+ 0.85 $\boxed{9,5}$ $\boxed{8,6}$

1 a In principle, there are N ~~4~~ "particles" thus N! ways to arrange them. However, particles that are in the same energylevel are indistinguishable. So we have to divide by the number of ways that we can arrange the ~~[illegible]~~ non excited particles (N-n particles, so $(N-n)!$ ways of arranging) and the excited particles (n particles, so $n!$ ways to arrange them). Furthermore, for each non excited particle we have 3 possible states, thus per particle in the ground state the total number of ~~[illegible]~~ combinations is multiplied by 3, which gives 3^{N-n} for all ground state particle, and for each excited one the total number of ~~[illegible]~~ combinations is multiplied by 2, which gives 2^n for all excited particles. Together this gives $\frac{N!\,3^{N-n}2^n}{(N-n)!\,n!}$ ~~[illegible]~~ possible combinations and thus the same number of microstates.

9

3

b $S = k\ln\Omega = k\ln\frac{N!\,3^{N-n}2^n}{N-n!\,n!} = k\left(\ln N! + \ln(3^{N-n}) + \ln(2^n) - \ln((N-n)!) - \ln(n!)\right) = k\left(N\ln N - N + (N-n)\ln 3 + n\ln 2 - (N-n)\ln(N-n) + N - n - n\ln n + n\right)$

$= k\left(N\ln N + (N-n)\ln 3 + n\ln 2 - (N-n)\ln(N-n) - n\ln n\right)$. $E = n\varepsilon \Rightarrow n = \frac{E}{\varepsilon}$. $\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial S}{\partial n}\frac{\partial n}{\partial E} = \frac{\partial S}{\partial n}\cdot\frac{1}{\varepsilon}$

$\Rightarrow \frac{1}{T} = \frac{\partial S}{\partial n}\cdot\frac{1}{\varepsilon} = k\left(-\ln 3 + \ln 2 + \ln(N-n) + (N-n)\cdot\frac{1}{N-n} - \ln n - n\cdot\frac{1}{n}\right)\cdot\frac{1}{\varepsilon} = k\left(-\ln 3 + \ln 2 + \ln(N-n) + 1 - \ln n - 1\right)\frac{1}{\varepsilon} = \frac{k}{\varepsilon}\left(\ln\left(\frac{2}{3}\right) + \ln\left(\frac{N-n}{n}\right)\right)$

$\Rightarrow \frac{\varepsilon}{kT} = \ln\frac{2}{3} + \ln\left(\frac{N-\frac{E}{\varepsilon}}{\frac{E}{\varepsilon}}\right) \Rightarrow e^{\varepsilon/kT} = \frac{2}{3}\cdot\frac{N-\frac{E}{\varepsilon}}{\frac{E}{\varepsilon}} \Rightarrow \frac{E}{\varepsilon}e^{\varepsilon/kT} = \frac{2}{3}N - \frac{2}{3}\frac{E}{\varepsilon} \Rightarrow \frac{E}{\varepsilon}\left(e^{\varepsilon/kT} + \frac{2}{3}\right) = \frac{2}{3}N$

$\Rightarrow E = \frac{\frac{2}{3}N\varepsilon}{e^{\varepsilon/kT} + \frac{2}{3}}$

3 ρ

c $C_v = \frac{\partial E}{\partial T} = \frac{\partial}{\partial T}\left(\frac{\frac{2}{3}N\varepsilon}{e^{\varepsilon/kT} + \frac{2}{3}}\right) = \frac{2}{3}N\varepsilon\cdot\frac{-1}{\left(e^{\varepsilon/kT} + \frac{2}{3}\right)^2}\cdot e^{\varepsilon/kT}\cdot\frac{-1\varepsilon}{kT^2} = \frac{\frac{2}{3}N\varepsilon^2 e^{\varepsilon/kT}}{kT^2\left(e^{\varepsilon/kT} + \frac{2}{3}\right)^2}$

