PHY252 Final Assessment

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Q1 a) $A \to B$: $U_A = 5(0.1)(2) + 10$

$U_B = 5(0.1)(8) + 10$

$\Delta U = U_B - U_A = 14 - 11 = 3\,J.$

W along $A \to B$ is $W = -P\Delta V = -0.1(8-2) = -\frac{1}{2}$

Then $\Delta U = Q + W \Rightarrow Q = \Delta U - W = 3 - (-\frac{1}{2}) = \frac{7}{2}$

$$\boxed{W_{A\to B} = -\frac{1}{2}\,J, \quad Q_{A\to B} = \frac{7}{2}\,J \text{ (emitted)}}$$

$B \to C$: $\Delta U = U_C - U_B = (5(0.4)(5) + 10) - (5(0.1)(8) + 10)$

$= 6\,J$

$$W_{B\to C} = -\int_{V_i}^{V_f} P(V)\,dV, = -\left(\frac{1}{2}(8-5)(0.4-0.1) + (0.1)(8-5)\right)$$

$$\boxed{W_{B\to C} = -\frac{3}{4}J \qquad Q_{B\to C} = \frac{27}{4}\,J \text{ (emitted)}}$$

$C \to D$: $\Delta U = U_D - U_C = (5(0.4)(2) + 10) - (5(0.4)(5) + 10)$

$= -6\,J$

$W_{C\to D} = -P\Delta V = -(0.4)(5-2) = -\frac{6}{5}J$

Then since $\Delta U = W + Q$, $Q = \Delta U - W = -6J - (-\frac{6}{5}J)$

Thus $\boxed{W_{C\to D} = -\frac{6}{5}J, \quad Q = -\frac{24}{5} \text{ (absorbed)}}$

Lastly, $D \to A$. $\Delta U = U_A - U_D = ((0.1)(2)5 + 10) - ((0.4)(2)(5) + 10)$

$= -3\,J.$

No change in volume, so $W_{D\to A} = 0$. Then $Q = \Delta U = -3J$

Therefore $\boxed{W_{D\to A} = 0\,J, \quad Q = -3J \text{ (absorbed)}}$

Q1 b) As from part (a), the change in energy remains the same. That is,

$\Delta U = U_C - U_B = 6\,J \Rightarrow \Delta U_{C\to B} = -6J.$

However, the work done is $W = -\int_{V_i}^{V_f} P(V)\,dV$. Here,

$$P(V) = \frac{0.4}{V-4}\left(\frac{kPa}{m^3}\right).$$

We have that $V_i = 5\,m^3$, $V_f = 8\,m^3$, so

$$W = -\int_5^8 \frac{0.4}{V-4}\,dV = -0.4\log(V-4)\Big|_5^8 = -0.4(\log 4 - \cancel{\log 1}^{\,0})$$

$$= -0.4\log 4\ J$$

note I use log = ln.

Then the heat is $Q = \Delta U - W = -6 - (-0.4\log 4)$.

Therefore $\boxed{W_{n,C\to B} = -0.4\log 4\ J,\quad Q = -6 + 0.4\log 4.}$

↑ absorbed throughout this process.

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Q2 | 2) Box: area A, indistinguishable particles, 2 dof.

In momentum hypersphere:

$$U = \frac{1}{2m}(p_x^2 + p_y^2) \Rightarrow \text{circle of radius } \sqrt{2mU}.$$

# of distinct position states (is quantized) is $\frac{L}{\Delta x}$, in momentum space, $\frac{L_p}{\Delta p}$. Then $\frac{L L_p}{\Delta p \Delta x} \approx \frac{L L_p}{h}$ by uncertainty principle. For N molecules,

$$\Omega_N = \frac{1}{N!}\frac{A^N}{h^{2N}} \cdot (\text{area of momentum circle})$$

The area of the momentum hypersphere, however, is just given by $\frac{2\pi^{d/2}}{(\frac{d}{2}-1)!} r^{d-1}$, with $d = 2N$, $r = \sqrt{2mU}$,

$$\Omega_N = \frac{1}{N!}\frac{A^N}{h^{2N}} \cdot \frac{2\pi^N}{(N-1)!}(\sqrt{2mU})^{2N-1}.$$

