Problem Set 2: Solutions

1) a)

$$\Delta E_{AB} = W_{AB} = -\int_A^B PdV = -\int_1^2 V^{-7/5}dV = \frac{5}{2}(2^{-2/5} - 1) = -0.605 atm\ m^3 \approx -60.5kJ$$

Along path a, we have $P = -0.621V + 1.621$. Then,

$$W_A = -\int_a PdV = -\int_1^2 (-0.621V + 1.621)dV = 0.621\ 1.5 - 1.621 = -0.689 atm\ m^3$$

Therefore, $Q_A = \Delta E_{AB} - W_A = 0.084$ atmm^3=8.4kJ=2.0kCal.

b)

$$W_B = -P_0\Delta V = -1 atm\ m^3$$

and then $Q_B = \Delta E_{AB} - W_B = -0.605 + 1 = 0.395$ atmm^3.

c)

$$W_C = -P_1\Delta V = -0.3789 atm\ m^3$$

and then $Q_C = \Delta E_{AB} - W_C = -0.605 + 0.3789 = -0.226$ atmm^3.

2) $PV = NkT$ and $E = \frac{5}{2}NkT = \frac{5}{2}PV$.

a) The heat is adsorbed during the horizontal path in b ($Q_{b,H}$) and the vertical path in c ($Q_{c,V}$):

$$Q_h = Q_{b,V} + Q_{c,H}$$

where,

$$Q_{b,H} = \Delta E_{b,H} - W_{b,H} = \frac{5}{2}\Delta(PV) + P_0\Delta V = \frac{5}{2}(2-1) + 1 = \frac{7}{2} atm\ m^3$$

and

$$Q_{c,V} = \Delta E_{c,H} - W_{c,H} = \frac{5}{2}\Delta(PV) + 0 = \frac{5}{2}(1 - 0.3789) = 1.553 atm\ m^3$$

Therefore, $Q_h = 5.053 atm\ m^3$. Then efficiency=$e = |W_{cycle}|/|Q_h| = |\Delta P \Delta V|/Q_h = 0.621/1.553 = 12.3\%$.

b) Here, $Q_h = Q_{c,V} = 1.553$ atmm^3. Furthermore,

$$W = W_{ad.path} + W_C = -\Delta E_{AB} + W_C = (-0.605) - (-P_1\Delta V)) = -0.605 + 0.3789 = -0.226 atm\ m^3$$

Therefore, $e = 0.226/1.553 = 14.5\%$.

c) No work is done by the system.

3) The total system is divided into 2 subsystems: the small part of the total system (with E,N,S,T_0,μ_0) , and the rest of it which acts as a reservoir (with E_R,N_R,S_R,T_0,μ_0). The reservoir keeps T_0 and μ_0 constant. If we have fluctuations in the reservoir: δE_R and δN_R ($\delta V_R = 0$ because volume is fixed), then the change in entropy of the reservoir will be

$$\Delta S_R = \frac{\delta E_R}{T_0} - \frac{\mu_0 \delta N_R}{T_0} = -\frac{\delta E}{T_0} + \frac{\mu_0 \delta N}{T_0} \tag{1}$$

The total change in entropy is,

$$\Delta S_T = \Delta S + \Delta S_R = \tag{2}$$

$$= \Delta S - \frac{\delta E}{T_0} + \frac{\mu_0 \delta N}{T_0} = \tag{3}$$

$$= -\frac{1}{T_0}\delta\left[E - T_0 S - \mu_0 N\right] \tag{4}$$

Note that because in any spontaneous process S_T increases, this eq. implies that $E - T_0 S - \mu_0 N$ decreases.

Expanding this expresion to 2nd. order (V=constant, $E = E(N, S)$), we have:

$$-T_0 \Delta S_T = \tag{5}$$

$$= \frac{\partial E}{\partial S}\delta S + \frac{\partial E}{\partial N}\delta N + \frac{1}{2}\frac{\partial^2 E}{\partial S^2}\delta S^2 + \frac{1}{2}\frac{\partial^2 E}{\partial N^2}\delta N^2 + \frac{\partial^2 E}{\partial S \partial N}\delta S \delta N - T_0 \delta S - \mu_0 \delta N \geq 0 \tag{6}$$

Linear terms cancel out because $\mu_0 = \frac{\partial E}{\partial N}$ and $T_0 = \frac{\partial E}{\partial S}$. The expresion above is valid for any δN and δS.

