\left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_S \left(\frac{\partial p}{\partial S}\right)_T = -1$$

Maxwell relation

$$\Rightarrow \kappa_T - \kappa_S = -\alpha_p \frac{T}{T\left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial p}{\partial S}\right)_T} = -\frac{T\alpha_p}{C_p}\left(\frac{\partial S}{\partial p}\right)_T \stackrel{\downarrow}{=} \frac{T\alpha_p}{C_p}\left(\frac{\partial V}{\partial T}\right)_p = \frac{TV\alpha_p^2}{C_p}$$

$$\Rightarrow C_p(\kappa_T - \kappa_S) = TV\alpha_p^2$$

c) (2) a) & b) $\Rightarrow \kappa_T (C_p - C_V) = C_p(\kappa_T - \kappa_S)$

$$\Rightarrow \kappa_T C_V = C_p \kappa_S$$

$$\Rightarrow \frac{C_p}{C_V} = \frac{\kappa_T}{\kappa_S}$$

Problem 8:

3 a)

$$\left(\frac{\partial U}{\partial X}\right)_T = \left(\frac{\partial U}{\partial X}\right)_S + \left(\frac{\partial U}{\partial S}\right)_X \left(\frac{\partial S}{\partial X}\right)_T = Y + T\left(\frac{\partial S}{\partial X}\right)_T = Y - T\left(\frac{\partial Y}{\partial T}\right)_X$$

3 b)

$$dU = \left(\frac{\partial U}{\partial T}\right)_{X,\{N_j\}} dT + \left(\frac{\partial U}{\partial X}\right)_{T,\{N_j\}} dX + \sum_j \left(\frac{\partial U}{\partial N_j}\right)_{T,X,\{N_{k \neq j}\}} dN_j$$

dU exact

$$\Rightarrow \left(\frac{\partial}{\partial X}\left(\frac{\partial U}{\partial T}\right)_{X,\{N_j\}}\right)_{T,\{N_j\}} = \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial X}\right)_{T,\{N_j\}}\right)_{X,\{N_j\}}$$

$$\underset{\uparrow \atop \text{def. } C_X}{\left(\frac{\partial C_X}{\partial X}\right)_T} = \left(\frac{\partial}{\partial T}\underset{\uparrow \atop a)}{\left[Y - T\left(\frac{\partial Y}{\partial T}\right)_X\right]}\right)_X$$

3 c) To be shown: $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$. Use b).

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \Rightarrow P = \frac{nRT}{V-nb} - \frac{n^2 a}{V^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V-nb} \Rightarrow (-P) + T\left(\frac{\partial P}{\partial T}\right)_V = -\frac{nRT}{V-nb} + \frac{n^2 a}{V^2} + T\frac{nR}{V-nb}$$

$$= \frac{n^2 a}{V^2}$$

$$\left(\frac{d C_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial T}\frac{n^2 a}{V^2}\right)_V = 0$$

3 d)

$$dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

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

$$\Rightarrow U(V,T) - U(V_0,T_0) = C_V (T - T_0) - n^2 a\left(\frac{1}{V} - \frac{1}{V_0}\right)$$

2 extra credit

e) 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) $\left(\frac{\partial V}{\partial P}\right)_T = -V\kappa_T = -nTf(P)$

$$\left(\frac{\partial V}{\partial T}\right)_P = V\alpha_P = \frac{nR}{P} + \frac{nA}{T^2}$$

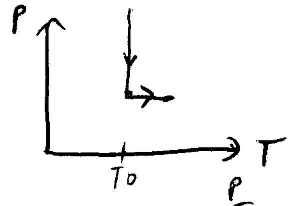
dV is exact

$$\Rightarrow \left(\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial P}\right)_T\right)_P = \left(\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial T}\right)_P\right)_T$$

$$-nf(P) = -\frac{nR}{P^2} \quad \Rightarrow \quad f(P) = \frac{R}{P^2}$$

b) (2) $dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT = -nT\frac{R}{P^2}\,dP + \left[\frac{nR}{P} + \frac{nA}{T^2}\right]dT$

assume $V = V_0$ at $T = T_0$ and $P = \infty$



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

$$= \frac{nRT_0}{P} + \frac{nR}{P}(T - T_0) - nA\left(\frac{1}{T} - \frac{1}{T_0}\right) + V_0$$

(2) $$= \frac{nRT}{P} - nA\left(\frac{1}{T} - \frac{1}{T_0}\right) + V_0$$