

Solutions to practice problems

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

$$S_0, \quad \left. \frac{\partial S}{\partial H} \right|_p = \frac{1}{T}$$

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

$$S_0, \quad \boxed{\left. \frac{\partial S}{\partial T} \right|_p = \frac{1}{T} \left. \frac{\partial H}{\partial T} \right|_p = \frac{C_p}{T}}$$

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

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

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

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

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

$$S_0, \quad \boxed{\left. \frac{\partial S}{\partial V} \right|_T = \frac{p}{T}}$$

d) applying Maxwell to the result of part b:

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

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

$$2) \quad \Omega_{\text{para}} = \frac{20!}{n_p! (20-n_p)!}$$

$$\Omega_{\text{exciton}} = \frac{(n_e+4-1)!}{n_e! (4-1)!} = \frac{(n_e+3)!}{n_e! 3!}$$

macrostate	Ω_p	Ω_{ex}	$\Omega_{\text{tot}} = \Omega_p \times \Omega_{\text{ex}}$
$n_p=0 \quad n_e=2$	1	10	10
$n_p=1 \quad n_e=1$	20	4	80
$n_p=2 \quad n_e=0$	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

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

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

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

combine with T from above to get

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

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

$q = \Delta H$ 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) $U = N\varepsilon_0$

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

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

$S = k_B \ln \Omega$

(Stirling)

$\approx k_B [M \ln M - N \ln N - (M-N) \ln (M-N)]$

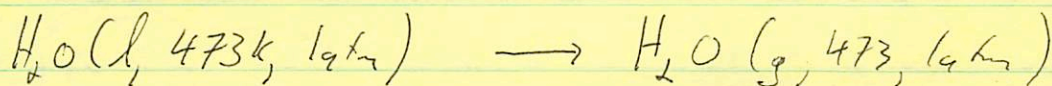
$T^{-1} = \frac{\partial S}{\partial N} \frac{\partial N}{\partial E}$

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

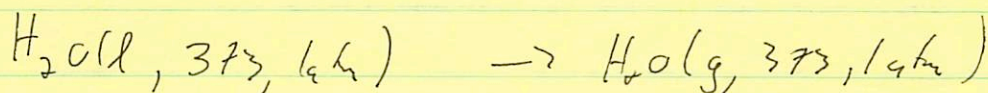
$T^{-1} = \frac{k_B}{\varepsilon_0} \ln \left(\frac{M-N}{N} \right)$

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

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



but are only given ΔH for



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

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

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

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

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

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

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