Therefore for an ideal monatomic gas with N particles in the box,

$$\boxed{\Omega_N = \frac{1}{N!}\frac{A^N}{h^{2N}} \cdot \frac{2\pi^N}{(N-1)!}(2mU)^{\frac{2N-1}{2}}}.$$

b) By Stirling, $N! \approx N^N e^{-N}\sqrt{2\pi N}$ so taking the natural log,

$$S = K \log \Omega_N = K \log\left[\frac{1}{N!}\frac{A^N}{h^{2N}} \cdot \frac{2\pi^N N}{N!}(2mU)^{\frac{2N-1}{2}}\right]$$

$$= K\left(\log\left[\frac{A^N}{h^{2N}}\right] + \log\left[\frac{\pi^N N}{N!}\right] + \log\left[(2mU)^{\frac{2N-1}{2}}\right]\right)$$

expand this term

$$\rightarrow = \log(\pi^N N) - \log N! \approx N\log(\pi) + \log N - N\log N + N$$

$$= (N(\log\pi + 1) + \log N(1-N))$$

drop small factor

$$S = K\left(N\log\left(\frac{A}{h^2}\right) + N[\log\pi + 1] + \log N\,(1-N) + \frac{2N-1}{2}\log(2mU)\right)$$

Therefore the entropy is approximately.

$$\boxed{S = K\left[N \log\left(\frac{2m\pi 2UA}{h^2 N}\right)\right]} \quad \text{(dropping small factors of } N, \log N, \dots)$$

c) Since $\frac{1}{T} = \frac{\partial S}{\partial U}$, then $\frac{1}{T} = KN \frac{\partial}{\partial U} \log\left(\frac{2m\pi 2UA}{h^2 N}\right)$

$$= KN \frac{h^2 N}{2m\pi 2UA} \cdot \frac{2m\pi A}{h^2 N}$$

$$= \frac{KN}{U}$$

Therefore $\boxed{T = U \cdot \frac{N}{K}}$

or $\boxed{U = NKT}$. Yes, this makes sense, given equipartition, since $f = 2$ and the number of particles is N, so $U = \frac{1}{2} \cdot N \cdot f \cdot KT = \frac{1}{2} \cdot 2 \cdot N \cdot KT = NKT$.

d) The pressure is given by $P = T\left(\frac{\partial S}{\partial V}\right)_U$ or $T\left(\frac{\partial S}{\partial A}\right)_U$, force per unit area. We have that

$$\left(\frac{\partial S}{\partial A}\right)_U = KN \frac{\partial}{\partial A} \log\left(\frac{A}{h^2} \cdot \pi\right) = KN \cdot \frac{W^2}{\pi A} \cdot \frac{\pi}{W^2} = \frac{KN}{A}.$$

Then $\boxed{P = T\frac{KN}{A}}$.

Like the ideal gas law $PV = NKT$, $\boxed{PA = KNT}$, so yes, this does make sense given the ideal gas law.

e) From (b), $S = kN\log\left(\frac{2u\pi 2uA}{h^2 N}\right)$, and $\mu = -T\left(\frac{\partial S}{\partial N}\right)_{N,u}$,

So $\mu = -T \cdot \frac{\partial}{\partial N} Nk \log\left(\frac{2\pi m 2u A}{h^2 N}\right)$

$= -TK\left[\log\left(\frac{2\pi m 2u A}{h^2 N}\right) + N \cdot \frac{h^2 N}{2\pi m 2u A} \cdot \left(-\frac{2\pi u A m}{h^2 N^2}\right)\right]$

then approximating again (since KT = const, energy only cares about difference)

$$\boxed{\mu = -KT \log\left[\frac{A}{N}\left(\frac{2\pi m 2u}{h^2}\right)\right]}$$

As $\frac{N}{A} \to \infty$, $\frac{A}{N} \to 0$ so then $\log\left(\frac{A}{N}\right) \to -\infty$ or $\mu \to \infty$,

so the chemical potential will increase.

f) Sackur - Tetrode:

$$S = NK\left[\log\left(\frac{V}{N}\left(\frac{4\pi m 2u}{3Nh^2}\right)^{3/2}\right) + \frac{5}{2}\right].$$

At first, $T_0 = 300K$, $P_0 = 10^5$ Pa → lower T when holding $\frac{N}{V}$ (density) fixed. with $2u = N \cdot 3 \cdot \frac{1}{2}KT = \frac{3}{2}NKT$,

$S = NK\left[\log\left(\frac{V}{N}\left(\frac{2\pi m KT}{h^2}\right)^{3/2}\right) + \frac{5}{2}\right]$. For negative S,

