

5.23) (a)
$$d\Phi = dU - TdS - (dT)S - (d\mu)N - \mu dN$$

$$= (TdS - PdV + \mu dN) - T(dS) - S(dT) - N d\mu - \mu(dN)$$

$$= -PdV - SdT - Nd\mu.$$

Thus, $\partial_T \Phi = -S$, $\partial_V \Phi = -P$, $\partial_\mu \Phi = -N$.

(b) $dS_{\text{univ.}} = dS_{\text{env.}} + dS = \frac{dU_{\text{env.}}}{T} + \frac{dQ}{T}$

The problem indicates that N and S can change, so we assume that V does not. So, $dU = TdS + \mu dN$. Thus,

$$dS_{\text{univ.}} = \frac{dU_{\text{env.}} - \mu dN_{\text{env.}}}{T} + dS = -\frac{(dU - \mu dN)}{T} + dS$$

$$= -\frac{(dU - TdS - \mu dN)}{T} = -\frac{d\Phi}{T}. \text{ Thus, for } dS_{\text{univ.}} > 0 \text{ we must have } d\Phi < 0.$$

(c) We know that the extensive expression for U which matches its differential expression and is in terms of other extensive quantities is $U = TS - PV + \mu N$. Thus, $\Phi = U - TS - \mu N = -PV$.

(d) Treating a one-electron H atom as a thermodynamic system makes very little sense. We can compute $\mu \equiv \left(\frac{\partial U}{\partial N}\right)_{S,V}$ since $S=0$ for both states and V does not change. Hence $\mu = -13.6 \text{ eV}$.

The idea that a single e^- constitutes an "ideal gas" is also far-fetched. And we should not use the Sackur-Tetrode equation because it starts with an approximate formula (2.40) and then makes another approximation: the Stirling approximation. And we are told that $\Omega = 1$ with and without the e^- , so $S=0$ either way. Better to wait for the Boltzmann Factor.