PHYSICS 210A : EQUILIBRIUM STATISTICAL PHYSICS
HW ASSIGNMENT #3 SOLUTIONS

(1) For an ideal gas, find the difference $C_\varphi - C_V$ for the following functions φ. You are to assume N is fixed in each case.

(a) $\varphi(p, V) = p^3 V^2$

(b) $\varphi(p, T) = p\, e^{T/T_0}$

(c) $\varphi(T, V) = V T^{-1}$

Solution :

In general,

$$ C_\varphi = T \left(\frac{\partial S}{\partial T} \right)_\varphi . $$

Note that

$$ \dbar Q = dE + p\, dV . $$

We will also appeal to the ideal gas law, $pV = Nk_{\mathrm{B}} T$. Below, we shall abbreviate $\varphi_V = \frac{\partial \varphi}{\partial V}$, $\varphi_T = \frac{\partial \varphi}{\partial T}$, and $\varphi_p = \frac{\partial \varphi}{\partial p}$.

(a) We have

$$ \dbar Q = \tfrac{1}{2} f N k_{\mathrm{B}}\, dT + p\, dV , $$

and therefore

$$ C_\varphi - C_V = p \left(\frac{\partial V}{\partial T} \right)_\varphi . $$

Now for a general function $\varphi(p, V)$, we have

$$ d\varphi = \varphi_p\, dp + \varphi_V\, dV $$
$$ = \frac{N k_{\mathrm{B}}}{V}\, \varphi_p\, dT + \left(\varphi_V - \frac{p}{V}\, \varphi_p \right) dV , $$

after writing $dp = d(N k_{\mathrm{B}} T / V)$ in terms of dT and dV. Setting $d\varphi = 0$, we then have

$$ C_\varphi - C_V = p \left(\frac{\partial V}{\partial T} \right)_\varphi = \frac{N k_{\mathrm{B}}\, p\, \varphi_p}{p\, \varphi_p - V \varphi_V} . $$

This is the general result. For $\varphi(p, V) = p^3 V^2$, we find

$$ C_\varphi - C_V = 3 N k_{\mathrm{B}} . $$

(b) We have

$$ \dbar Q = \left(\tfrac{1}{2} f + 1 \right) N k_{\mathrm{B}}\, dT - V\, dp , $$

1

and therefore

$$C_\varphi - C_V = Nk_{\mathrm{B}} - V \left(\frac{\partial p}{\partial T} \right)_\varphi .$$

For a general function $\varphi(p, T)$, we have

$$d\varphi = \varphi_p \, dp + \varphi_T \, dT \quad \Longrightarrow \quad \left(\frac{\partial p}{\partial T} \right)_\varphi = -\frac{\varphi_T}{\varphi_p} .$$

Therefore,

$$C_\varphi - C_V = Nk_{\mathrm{B}} + V \frac{\varphi_T}{\varphi_p} .$$

This is the general result. For $\varphi(p, T) = p \, e^{T/T_0}$, we find

$$C_\varphi - C_V = Nk_{\mathrm{B}} \left(1 + \frac{T}{T_0} \right) .$$

(c) We have

$$C_\varphi - C_V = p \left(\frac{\partial V}{\partial T} \right)_\varphi ,$$

as in part (a). For a general function $\varphi(T, V)$, we have

$$d\varphi = \varphi_T \, dT + \varphi_V \, dV \quad \Longrightarrow \quad \left(\frac{\partial V}{\partial T} \right)_\varphi = -\frac{\varphi_T}{\varphi_V} ,$$

and therefore

$$C_\varphi - C_V = -p \frac{\varphi_T}{\varphi_V} .$$

This is the general result. For $\varphi(T, V) = V/T$, we find

$$C_\varphi - C_V = Nk_{\mathrm{B}} .$$

($\mathbf{2}$) Consider a thermodynamic system for which $E(S, V, N) = aS^4/NV^2$.

