Problem 1

(a) $$W_{34} = \int_{V}^{10V} P\,dV = Nk \cdot 1.5T \cdot \int_{V}^{10V} \frac{dV}{V} = 1.5NkT\ln 10$$

$$W_{12} = \int_{10V}^{V} P\,dV = Nk \cdot T \cdot \int_{10V}^{V} \frac{dV}{V} = -NkT\ln 10$$

Total work: $$\boxed{\oint P\,dV = W_{12} + W_{34} = 0.5NkT \ln 10}$$

(since no work is done in 2-3 and 4-1)

(b) $\Delta U = Q + W$, $\Delta U = 0$ in 3-4 since temperature doesn't change

$\Rightarrow Q_{34} = W_{34} = 1.5NkT\ln 10$

(c) $Q_{23} = \Delta U$ since no work is done. $U = \frac{3}{2}NkT \Rightarrow$

$$Q_{23} = \frac{3}{2}Nk(1.5T - T) = \boxed{\frac{3}{4}NkT}$$

(d) Total heat absorbed $= Q_{34} + Q_{23} = NkT(1.5\ln 10 + 0.75)$

$$\boxed{e = \frac{\text{work performed}}{\text{heat absorbed}} = \frac{0.5NkT\ln 10}{1.5NkT\ln 10 + 0.75NkT}}$$

(e) For a Carnot engine:

$$e_{carnot} = 1 - \frac{T_{low}}{T_{high}} = 1 - \frac{T}{1.5T} = \frac{0.5}{1.5} = \boxed{33.3\%}$$

here, $$e = \frac{0.5}{1.5 + 0.75/\ln 10} = \frac{0.5}{1.5 + 0.326} = \boxed{27.4\% < 33.3\%}$$

That's because some heat is absorbed at temperatures smaller than the highest temperature in the step 2-3.

Problem 2

N atoms, n in excited state of energy ε, N-n in state of energy 0.

For $n=0$, $\Omega(n=0)=1$

$n=1$, $\Omega(n=1)=N$ (excited atom can be one of N)

$n=2$ $\quad \Omega(n=2)=\frac{N(N-1)}{2}$

$n=N-1$ $\quad \Omega(N-1)=N$

$n=N$ $\quad \Omega(N)=1$

(b) $\Omega(n)=\frac{N!}{n!(N-n)!}$; using $n!\doteq n^n e^{-n}$,

$$\Omega(n)=\frac{N^N e^{-N}}{n^n e^{-n}(N-n)^{N-n}e^{-N+n}}=\boxed{\frac{N^N}{n^n(N-n)^{N-n}}}$$

(c) $\ln\Omega(n)=N\ln N-n\ln n-(N-n)\ln(N-n)$

$$\frac{\partial\ln\Omega}{\partial n}=-\ln n-1+\ln(N-n)+1=\ln\left(\frac{N-n}{n}\right)$$

maximum is for $\frac{\partial\ln\Omega}{\partial n}=0=\ln\frac{N-n}{n}\Rightarrow\frac{N-n}{n}=1\Rightarrow N-n=n\Rightarrow\boxed{n=\frac{N}{2}}$

(d) $\frac{1}{T}=k\frac{\partial\ln\Omega}{\partial(n\varepsilon)}=\frac{k}{\varepsilon}\frac{\partial\ln\Omega}{\partial n}=\frac{k}{\varepsilon}\ln\left(\frac{N-n}{n}\right)\Rightarrow\boxed{T=\frac{\varepsilon}{k\ln\left(\frac{N-n}{n}\right)}}$

(e) $\frac{\varepsilon}{kT}=\ln\frac{N-n}{n}\Rightarrow N-n=ne^{\varepsilon/kT}\Rightarrow n(1+e^{\varepsilon/kT})=N\Rightarrow\boxed{n=\frac{N}{e^{\varepsilon/kT}+1}}$

(f) $T_1=\frac{\varepsilon}{k\ln\left(\frac{990}{10}\right)}=0.218\,\frac{\varepsilon}{k}$

$T_2=\frac{\varepsilon}{k\ln\frac{999{,}000}{1000}}=0.145\,\frac{\varepsilon}{k}$; since $T_2<T_1$, energy will flow from 1 to 2.