$0 > NK\cdot\frac{5}{2} + NK\log\left(\frac{V}{N}\left(\frac{2\pi m KT}{h^2}\right)^{3/2}\right)$

so $-\frac{5}{2} > \log\left(\frac{V}{N}\left(\frac{2\pi m KT}{h^2}\right)^{3/2}\right)$

$e^{-5/2} > \frac{V}{N} \cdot \left(\frac{2\pi m KT}{h^2}\right)^{3/2} \to e^{-5/2 \cdot \frac{2}{3}} > \left(\frac{V}{N}\right)^{2/3} \cdot \frac{2\pi m KT}{h^2}$

So $$\boxed{T < e^{-\frac{5}{3}}\left(\frac{V}{N}\right)^{-\frac{2}{3}} \cdot \frac{h^2}{2\pi m K}}$$ predicts negative S.

with $\left(\frac{V}{N}\right)^{-2/3} = \left(\frac{kT}{P}\right)^{-2/3}$,

$h = 6.63 \times 10^{-34}$ J·s,

$k = 1.38 \times 10^{-23}$ J/K,

$P = 10^5$ Pa,

$T = 300$K

Then $T < e^{-5/3} \left(\frac{1.38 \times 10^{-23} \frac{J}{K} \cdot 300K}{10^5 \text{ Pa}} \right)^{-2/3} \cdot \frac{(6.63 \times 10^{-34})^2 \, J^2/s^2}{2\pi(4)(1.66 \times 10^{-27} kg)(1.38 \times 10^{-23} \frac{J}{K})}$

Numerically, $\boxed{T < 0.0559 \text{ K}}$ (at very low T)

PH4252 final

Q3] a) $N = N_g + N_\ell$ (gas ↓, liquid ↓) Vapour + liquid in equilibrium.

The Gibbs free energy can be given by

$$dG = \sum_i \mu_i \, dN_i \,, \quad \text{so}$$

$$G = \mu_g N_g + \mu_\ell N_\ell \,. \quad \text{This also implies}$$

$$\boxed{G = \mu_g N_g + \mu_\ell (N - N_g)}$$

b) If the radius of the bubble is r, then $V = \frac{4}{3}\pi r^3$.

If each gas molecule takes up v_g amount of volume, then

$$N_g = \frac{V}{v_g} = \frac{4\pi r^3}{3 v_g} \,. \quad \text{Then}$$

$$\boxed{G = \mu_g \left(\frac{4\pi r^3}{3 v_g}\right) + \mu_\ell \left(N - \frac{4\pi r^3}{3 v_g}\right).}$$

c) The surface area of the bubble is $4\pi r^2$, so

$$G = \mu_g \left\{\frac{4\pi r^3}{3 v_g}\right) + \mu_\ell \left(N - \frac{4\pi r^3}{3 v_g}\right) + G_{\partial\text{-Boundary}}$$

$$\boxed{G = \mu_g \left(\frac{4\pi r^3}{3 v_g}\right) + \mu_\ell \left(N - \frac{4\pi r^3}{3 v_g}\right) + 4\pi r^2 \sigma \,.}$$

d) The critical radius is the value r_c for which $\left.\frac{dG}{dr}\right|_{r_c} = 0$.

We have that

$$\frac{dG}{dr} = \mu_g \cdot \frac{4\pi r^2}{v_g} - \mu_\ell \frac{4\pi r^2}{v_g} + 8\pi r \sigma = 0$$

$$\Rightarrow \cancel{8}\pi r \sigma = \frac{4\pi r^2}{v_g} (\mu_\ell - \mu_g)$$

e) The two states are given when the electron is ionized and when the electron is bound,

ion: $E=0,\ N=0$

bound: $E=-I,\ N=1$ so the grand partition function is

$$\mathcal{Z} = 1 + \exp\left[-\frac{1}{kT}\left[-I-\mu_e\right]\right]$$

f) The probability of measuring an ionized atom is having $E=0,\ n=0,$ which then is

$$P(\text{ionized}) = \frac{1}{1+e^{-\frac{1}{kT}\left[-I-\mu_e\right]}}$$

g) For electrons, the chemical potential can be determined by

$$\mu = -kT \log\left(\frac{V}{N}\cdot\frac{\cancel{Z_{int}}}{V_Q}\right)$$ → neglect internal contributions