If $\delta S = 0$ then we get

$$\frac{\partial^2 E}{\partial N^2} = \frac{\partial \mu}{\partial N} \geq 0$$

If $\delta N = 0$ then we get

$$\frac{\partial^2 E}{\partial S^2} = \frac{\partial T}{\partial S} \equiv \frac{T}{C_v(T)} \geq 0$$

If $\delta S = \sqrt{\frac{1}{2}\frac{\partial^2 E}{\partial N^2}}$ and $\delta N = -\sqrt{\frac{1}{2}\frac{\partial^2 E}{\partial S^2}}$ then we get

$$\frac{\partial^2 E}{\partial S^2}\frac{\partial^2 E}{\partial N^2} - \left(\frac{\partial^2 E}{\partial S \partial N}\right)^2 \geq 0 \tag{7}$$

$$\frac{\partial T}{\partial S}\frac{\partial \mu}{\partial N} - \left(\frac{\partial \mu}{\partial S}\right)^2 \geq 0 \tag{8}$$

$$\frac{T}{Cv}\frac{\partial \mu}{\partial N} \geq \left(\frac{\partial \mu}{\partial S}\right)^2 \tag{9}$$

4)

$$\left(\frac{\partial^2 E}{\partial S^2}\right)_V \left(\frac{\partial^2 E}{\partial V^2}\right)_S - \left(\frac{\partial^2 E}{\partial S \partial V}\right)^2 \geq 0 \tag{10}$$

$$-\left(\frac{\partial T}{\partial S}\right)_V \left(\frac{\partial P}{\partial V}\right)_S + \left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial P}{\partial S}\right)_V \geq 0 \tag{11}$$

$$\tag{12}$$

In terms of the Jacobian, it can be re-written as:

$$\frac{\partial(T, P)}{\partial(S, V)} \leq 0$$

Therefore,

$$\frac{\partial(T, P)}{\partial(S, V)}\frac{\partial(T, V)}{\partial(T, V)} \leq 0 \tag{13}$$

$$\frac{\partial(T, P)}{\partial(T, V)}\frac{\partial(T, V)}{\partial(S, V)} \leq 0 \tag{14}$$

$$\tag{15}$$

or,

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial T}{\partial S}\right)_V \leq 0 \tag{16}$$

$$\left(\frac{\partial P}{\partial V}\right)_T \frac{T}{C_v} \leq 0 \tag{17}$$

$$\tag{18}$$

Then, assuming $T > 0$ and because $C_v > 0$ we get

$$\left(\frac{\partial P}{\partial V}\right)_T \leq 0$$

5)a)

$$P = -\left(\frac{\partial A}{\partial V}\right)_T = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}$$

b)

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(\frac{\partial P}{\partial V}\right)_T^{-1}$$

But from a),

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{NkT}{(V - Nb)^2} + 2\frac{aN^2}{V^3}$$

Therefore,

$$K_T = \left[\frac{NkTV}{(V - Nb)^2} - 2\frac{aN^2}{V^2}\right]^{-1}$$

So, $K_T \geq 0$ iff

$$\frac{NkT}{(V - Nb)^2} \geq 2\frac{aN^2}{V^3}$$

This condition is not satisfied for low T.

c)

$$S = -\left(\frac{\partial A}{\partial T}\right)_V = Nk\ln\left[T^{3/2}(V - Nb)d/N\right] + \frac{3}{2}Nk$$

Then, $C_v = T\left(\frac{\partial S}{\partial T}\right)_V = 3/2Nk \geq 0$, and

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_V + T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

Now, $\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial T}{\partial V}\right)_P^{-1}$. From

$$T = \frac{P(V - Nb)}{Nk} + \frac{aN(V - Nb)}{V^2k},$$

we get

$$\left(\frac{\partial T}{\partial V}\right)_P = \frac{P}{Nk} - \frac{2aN(V - Nb)}{V^3k} + \frac{aN}{V^2k} = \frac{P}{Nk} + \frac{aN}{kV^3}\left[-2(V - Nb) + V\right] = \tag{19}$$

$$\frac{P}{Nk} - \frac{aN}{kV^3}\left[V + 2Nb\right] = \frac{T}{V - Nb} - \frac{aN}{kV^2} - \frac{aN}{kV^3}\left[V + 2Nb\right] = \tag{20}$$

$$\frac{T}{V - Nb} - \frac{2aN}{kV^2} - \frac{2abN^2}{kV^3} \tag{21}$$

Therefore,

$$C_p = \frac{3}{2}Nk + \frac{TNk}{V - Nb}\left[\frac{T}{V - Nb} - \frac{2aN}{kV^2}(1 + \frac{bN}{V})\right]^{-1}$$

Then ($n = N/V$),

$$\frac{C_p}{Nk} = \frac{3}{2} + \left[1 - \frac{2aN(V - Nb)}{kV^2T}(1 + \frac{bN}{V})\right]^{-1} = \frac{3}{2} + \left[1 - \frac{2an}{kT}(1 + bn)(1 - nb)\right]^{-1} = \frac{3}{2} + \left[1 - \frac{2an}{kT}(1 - b^2n^2)\right]^{-1}$$

There is a range of n and T where $C_P < 0$ for any positive non-zero a and b. To see this choose some value of n small enough that $1 - b^2n^2 > 0$. Then the denominator in the second term in the final expression of C_P vanishes at a particular value of T, $T = 2an(1 - b^2n^2)/k$. At this point C_P diverges! For a slightly smaller value of T the second term in C_P will be very large and negative so that $C_P < 0$. Of course, this problem is not present when $a = 0$, in which case $C_P/kN = 5/2$, independent of b.