Problem 3

(a) $H = U + PV$, $dU = TdS - PdV \Rightarrow \boxed{dH = TdS + VdP}$

(b) $dS = \left.\frac{\partial S}{\partial T}\right)_P dT + \left.\frac{\partial S}{\partial P}\right)_T dP \Rightarrow$

$$\boxed{dH = T\left.\frac{\partial S}{\partial T}\right)_P dT + \left(T\left.\frac{\partial S}{\partial P}\right)_T + V\right) dP}$$

(c) $T\left.\frac{\partial S}{\partial T}\right)_P = C_P$ by definition

$\left.\frac{\partial S}{\partial P}\right)_T = -\left.\frac{\partial V}{\partial T}\right)_P$ by a Maxwell relation. Since $\beta = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right)_P \Rightarrow$

$\left.\frac{\partial S}{\partial P}\right)_T = -V \cdot \beta$

$\Rightarrow dH = C_P\, dT + (V - T \cdot V \cdot \beta)\, dP$

$\Rightarrow \boxed{dH = C_P\, dT + V(1 - T\beta)\, dP}$

(d) For process at constant H, $dH = 0 \Rightarrow$

$\Rightarrow C_P\, dT + V(1 - T\beta)\, dP = 0 \Rightarrow \boxed{\left.\frac{\partial T}{\partial P}\right)_H = \frac{V}{C_P}(T\beta - 1)}$

$\Rightarrow \boxed{\mu_{JT} = \frac{V}{C_P}(T\beta - 1)}$

For ideal gas: $V = \frac{NkT}{P} \Rightarrow \left.\frac{\partial V}{\partial T}\right)_P = \frac{Nk}{P} \Rightarrow \beta = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right)_P = \frac{Nk}{PV} = \frac{1}{T}$

So $\beta = \frac{1}{T} \Rightarrow \boxed{\mu_{JT} = \frac{V}{C_P}\left(T \cdot \frac{1}{T} - 1\right) = 0}$

Problem 4

$$\bar{E} = \frac{2\varepsilon e^{-\beta\varepsilon} + 2\cdot 10\varepsilon e^{-10\beta\varepsilon}}{2 + 2e^{-\beta\varepsilon} + 2e^{-10\beta\varepsilon}} = \boxed{\varepsilon \frac{e^{-\beta\varepsilon} + 10 e^{-10\beta\varepsilon}}{1 + e^{-\beta\varepsilon} + e^{-10\beta\varepsilon}}}$$

(i) $T = \infty \Rightarrow \beta = 0 \Rightarrow \bar{E} = \varepsilon \frac{1+10}{3} = \frac{11}{3}\varepsilon = \boxed{3.67\,\varepsilon}$

(ii) $T = 0, \beta \to \infty, e^{-\beta\varepsilon} \to 0, e^{-10\beta\varepsilon} \to 0 \Rightarrow \boxed{\bar{E} = 0}$

(iii) if $\bar{E} = \varepsilon \Rightarrow 1 + \cancel{e^{-\beta\varepsilon}} + e^{-10\beta\varepsilon} = \cancel{e^{-\beta\varepsilon}} + 10 e^{-10\beta\varepsilon} \Rightarrow$

$$9 e^{-10\beta\varepsilon} = 1 \Rightarrow 10 \frac{\varepsilon}{kT} = \ln 9 \Rightarrow \boxed{kT = \frac{10}{\ln 9}\varepsilon = 4.55\varepsilon}$$

