Solutions to practice problems

1) a) $dH = TdS + Vdp \rightarrow dS = \frac{1}{T}dH - \frac{V}{T}dp$

$$\text{So,} \quad \left.\frac{\partial S}{\partial H}\right|_p = \frac{1}{T}$$

Chain rule: $\left.\frac{\partial S}{\partial H}\right|_p = \left.\frac{\partial S}{\partial T}\right|_p \left.\frac{\partial T}{\partial H}\right|_p = \frac{1}{T}$

$$\text{So,} \quad \boxed{\left.\frac{\partial S}{\partial T}\right|_p = \frac{1}{T}\left.\frac{\partial H}{\partial T}\right|_p = \frac{C_p}{T}}$$

b) $dS = \left.\frac{\partial S}{\partial T}\right|_p dT + \left.\frac{\partial S}{\partial p}\right|_T dp$ $\quad \left.\frac{\partial S}{\partial p}\right|_T = -\left.\frac{\partial V}{\partial T}\right|_p$

$= \frac{C_p}{T}dT + \left(-\left.\frac{\partial V}{\partial T}\right|_p\right)dp$ $\quad \beta \equiv \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_p$

$$\boxed{dS = \frac{C_p}{T}dT - V\beta\, dp}$$

c) $dA = -SdT - pdV \overset{\text{Maxwell}}{\Rightarrow} \left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial p}{\partial T}\right|_V$

for ideal gas: $p = \frac{nRT}{V} \Rightarrow \left.\frac{\partial p}{\partial T}\right|_V = \frac{nR}{V} = \frac{p}{T}$

$$\text{So,} \quad \boxed{\left.\frac{\partial S}{\partial V}\right|_T = \frac{p}{T}}$$

d) applying Maxwell to the result of part b:

$$\frac{\partial}{\partial p}\left(\frac{C_p}{T}\right)\bigg|_T = -\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial T}\bigg|_p\right)_p$$

$$\boxed{\frac{1}{T}\frac{\partial C_p}{\partial p}\bigg|_T = -\frac{\partial^2 V}{\partial T^2}\bigg|_p}$$

2) $\Omega_{para} = \dfrac{20!}{n_p!\,(20-n_p)!}$

$\Omega_{einstein} = \dfrac{(n_e+4-1)!}{n_e!\,(4-1)!} = \dfrac{(n_e+3)!}{n_e!\,3!}$

macrostate	Ω_p	Ω_{ein}	$\Omega_{TOT} = \Omega_p \times \Omega_{ein}$
$n_p=0$ $n_e=2$	1	10	10
$n_p=1$ $n_e=1$	20	4	80
$n_p=2$ $n_e=0$	190	1	190

Most microstates associated with $n_p=2$, $n_e=0$

The division of energy with both excitations in the paramagnet is the most probable.

3) from $dS = \frac{1}{T}dE + \frac{P}{T}dV$ we know

$$\left.\frac{\partial S}{\partial E}\right|_V = \frac{1}{T} \qquad \left.\frac{\partial S}{\partial E}\right|_V = \frac{3}{4}a\left(\frac{V}{U}\right)^{1/4}$$

$$\Rightarrow \boxed{T = \frac{4}{3a}\left(\frac{U}{V}\right)^{1/4}}$$

$$\left.\frac{\partial S}{\partial V}\right|_E = \frac{P}{T} = \frac{a}{4}\left(\frac{U}{V}\right)^{3/4}$$

combine with T from above to get

$$\boxed{P = \frac{1}{3}\frac{U}{V}}$$

4) $$C_p = \frac{dq_p}{dT} \qquad q_p = \int_{T_1}^{T_2} C_p\,dT = C_p(T_2 - T_1)$$

$q = \Delta H$ at const. P; H is state function

$$dS = \frac{dq_{rev}}{T} = \frac{dq_p}{T} = \frac{C_p\,dT}{T}$$

$$\Delta S_{sys} = \int_{T_1}^{T_2} \frac{C_p\,dT}{T} = C_p \ln(T_2/T_1)$$

$$\Delta S_{res.} = \frac{q_{res}}{T_2} = \frac{-q_p}{T_2} = -C_p\frac{(T_2 - T_1)}{T_2}$$

$$\boxed{\Delta S_{TOT} = \Delta S_{sys} + \Delta S_{res} = C_p \ln(T_2/T_1) - C_p\frac{(T_2 - T_1)}{T_2}}$$

5) a) $\boxed{U = N\varepsilon_0}$

b) $\boxed{\frac{M!}{(M-N)!\,N!} = \Omega(M,N)}$

c) $T^{-1} = \frac{\partial S}{\partial E}$ $\qquad S = k_B \ln \Omega$

$\overset{\text{(Stirling)}}{\approx} k_B\left[M\ln M - N\ln N - (M-N)\ln(M-N)\right]$

$T^{-1} = \frac{\partial S}{\partial N}\frac{\partial N}{\partial E}$

$T^{-1} = \frac{\partial S}{\partial N}\frac{1}{\varepsilon_0} = \frac{k_B}{\varepsilon_0}\left[-\ln N - 1 + \ln(M-N) + 1\right]$

$T^{-1} = \frac{k_B}{\varepsilon_0}\ln\left(\frac{M-N}{N}\right)$

$\boxed{T = \frac{\varepsilon_0}{k_B}\left[\ln\left(\frac{M-N}{N}\right)\right]^{-1}}$

6) We want to calculate ΔH for $\quad (\Delta H = q_p)$

$H_2O(l, 473k, 1atm) \longrightarrow H_2O(g, 473, 1atm)$

but are only given ΔH for

$H_2O(l, 373, 1atm) \longrightarrow H_2O(g, 373, 1atm)$

but since H is a state function we can calculate the desired quantity as:

$\Delta H_{473\,\text{boil}} = \Delta H_{\text{cool}}\text{ liquid} + \Delta H_{373\,\text{boil}} + \Delta H_{\text{heat}}\text{ gas}$

$$\Delta H_{\substack{cool \\ liq}} = C_{p(\ell)}(373-473) = -7500 \text{ J/mol}$$

$$\Delta H_{\substack{heat \\ gas}} = C_{p(g)}(473-373) \quad +350 \text{ J/mol}$$

$$q_{\substack{473 \\ boil}} = \Delta H_{\substack{473 \\ boil}} = -7500 + 40700 + 350 \quad \text{J/mol}$$

$$= \boxed{33{,}600 \text{ J/mol}}$$