$$\mu_e = -kT \log\left(\frac{V}{N_c}\cdot\frac{1}{V_Q}\right)$$

h) Now $N_c = P_{\text{ionized}}\, N = \dfrac{N}{1+e^{-\frac{1}{kT}\left(-I+kT\log\left(\frac{V}{N_c}\cdot\frac{1}{V_Q}\right)\right)}}$

so $N_c = \dfrac{N}{1+e^{I/kT}\cdot\left(\frac{V}{N_c}\cdot\frac{1}{V_Q}\right)^{-1}} \Rightarrow N_c\left(1+e^{I/kT}\left(\frac{V}{N_c}\cdot\frac{1}{V_Q}\right)^{-1}\right) = N$

$$N_c + e^{I/kT}\, N_c^2 \cdot \frac{V_Q}{V} = N.$$

Q4) 2) $Z = e^{-\beta E(S_1)} + e^{-\beta E(S_2)}$

$$P(\text{excited}) = \frac{e^{-\beta E(S_2)}}{e^{-\beta E(S_1)} + e^{-\beta E(S_2)}}$$

$$P(\text{ground}) = \frac{e^{-\beta E(S_1)}}{e^{-\beta E(S_1)} + e^{-\beta E(S_2)}}$$

$P_{ground} + P_{excited} = 1$

$N_1 = P_{ground}\, N, \quad N_2 = P_{excited}\, N \qquad N = N_1 + N_2 = \text{const.}$

$$\Rightarrow \frac{dN_1}{dt} = A N_2, \quad \frac{dN_2}{dt} = \frac{B}{u(f)} N_1 \qquad \Rightarrow \frac{dN_1}{dt} = -\frac{dN_2}{dt}$$

$$\boxed{\frac{dN_1}{dt} = \left(\frac{BN_2}{u(f)} - AN_1\right)} = \frac{\text{photons given} - \text{photons taken away}}{\text{unit time}}$$

b) $$u(f) = \frac{8\pi}{(hc)^3} \frac{\epsilon^3}{e^{\epsilon/kT} - 1}$$

At equilibrium, $\dot{N}_1 = 0$.

And $\frac{N_2}{N_1} = e^{-\beta[E(S_2) - E(S_1)]} = e^{-\beta\epsilon}$

$$AN_1 = BN_2 \cdot \frac{e^{\epsilon/kT} - 1}{\epsilon^3} \cdot \frac{(hc)^3}{8\pi}$$

Then $\frac{A}{B} = \frac{N_2}{N_1}$

$$\boxed{\frac{A}{B} = e^{-\beta\epsilon} \cdot \frac{(hc)^3}{8\pi} \frac{\epsilon^3}{e^{\epsilon/kT} - 1}}$$

c) Photon gas in a box:

$$F = U - TS$$

P.245, entropy of photon gas is

$$S(T) = \frac{32\pi^5}{45} V \left(\frac{kT}{hc}\right)^3 K$$

Total E given by Planck: $U = \frac{8\pi^5 (kT)^4}{15 (hc)^3} V$

Thus

$$\boxed{F = \frac{8\pi^5 (kT)^4}{15 (hc)^3} V - TV \cdot \frac{32\pi^5}{45} \left(\frac{kT}{hc}\right)^3 K}$$

d) Since $U = \frac{8\pi^5}{15} \frac{(kT)^4}{(hc)^3} V$, thus

$$F = U - \frac{32\pi^5}{45} \cdot \frac{(kT)^4}{(hc)^3} \cdot V$$

$$\frac{32}{45} = \frac{32}{3 \cdot 15}$$

$$= U - \frac{32}{3 \cdot 8} \cdot \frac{8}{15} \pi^5 \frac{(kT)^4}{(hc)^3} \cdot V$$

$$= U - \frac{32}{24} U$$

$$\boxed{F = -\frac{1}{3} U}$$

e) $$S = -\left(\frac{\partial F}{\partial T}\right)_V = -\frac{11}{24}\left(\frac{\partial U}{\partial T}\right)_V = -\frac{1}{3} \cdot \left(\frac{\partial}{\partial T} \frac{8\pi^5 (kT)^4}{15 (hc)^3} V\right)_V$$

$$\boxed{S = -\frac{32}{45} K \cdot \pi^5 \left(\frac{kT}{hc}\right)^3 V}$$ ✓

f) $$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$

$$= -\frac{\partial}{\partial V}\left(-\frac{1}{3}\frac{8\pi^5 (kT)^4}{15 (hc)^3} V\right)$$

$$\boxed{P = \frac{8\pi^5 (kT)^4}{45 (hc)^3}}$$