(b) $\boxed{U = N\bar{E} = N\varepsilon \frac{e^{-\beta\varepsilon} + 10 e^{-10\beta\varepsilon}}{1 + e^{-\beta\varepsilon} + e^{-10\beta\varepsilon}}}$; $\boxed{Z = \left(2 + 2e^{-\beta\varepsilon} + 2e^{-10\beta\varepsilon}\right)^N}$

$$\boxed{F = -kT\ln Z = -NkT\ln\left(2 + 2e^{-\beta\varepsilon} + 2e^{-10\beta\varepsilon}\right)}$$

$$F = U - TS \Rightarrow TS = U - F \Rightarrow \boxed{S = \frac{U-F}{T}}$$

(c) For $T \to 0$: $\frac{U}{T} \to \frac{N\varepsilon e^{-\beta\varepsilon}}{T} \to 0$

$$\frac{F}{T} \to -Nk\ln(2 + 2\cdot 0 + 2\cdot 0) = -Nk\ln 2 \Rightarrow \boxed{S = Nk\ln 2}$$

For $T \to \infty$, $\frac{U}{T} \to \frac{N\varepsilon\cdot 11}{3T} \to 0$, $\frac{F}{T} \to -Nk\ln(2+2+2) \Rightarrow \boxed{S = Nk\ln 6}$

(d) For $T \to 0$, $U \to N\varepsilon e^{-\varepsilon/kT}$, $\boxed{\frac{\partial U}{\partial T} = C \to 0}$

For $T \to \infty$, $U \to N\frac{\left[\varepsilon\left(1 - \frac{\varepsilon}{kT}\right) + 10\varepsilon\left(1 - 10\frac{\varepsilon}{kT}\right)\right]}{1 + 1 - \varepsilon/kT + 1 - 10\frac{\varepsilon}{kT}}$, $\boxed{\frac{\partial U}{\partial T} = C \to 0}$

(e) For low T, $U = N\varepsilon e^{-\varepsilon/kT}$, $C = N\left(\frac{\varepsilon}{kT}\right)^2 k e^{-\varepsilon/kT} = Nk\cdot 10^2 e^{-10} = \boxed{0.0045\,Nk}$

Problem 5

$$\mathcal{Z} = \sum_s e^{-\beta(E(s)-\mu N(s))} = \sum_n e^{-\beta(n\varepsilon - n\mu)}$$ for a single state.

i.e.: S are the states of the system with n particles in energy state ε. So

$E(s) - \mu N(s) = 0$ if there is no particle

$\varepsilon - \mu$ if there is $n=1$ particle

$2\varepsilon - 2\mu = 2(\varepsilon-\mu)$ if there are $n=2$ particles.

$$\Rightarrow \boxed{\mathcal{Z} = 1 + e^{-\beta(\varepsilon-\mu)} + e^{-2\beta(\varepsilon-\mu)}} \quad (a)$$

(b) $$\boxed{P(n) = e^{-\beta n(\varepsilon-\mu)} / \mathcal{Z}}$$

(c) $$\bar{n} = \sum_{n=0}^{2} n P(n) = \sum_{n=1}^{2} n P(n) = \boxed{\frac{e^{-\beta(\varepsilon-\mu)} + 2e^{-2\beta(\varepsilon-\mu)}}{1+e^{-\beta(\varepsilon-\mu)} + e^{-2\beta(\varepsilon-\mu)}}}$$

(d) At very low temperatures:

$e^{-\beta(\varepsilon-\mu)} \approx 0$ for $\varepsilon > \mu$

$e^{-2\beta(\varepsilon-\mu)} \gg e^{-\beta(\varepsilon-\mu)}$ for $\varepsilon < \mu$