3 4

6

2a $Z = \sum_r e^{-\beta\varepsilon_r} = \sum_0^\infty e^{-\beta(\hbar\omega(r+\frac{1}{2}))} = e^{-\frac{1}{2}\beta\hbar\omega} \sum_0^\infty e^{-\beta\hbar\omega r}$ $\quad \beta = kT > 0$, $\hbar > 0$, $\omega > 0$ and r goes from zero to infinity

$\Rightarrow$ $-\beta\hbar\omega < 0$, thus $e^{-\beta\hbar\omega} < 1$, thus $(e^{-\beta\hbar\omega})^r$ is a geometric series that converges $\Rightarrow \sum_0^\infty e^{-\beta\hbar\omega r} = \frac{1}{1-e^{-\beta\hbar\omega}}$

2 $\quad \Rightarrow Z = e^{-\frac{\beta\hbar\omega}{2}} \cdot \frac{1}{1-e^{-\beta\hbar\omega}} = \frac{e^{-\frac{\beta\hbar\omega}{2}}}{1-e^{-\beta\hbar\omega}}$

b $\bar{\varepsilon} = \frac{-\partial \ln Z}{\partial\beta} = -\frac{\partial}{\partial\beta}\left(\ln e^{-\beta\hbar\omega/2} - \ln|1-e^{-\beta\hbar\omega}|\right) = \frac{\partial}{\partial\beta}\left(\frac{\beta\hbar\omega}{2}\ln e + \ln|1-e^{-\beta\hbar\omega}|\right) = \frac{\hbar\omega}{2}\cdot 1 + \frac{1}{1-e^{-\beta\hbar\omega}} \cdot e^{-\beta\hbar\omega}\cdot\hbar\omega$

$= \hbar\omega\left(\frac{1}{2} + \frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right)$

2½

c $Z_{tot} = \frac{1}{N!}\left(Z_{vib}\cdot Z_{rot}\cdot Z_{tr}\right)^N$

0

d ~~$F = -kT\ln Z$ and $F = E - TS = N\bar{E} - TS \Rightarrow TS = kT\ln Z + N\bar{E} \Rightarrow S = \frac{kT\ln Z + N\bar{E}}{T}$~~

~~$\Rightarrow S = \frac{kT\left(\frac{\beta\hbar\omega}{2}\ln e + \ln|1-e^{-\beta\hbar\omega}|\right) + N\hbar\omega\left(\frac{1}{2} + \frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right)}{T} = k\left(\frac{\beta\hbar\omega}{2} + \ln|1-e^{-\beta\hbar\omega}|\right) + \frac{N\hbar\omega}{T}\left(\frac{1}{2} + \frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right)$~~

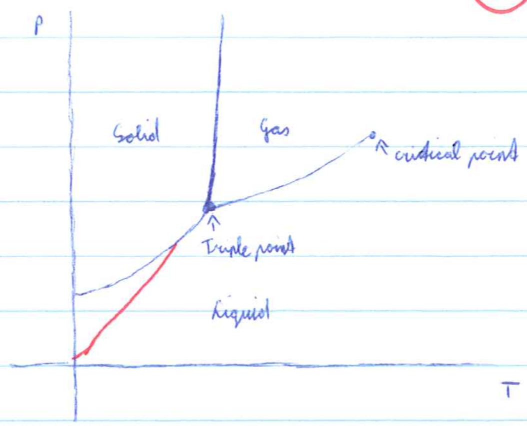
or $\quad F = E - TS \Rightarrow dF = TdS - pdV - TdS - SdT = -pdV - SdT \Rightarrow S = -\left(\frac{\partial F}{\partial T}\right)_V$

$\Rightarrow S = \frac{+\partial(kT\ln Z)}{\partial T} = \frac{\partial}{\partial T}\left(-\frac{\hbar\omega}{2} + kT\ln(1-e^{-\beta\hbar\omega})\right) = k\ln(1-e^{-\beta\hbar\omega}) + kT\frac{1}{1-e^{-\beta\hbar\omega}}\cdot e^{-\beta\hbar\omega}\cdot -\frac{\hbar\omega}{kT^2}$ $= \left(k\ln(1-e^{-\beta\hbar\omega}) - \frac{\hbar\omega}{T}\cdot\frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right)(-N$