(a) Find the equation of state $p = p(T, V, N)$.

(b) Find the equation of state $\mu = \mu(T, p)$.

(c) ν moles of this substance are taken through a Joule-Brayton cycle (see §2.6.7 of the Lecture Notes). The upper isobar lies at $p = p_2$ and extends from volume V_{A} to V_{B}. The lower isobar lies at $p = p_1$. Find the volumes V_{C} and V_{D}.

(d) Find the work done per cycle W_{cyc}, the heat Q_{AB}, and the cycle efficiency.

(a) We can find

$$p = -\left(\frac{\partial E}{\partial V}\right)_{S,N} = \frac{2aS^4}{NV^3} \quad , \quad T = \left(\frac{\partial E}{\partial S}\right)_{V,N} = \frac{4aS^3}{NV^2} \quad , \quad \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V} = -\frac{aS^4}{N^2V^2} \quad ,$$

but we need to eliminate the inconvenient variable S from these equations. To do this, we construct the ratio p^3/T^4, in which the S factors manifestly cancel. One then finds $32a\,p^3V = NT^4$, i.e.

$$p(T, V, N) = (32a)^{-1/3}\left(\frac{N}{V}\right)^{1/3} T^{4/3} \ .$$

This means, for example, that the equation for an isotherm (at fixed N) is $pV^{1/3} = \text{const.}$, in contrast to the result for the ideal gas isotherm, $pV = \text{const.}$ Note also that p, being intensive, must be expressible as $p(T, V/N)$, which it is.

(b) To obtain $\mu(T, p)$, note that $2N\mu = -pV$, and from our result for $p(T, V/N)$ we have $V/N = T^4/32ap^3$. Thus,

$$\mu(T, p) = -\frac{T^4}{64a\,p^2} \ .$$

(c) The equilibrium adiabatic equation of state for this system is $dS = 0$. From (a), we see that at fixed N this means $pV^3 = \text{const.}$, so we must have $p_2 V_B^3 = p_1 V_C^3$ and $p_2 V_A^3 = p_1 V_D^3$. Hence

$$V_C = V_B \cdot (p_2/p_1)^{1/3} \quad , \quad V_D = V_A \cdot (p_2/p_1)^{1/3} \ .$$

(d) From part (a), the energy for our system is $E = \frac{1}{2}pV$. Along the upper (p_2) isochore,

$$W_{AB} = \int_A^B dV\, p_2 = p_2(V_B - V_A) \quad , \quad \Delta E_{AB} = E_B - E_A = \frac{1}{2}p_2\,(V_B - V_A) \quad ,$$

hence

$$Q_{AB} = \Delta E_{AB} + W_{AB} = \frac{3}{2}p_2\,(V_B - V_A) \ .$$

The work along the lower (p_1) isochore is

$$W_{CD} = p_1(V_D - V_C) = p_2\,(V_A - V_B)\left(\frac{p_1}{p_2}\right)^{2/3} \ .$$

Along the BC adiabat,

$$W_{BC} = \int_B^C p\,dV = p_2 V_B^3 \int_{V_B}^{V_C} \frac{dV}{V^3} = \frac{1}{2}p_2 V_B\left(1 - \frac{V_B^2}{V_C^2}\right) = \frac{1}{2}p_2 V_B\left[1 - \left(\frac{p_1}{p_2}\right)^{2/3}\right] \ .$$

Similarly,

$$W_{\text{DA}} = \int_{\text{D}}^{\text{A}} p\,dV = p_2 V_{\text{A}}^3 \int_{V_{\text{D}}}^{V_{\text{A}}} \frac{dV}{V^3} = \tfrac{1}{2} p_2 V_{\text{A}} \left(\frac{V_{\text{A}}^2}{V_{\text{D}}^2} - 1 \right) = \tfrac{1}{2} p_2 V_{\text{A}} \left[\left(\frac{p_1}{p_2} \right)^{2/3} - 1 \right].$$

