Problem A

A model thermodynamic system has the internal energy

$$U(S,V,N) = \frac{\alpha S^3}{NV} \tag{1}$$

where α is a constant.

A.1 Obtain expressions for temperature T, pressure P and chemical potential μ in terms of entropy S, volume V , and number of particles N.

Solution:
We can write the total differential of U as

$$\mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_{V,N} \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_{S,N} \mathrm{d}V + \left(\frac{\partial U}{\partial N}\right)_{S,V} \mathrm{d}N \tag{2}$$

Using the Born Square, we obtain

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N \tag{3}$$

Comparing these two equations, we get the following relations:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N}, \qquad P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}, \qquad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \tag{4}$$

Substituting Eq. (1) into these relations, we obtain expressions T, P, and μ:

$$T = \frac{3\alpha S^2}{NV} \tag{5}$$

$$P = \frac{\alpha S^3}{NV^2} \tag{6}$$

$$\mu = -\frac{\alpha S^3}{N^2 V} \tag{7}$$

A.2 The entropy is not a suitable thermodynamic variable for experimental purposes. Eliminate S in the equations in (A.1) and obtain three equations of state.

Solution:
An equation of state is a thermodynamic relation that models the dependency of state variables (*e.g.* pressure, volume, temperature) with each other. Generally, it is often in the form of

$$f(P,V,T) = 0 \tag{8}$$

To get the three equations of state in this case, we isolate S in the expression of T in Eq. (5),

$$S = \sqrt{\frac{NVT}{3\alpha}} \tag{9}$$

and substitute this into the expressions for P and μ

$$P = \frac{\alpha\left(\sqrt{\frac{NTV}{3\alpha}}\right)^3}{NV^2} = \sqrt{\frac{NT^3}{27\alpha V}} \tag{10}$$

$$\mu = -\frac{\alpha\left(\sqrt{\frac{NTV}{3\alpha}}\right)^3}{N^2V} = -\sqrt{\frac{T^3V}{27\alpha N}} \tag{11}$$

in which we obtain two of them. For the third equation, we isolate again S in the expression of P in Eq. (6):

$$S = \sqrt[3]{\frac{PNV^2}{\alpha}} \tag{12}$$

Equating Eqs. (9) and (12), we get

$$\frac{NVT}{3\alpha} = \left(\sqrt[3]{\frac{NPV^2}{\alpha}}\right)^2 \quad\longrightarrow\quad T = 3\sqrt{\frac{\alpha P^2 V}{N}} \tag{13}$$

Therefore, Eqs. (10), (11), and (13) are the equations of state that relate state variables in the given system.

A.3 Obtain the ratio between heat capacity at constant pressure C_P and at constant volume C_V.

Solution:
Substituting the expression for S from Eq. (12) into U, we have

$$U = \frac{\alpha}{NV}\left(\sqrt[3]{\frac{NPV^2}{\alpha}}\right)^3 = PV \tag{14}$$

Then, substituting this to get the heat capacity at constant volume, we have

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = \left(\frac{\partial (PV)}{\partial T}\right)_{N,V} = V\frac{\partial P}{\partial T} \tag{15}$$

where we factor out V since it is constant as mentioned. Substituting in Eq. (10), we obtain

$$C_V = V\frac{\partial}{\partial T}\left(\sqrt{\frac{NT^3}{27\alpha V}}\right) = \frac{3}{2}\sqrt{\frac{NTV}{27\alpha}} \tag{16}$$

As for the heat capacity at constant pressure, note that the enthalpy is defined as $H \equiv U + PV$. Thus,

$$C_P = \left(\frac{\partial H}{\partial T}\right)_{N,P} = \left(\frac{\partial (U+PV)}{\partial T}\right)_{N,P} = \left(\frac{\partial (PV+PV)}{\partial T}\right)_{N,P} = 2P\frac{\partial V}{\partial T} \tag{17}$$

in which we again substitute in U and factor out P. We can rearrange Eq. (10) to get an expression for V

$$V = \frac{NT^2}{27\alpha P^2}. \tag{18}$$

Using this, C_P becomes

$$C_P = 2P\frac{\partial}{\partial T}\left(\frac{NT^2}{27\alpha P^2}\right) = (2\cdot 3)\frac{1}{P}\frac{NT^2}{27\alpha} = (2\cdot 3)\sqrt{\frac{27\alpha V}{NT^3}}\frac{NT^2}{27\alpha} = (2\cdot 3)\sqrt{\frac{NTV}{27\alpha}} \tag{19}$$

after replacing P with the relation in Eq. (10). Therefore,

$$\frac{C_P}{C_V} = \frac{(2\cdot 3)\sqrt{\frac{NTV}{27\alpha}}}{\frac{3}{2}\sqrt{\frac{NTV}{27\alpha}}} = 4 \tag{20}$$

which shows that the ratio between C_P and C_V is 4.

Problem B

Obtain the Maxwell's relations that can be derived from the enthalpy $H \equiv H(S, P, N)$.

Solution:

The total differential of H can be written as

$$\mathrm{d}H = \left(\frac{\partial H}{\partial S}\right)_{P,N}\mathrm{d}S + \left(\frac{\partial H}{\partial P}\right)_{S,N}\mathrm{d}P + \left(\frac{\partial H}{\partial N}\right)_{P,S}\mathrm{d}N \tag{21}$$

Using the Born Square, we get

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P + \mu\mathrm{d}N \tag{22}$$

Comparing these two equations, we have the following relations

$$T = \left(\frac{\partial H}{\partial S}\right)_{P,N}, \qquad V = \left(\frac{\partial H}{\partial P}\right)_{S,N}, \qquad \mu = \left(\frac{\partial H}{\partial N}\right)_{P,S} \tag{23}$$

Making use of the symmetry of the second derivatives and applying the relations in Eq. (23), we obtain

$$\left(\frac{\partial}{\partial P}\frac{\partial H}{\partial S}\right)_{S,N} = \left(\frac{\partial}{\partial S}\frac{\partial H}{\partial P}\right)_{P,N} \longrightarrow \left(\frac{\partial T}{\partial P}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{P,N} \tag{24}$$

$$\left(\frac{\partial}{\partial P}\frac{\partial H}{\partial N}\right)_{S,N} = \left(\frac{\partial}{\partial N}\frac{\partial H}{\partial P}\right)_{P,S} \longrightarrow \left(\frac{\partial \mu}{\partial P}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{P,S} \tag{25}$$

$$\left(\frac{\partial}{\partial S}\frac{\partial H}{\partial N}\right)_{P,N} = \left(\frac{\partial}{\partial N}\frac{\partial H}{\partial S}\right)_{P,S} \longrightarrow \left(\frac{\partial \mu}{\partial S}\right)_{P,N} = \left(\frac{\partial T}{\partial N}\right)_{P,S} \tag{26}$$

which are the Maxwell's relations derived from the enthalpy.