1½

9

3 a



4

b $\frac{dP}{dT} = \frac{L_{12}}{T\Delta V}$ assuming a perfect gas: $pV = nRT$, 1 mole, so $pV = RT$. Because gas is involved, $\Delta V \approx V_{gas} = \frac{RT}{p}$

$d p = \frac{L_{12}}{T} \frac{p}{RT} dT \Rightarrow \frac{1}{p} dp = \frac{L_{12}}{RT^2} dT \Rightarrow \int \frac{1}{p} dp = \int \frac{L_{12}}{RT^2} dT$

5

$\Rightarrow \ln\left(\frac{p_2}{p_1}\right) = \frac{-L_{12}}{RT_2} + \frac{L_{12}}{RT_1}$

$\Rightarrow \frac{p_2}{p_1} = e^{-L_{12}/RT} \cdot e^{L_{12}/RT_1}$

$\Rightarrow p_2 = p_1 e^{-L_{12}/RT} \cdot e^{L_{12}/RT_1} p_1$

Because $L_{12} = \Delta_{vap}H$, and (T_B, p_0) is a point on the curve, we can simplify:

$\Rightarrow p_2 = e^{-L_{12}/RT} \cdot e^{L_{12}/RT_B} p_0 = e^{-\frac{\Delta_{vap}H}{RT}} \cdot e^{\frac{\Delta_{vap}H}{RT_B}} p_0$

Define now $C := e^{\frac{\Delta_{vap}H}{RT_B}} \cdot p_0$, then $\Rightarrow p_2 = p = C \cdot e^{-\frac{\Delta_{vap}H}{RT}}$

5

(6)

4 a The average of a quantity: $\frac{\Sigma \text{ quantity} \cdot \text{weight}}{\Sigma \text{ weights}}$. With statistical Physics, Σ weights $= Z$ because the weights are $e^{-\beta n_i \varepsilon_i}$

So in our case, $\bar{n}_i = \frac{\sum_{n_1,n_2,n_3\dots} n_i \, e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+n_3\varepsilon_3)}}{\sum_{n_1,n_2,n_3} e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+n_3\varepsilon_3)}}$. The numerator looks similar to $\frac{\partial Z}{\partial \varepsilon_i} = \sum_{n_1,n_2,n_3\dots} -\beta n_i e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2\dots)}$

which only differs a constant factor. ~~So $\bar{n}_i =$~~ which we can pull out: $\frac{\partial Z}{\partial \varepsilon_i} = -\beta \sum_{n_1,n_2,n_3\dots} n_i e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2\dots)}$

So $\bar{n}_i = \frac{-1}{\beta}\left(\frac{\partial Z}{\partial \varepsilon_i}\right)\cdot\frac{1}{Z}$. But $\frac{1}{Z}$ is the anti-derivative of $\ln Z$, so we can write this nicer as

2 $\bar{n}_i = \frac{-1}{\beta}\left(\frac{\partial \ln Z}{\partial \varepsilon_i}\right)$

b Because a photon gas has no fixed number of particles, n_1 can run from 0 to ∞, n_2 can run from 0 to ∞, ..., n_i from 0 to ∞, ...

So $Z_{PH} = \sum_{n_1,n_2,n_3} e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2\dots)} = \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\dots e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2\dots)} = \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\dots\dots e^{-\beta n_1\varepsilon_1}\cdot e^{-\beta n_2\varepsilon_2}\cdot e^{\dots}\dots = \sum_{n_1=0}^{\infty} e^{-\beta n_1\varepsilon_1}\sum_{n_2=0}^{\infty} e^{-\beta n_2\varepsilon_2}\sum_{n_3=0}^{\infty}\dots\dots$

$= \prod_{z=1}^{\infty}\sum_{n_z=0}^{\infty} e^{-\beta n_z\varepsilon_z}$. But because $\beta>0, \varepsilon_z>0$, $e^{-\beta\varepsilon_z}<1$ and thus is $\left(e^{-\beta\varepsilon_z}\right)^{n_z}$ a converging series $e^{-\beta\varepsilon_z n_z} = \frac{1}{1-e^{-\beta\varepsilon_z}}$