Adding up all the individual works, we get

$$W_{\text{cyc}} = W_{\text{AB}} + W_{\text{BC}} + W_{\text{CD}} + W_{\text{DA}}$$

$$= \tfrac{3}{2} p_2 (V_{\text{B}} - V_{\text{A}}) \left[1 - \left(\frac{p_1}{p_2} \right)^{2/3} \right].$$

Dividing by Q_{AB}, we obtain the efficiency,

$$\eta = \frac{W_{\text{cyc}}}{Q_{\text{AB}}} = 1 - \left(\frac{p_1}{p_2} \right)^{2/3}.$$

(3) Show that

$$\left(\frac{\partial \mu}{\partial T} \right)_{S,N} = \frac{C_p}{NT\alpha_p} - \frac{S}{N} \quad .$$

Solution :

$$\left(\frac{\partial \mu}{\partial T} \right)_{S,N} = \frac{\partial(\mu, S, N)}{\partial(T, S, N)} = \overbrace{\frac{\partial(\mu, S, N)}{\partial(p, S, V)}}^{=1} \cdot \frac{\partial(p, S, V)}{\partial(p, T, N)} \cdot \frac{\partial(p, T, N)}{\partial(p, V, N)}$$

$$= \left[\left(\frac{\partial S}{\partial T} \right)_{p,N} \left(\frac{\partial V}{\partial N} \right)_{p,T} - \left(\frac{\partial S}{\partial N} \right)_{p,T} \left(\frac{\partial V}{\partial T} \right)_{p,N} \right] \cdot \left(\frac{\partial T}{\partial V} \right)_{p,N} = \frac{C_p}{NT\alpha_p} - \frac{S}{N} \quad .$$

Equivalently, from Gibbs-Duhem we have $N d\mu = -S\,dT + V\,dp$ hence

$$\left(\frac{\partial \mu}{\partial T} \right)_{S,N} = -\frac{S}{N} + \frac{V}{N} \left(\frac{\partial p}{\partial T} \right)_{S,N}$$

But now

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

and invoking the Maxwell relation (from dG) $\left(\frac{\partial S}{\partial p} \right)_T = -\left(\frac{\partial V}{\partial T} \right)_p$ gives us

$$\left(\frac{\partial p}{\partial T} \right)_S = \frac{C_p}{TV\alpha_p}$$

and we are once again done.

(4) A solution of $4.00\,\mathrm{g}$ of hemoglobin in 100 mL of water was prepared and its osmotic pressure was measured to be $\pi = 0.0130\,\mathrm{atm}$ at $T = 280\,\mathrm{K}$. Estimate the molecular mass of hemoglobin.

Solution :

We use the formula $\pi v = xRT$ for the osmotic pressure π of weak solutions. Here v is the molar volume of the solvent, and x is the molar fraction of solute. If M is the molar mass of hemoglobin, then

$$x = \frac{4.00\,\mathrm{g}}{M} \bigg/ \frac{100\,\mathrm{g}}{18\,\mathrm{g}} = \frac{18\,\mathrm{g}}{25\,M} \,,$$

since the density of water is $1.0\,\mathrm{g/cm^3} = 1\,\mathrm{g/mL}$. We then have

$$
\begin{aligned}
M &= \tfrac{18}{25}\,\mathrm{g} \cdot \frac{RT}{\pi v} \\
&= \frac{18\,\mathrm{g}}{25} \cdot \frac{(8.314 \times 10^7\,\mathrm{erg/mol\,K})(280\,\mathrm{K})}{(0.013\,\mathrm{atm})(1.013 \times 10^6\,\mathrm{g/cm\,s^2\,atm})(18\,\mathrm{cm^3/mol})} = 70710\,\mathrm{g}\,.
\end{aligned}
$$

The actual value is $M = 65706\,\mathrm{g}$.