Problem 8.3

Use $\ell_s = \ell_m + \ell_v$

and $\ell = T \Delta V \left(\frac{dP}{dT}\right)$

$$\Rightarrow \quad T_0 (v_{gas} - v_{sol}) \left(\frac{dP}{dT}\right)_s$$

$$= T_0 (v_{liq} - v_{sol}) \left(\frac{dP}{dT}\right)_m + T_0 (v_{gas} - v_{liq}) \left(\frac{dP}{dT}\right)_v.$$

It's easy to solve for $\left(\frac{dP}{dT}\right)_s$ from above.

Problem 8.10.

Let's divide the substance into small volume elements V_i which contains E_i energy and N_i particles.

Then the total entropy

$$S = \sum_i S_i (E_i, N_i)$$

In equilibrium any exchange of energy between volume elements must result in zero entropy change:

$$dS = 0 = \frac{\partial S_i}{\partial E_i} dE_i + \frac{\partial S_j}{\partial E_j} dE_j$$

But $dE = dE_i + dE_j = 0$

$$\Rightarrow \frac{\partial S_i}{\partial E_i} = \frac{\partial S_j}{\partial E_j}$$

$$\Rightarrow T_i = T_j \quad \left(\text{notice } S \propto \log \Omega \Rightarrow \frac{\partial S}{\partial E} \propto T^{-1}\right).$$

Similarly, for exchange of particles between volume elements

$$dS = \frac{\partial S_i}{\partial N_i} dN_i + \frac{\partial S_j}{\partial N_j} dN_j = 0 \quad , \text{ use } dN_i = -dN_j$$

$$\Rightarrow \frac{\partial S_i}{\partial N_i} = \frac{\partial S_j}{\partial N_j}$$

$$\Rightarrow \mu_i = \mu_j$$

Problem 8.11

(a) Chemical potential $\mu = \frac{\partial F}{\partial N}$.

$$F = -kT \log Z.$$

The partition function

$$Z = \frac{1}{h_0^{3N}} \int d^3\vec{r}_1 \cdots d^3\vec{r}_N \, d^3\vec{p}_1 \cdots d^3\vec{p}_N \, e^{-\beta E}$$

where $E = \sum_i \left(\frac{\vec{p}_i^{\,2}}{2m} + mg z_i \right) \rightarrow$ potential energy.

Consider a small volume element such that the potential energy is approximately constant:

$$E = \left(\sum_i \frac{\vec{p}_i^{\,2}}{2m} \right) + N mg z_0$$

$\hookrightarrow$ assume all $z_i \approx z_0$

$$\Rightarrow \quad Z = \left(\zeta \cdot e^{-\beta m g z_0} \right)^N / N!$$

where ζ is the single-particle partition function for ideal gases in the absence of gravity. (See (7.2.5)).

$$\Rightarrow \quad F = -kT \log Z$$

$$= -kTN \left[\log \frac{V}{h_0^3} - \frac{3}{2} \log \beta + 1 + \frac{3}{2} \log \frac{2\pi m}{h_0^2} \right] + mg z_0 \beta$$

$$\mu = \frac{\partial F}{\partial N} = mgz_0 - kT\left[\log\frac{V}{N} - \frac{3}{2}\log\beta + \frac{3}{2}\log\frac{2\pi m}{h_0^2}\right]$$

use equation of state we have

$$\frac{V}{N} = \frac{kT}{P}$$

$$\Rightarrow \mu = mgz_0 - kT\left[\log\frac{kT}{P} + \frac{3}{2}\log kT + \frac{3}{2}\log\frac{2\pi m}{h_0^2}\right]$$

(b) $\frac{\partial\mu}{\partial z_0} = 0 \Rightarrow \quad mg + \frac{kT}{P}\frac{dP}{dz_0} = 0.$

$$\Rightarrow \quad \frac{dP}{P} = \frac{mg}{kT}dz_0$$

or $\quad P = P(0)\, e^{-\frac{mgz_0}{kT}}$

<u>Problem 9.2</u>

(a) $\log Z_{FD} = -\beta\mu N + \sum_r \log\left(1 + e^{-\beta(\varepsilon_r - \mu)}\right)$

$$\bar{n}_r = \frac{1}{e^{\beta(\varepsilon_r-\mu)}+1}$$

$\bar{E} = \sum_r \varepsilon_r \bar{n}_r \; ; \; \sum_r \bar{n}_r = N.$

$$S = k(\log Z + \beta\bar{E})$$

$$= k\left[\sum_r \bar{n}_r \beta(\varepsilon_r - \mu) + \sum_r \log\left(1 + e^{-\beta(\varepsilon_r-\mu)}\right)\right]$$

But since $e^{\beta(\varepsilon_r - \mu)} = \frac{1}{\bar{n}_r} - 1$

$$\Rightarrow S_{FD} = -k \sum_r \left[\bar{n}_r \log \bar{n}_r + (1-\bar{n}_r) \log(1-\bar{n}_r) \right]$$

(b) For BE statistics, it's easy to repeat (a) to obtain

$$S_{BE} = -k \sum_r \left[\bar{n}_r \log \bar{n}_r + (1+\bar{n}_r) \log(1+\bar{n}_r) \right]$$

(c). For $\bar{n}_r \ll 1$

$$\left.\begin{matrix} S_{FD} \\ S_{BE} \end{matrix}\right\} \longrightarrow -k \sum_r \bar{n}_r \log \bar{n}_r$$