2 $\Rightarrow Z_{PH} = \prod_{z=1}^{\infty}\frac{1}{1-e^{-\beta\varepsilon_z}}$

$\times$

$\Sigma_i \quad \prod_{i=1}$

c With photons, $\varepsilon = \hbar\omega$ so: $\bar{n}(\omega) = \bar{n}_i = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \varepsilon_i} = -\frac{1}{\beta}\frac{\partial}{\partial \varepsilon_i}\ln\left(\prod_{i=1}^{\infty}\frac{1}{1-e^{-\beta\varepsilon_i}}\right) = -\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_i}\sum_{i=1}^{\infty}\ln\frac{1}{1-e^{-\beta\varepsilon_i}} = -\frac{1}{\beta}\cancel{\sum_{i=1}^{\infty}}\left(1-e^{-\beta\varepsilon_i}\right)\cdot e^{-\beta\varepsilon_i}\cdot\beta$

0 $= \sum_{i=1}^{\infty}\left(e^{-\beta\varepsilon_i}-1\right)e^{-\beta\varepsilon_i} = \sum_{i=1}^{\infty} e^{-2\beta\varepsilon_i} - e^{-\beta\varepsilon_i} = \sum_{i=1}^{\infty}\left(e^{-2\beta}-e^{-\beta}\right)^{\varepsilon_i}$

$\times 2$ polarisati

d $f(p)dp = \frac{4\pi V p^2 dp}{h^3}$, $p = \frac{\varepsilon}{c} = \frac{\hbar\omega}{c}$, $\frac{dp}{d\omega} = \frac{\hbar}{c} \Rightarrow f(\omega)d\omega = \frac{4\pi V\hbar^2\omega^2\hbar\,d\omega}{h^3 c^2\cdot c} = \frac{4\pi\, V\omega^2 d\omega}{(2\pi)^3\, c^3} = \frac{V\omega^2 d\omega}{2\pi^2c^3}$

2 $N = \int_{\omega=0}^{\infty}\bar{n}(\omega)f(\omega)d\omega = \int_{\omega=0}^{\infty}\frac{1}{e^{\beta\hbar\omega}-1}\cdot\frac{V\omega^2 d\omega}{2\pi^2c^3} = \frac{V}{2\pi^2c^3}\int_{\omega=0}^{\infty}\frac{\omega^2 d\omega}{e^{\beta\hbar\omega}-1} = \frac{V}{2\pi^2c^3}\int_{x=0}^{\infty}\frac{\left(\frac{x}{\beta\hbar}\right)^2\frac{1}{\beta\hbar}dx}{e^x-1} = \frac{V}{2\pi^2c^3\beta^3\hbar^3}\int_{x=0}^{\infty}\frac{x^2dx}{e^x-1}$

$x = \beta\hbar\omega$, $\frac{\partial\omega}{\partial x} = \frac{1}{\beta\hbar}$

$= 2{,}404\cdot\frac{V\,k^3T^3}{2\pi^2c^3\hbar^3} = 1{,}404\cdot\frac{Vk^3T^3}{\pi^2c^3\hbar^3}$

looked up on last page

8

5 a To know how big the density of states is, we look in 3 dimensional p space. Classically, every point in this space is possible, but quantum mechanically, each component of p is quantisized in h. Thus to find the density of states, we look at a shell around the origin in which $|\vec{p}|$ lies between p and $p+dp$ and divide that by the volume in which the p space is quantisized, h^3: $f(p)dp = \frac{\text{volume of shell}}{\text{volume of quanta}} = \frac{4\pi V p^2 dp}{h^3}$. Than we multiply by 2 to account for spin up and spin down states: $f(p) = \frac{8\pi V p^2 dp}{h^3}$