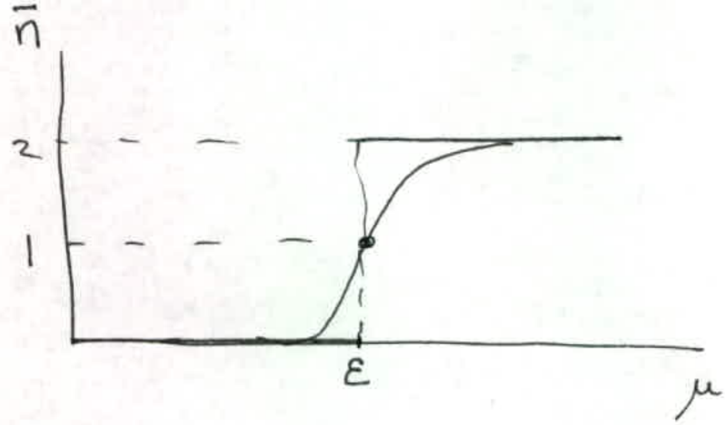
$\Rightarrow$ for $\varepsilon < \mu$

$$\bar{n} \approx \frac{2e^{-2\beta(\varepsilon-\mu)}}{e^{-2\beta(\varepsilon-\mu)}} \cong 2$$

for $\varepsilon > \mu$ $\quad \bar{n} \cong 0$

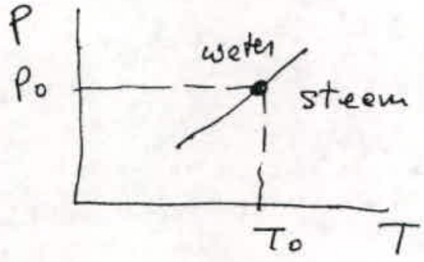
for $\varepsilon = \mu$: $\bar{n} = \frac{1+2}{3} = 1$

for any β



Problem 6

(a) The phase diagram is



$T_0 = 423°K$

For each T there is one P where the two phases coexist.

Initially, $T_0 = 150°C$, P_0 is the external pressure

(a) If $T < T_0$, the coexistence can only occur at a $P < P_0$.

Since the external pressure is larger, piston moves down and all the steam condenses into liquid water.

Hence $n_{steam} = 0$, $n_{water} = 2$

(b) Similarly, $n_{steam} = 2$, $n_{water} = 0$. Piston moves up, all the water evaporates.

(c) The heat goes into latent heat of vaporization, since temperature doesn't change. As more water evaporates, piston moves up, so work is done by the system. $W = P_0 V - P_0 V_0 = RT_0(n - n_0)$

So $Q = 10{,}000\,J = L(n-n_0) + RT_0(n-n_0) = (L + RT_0)(n-n_0) =$

$= (38{,}090 + 8.31 \times 423)\,J\,(n-n_0) = 41{,}605\,(n-n_0) \Rightarrow$

$n - n_0 = 0.24 \Rightarrow 0.24$ moles of water evaporate $\Rightarrow$

$\boxed{n_{steam} = 1.24 \text{ moles}, \quad n_{water} = 0.76 \text{ moles}}$

(d) The equilibrium temperature and pressure satisfy

$$P = C e^{-L/RT} \quad \text{where } C \text{ is a constant.}$$

initially $\quad P_0 = C e^{-L/RT_0} \quad$ with $T_0 = 423\,°K$

then, $\quad P_1 = C e^{-L/RT_1} \quad$ with $T_1 = 433\,°K$

$$\Rightarrow \quad P_1 = P_0 e^{\frac{L}{R}\left(\frac{1}{T_0} - \frac{1}{T_1}\right)}$$

$$\frac{L}{R}\left(\frac{1}{T_0} - \frac{1}{T_1}\right) = \frac{38{,}090}{8.31}\left(\frac{1}{423} - \frac{1}{433}\right) = 0.250$$

$$\Rightarrow \boxed{P_1 = P_0 e^{0.25} = 1.284 P_0}$$

From $PV = nRT \Rightarrow n = \frac{PV}{RT} \Rightarrow$

$$n_0 = 1\,\text{mol} = \frac{P_0 V}{RT_0}$$

$$n_1 = \frac{P_1 V}{RT_1} = \frac{P_1}{P_0} \cdot \frac{T_0}{T_1} \cdot \frac{P_0 V}{RT_0} = 1.284 \cdot \frac{423}{433} \cdot 1\,\text{mol}$$

$$\Rightarrow \boxed{\boxed{n_1 = 1.254 \text{ moles}} \text{ of steam} \quad n_{water} = 0.746 \text{ moles}}$$