1

b $\epsilon_F = \mu(T=0)$. $f(\epsilon)d\epsilon = \frac{8\pi V \left(\frac{\epsilon}{c}\right)^2 \cdot \frac{1}{c} d\epsilon}{h^3} = \frac{8\pi V \epsilon^2 d\epsilon}{(ch)^3}$

$N = \int_0^\infty n(\epsilon) f(\epsilon) d\epsilon = \int_0^\infty \frac{1}{e^{\beta(\epsilon-\mu)}+1} \cdot \frac{8\pi V \epsilon^2 d\epsilon}{(ch)^3} = \frac{8\pi V}{(ch)^3} \int_0^\infty \frac{\epsilon^2 d\epsilon}{e^{\beta(\epsilon-\mu)}+1}$. Take $T=0$, then $\frac{1}{e^{\beta(\epsilon-\mu)}+1} = \frac{1}{e^{\beta(\epsilon_p-\epsilon_F)}+1}$ is $\frac{1}{0+1} = 1$ for $\epsilon < \epsilon_F$ (for $\frac{\epsilon-\epsilon_F}{kT}$ goes to minus infinity then, so $e^{\frac{\epsilon-\epsilon_F}{kT}}$ goes to 0), and it is $\frac{1}{\infty+1} = 0$ for $\epsilon > \epsilon_F$ (for $\frac{\epsilon-\epsilon_F}{kT}$ goes to infinity then, so $e^{\frac{\epsilon-\epsilon_F}{kT}}$ does too). so $N = \frac{8\pi V}{c^3h^3} \int_0^{\epsilon_F} \epsilon^2 d\epsilon = \frac{8\pi V}{3c^3h^3} [\epsilon^3]_0^{\epsilon_F} = \frac{8\pi V}{3c^3h^3} \epsilon_F^3$

3 $\Rightarrow \epsilon_F = \sqrt[3]{\frac{N 3c^3 h^3}{8\pi V}} = \sqrt[3]{\frac{3N}{8\pi V}}\, ch$

c $E = \int_0^\infty \epsilon \cdot n(\epsilon) f(\epsilon) d\epsilon = \frac{8\pi V}{(ch)^3} \int_0^\infty \frac{\epsilon^3 d\epsilon}{e^{\beta(\epsilon-\mu)}+1}$, with same reasoning as with 5b, this gives

$2\frac{1}{2}$ $E = \frac{8\pi V}{(ch)^3} \int_0^{\epsilon_F} \epsilon^3 d\epsilon = \frac{8\pi V}{4c^3h^3} \epsilon_F^4 = \frac{3N\epsilon_F}{4}$

d $dE = TdS - pdV \Rightarrow p = -\left(\frac{\partial E}{\partial V}\right)_S = -\frac{\partial}{\partial V}\left(\frac{8\pi V}{4c^3h^3}\epsilon_F^4\right) =$

$1\frac{1}{2}$

$p = \frac{-8\pi}{4c^3h^3}\epsilon_F^4 + \frac{-8\pi V}{4c^3h^3} 4\epsilon_F^3 \cdot \frac{\partial \epsilon_F}{\partial V}$, $\frac{\partial \epsilon_F}{\partial V} = -ch \sqrt[3]{\frac{3N}{8\pi}} \frac{1}{3} V^{-\frac{4}{3}}$

$\Rightarrow p = \frac{-8\pi}{4c^3h^3} \frac{3N}{8\pi V} c^3h^3 \sqrt[3]{\frac{3N}{8\pi V}}\, ch + ch \sqrt[3]{\frac{3N}{8\pi}} \cdot \frac{1}{3} \cdot V^{-\frac{4}{3}} \cdot \frac{8\pi V}{4c^3h^3} \cdot 4 \cdot \frac{3N}{8\pi V} c^3h^3 = \frac{-3Nch}{4V}\sqrt[3]{\frac{3N}{8\pi V}} + \frac{Nch}{V^{4/3}}\sqrt[3]{\frac{3N}{8\pi V}} = \sqrt[3]{\frac{3N}{8\pi V}} \cdot \frac{Nch}{V}\left(\frac{1}{V^{1/3}} - \frac{3}{4}\right)$