Solutions to Problem Set 8

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8.1 Chemical Equilibrium

Reif §8.12: At a fixed temperature $T = 1200K$ the gases

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

are in chemical equilibrium in a vessel of volume V. If the volume of this vessel is increased, its temperature being maintained constant, does the relative concentration of CO_2 increase, decrease, or remain the same?

At constant V, T in equilibrium, F is minimized. This imples that

$$dF = 0 = -S\cancelto{0}{dT} - p\cancelto{0}{dV} + \sum_i \mu_i dN_i = \mu_{CO_2} dN_{CO_2} + \mu_{H_2} + dN_{H_2} + \mu_{CO} dN_{CO} + \mu_{H_2O} dN_{H_20}$$

From the chemical equation we know that $dN_{CO_2} = dN_{H_2} = -dN_{CO} = -dN_{H_2O}$ and thus

$$\mu_{CO_2} + \mu_{H_2} - \mu_{CO} - \mu_{H_2O} = 0$$

But we also know (from Reif §8.10.24) that

$$\mu = -kT \ln \frac{\zeta'(T)V}{N}$$

where ζ' is the single species partition function with the volume dependance removed. Hence we have

$$\ln \frac{\zeta'_{CO_2}(T)V}{N_{CO_2}} + \ln \frac{\zeta'_{H_2}(T)V}{N_{H_2}} - \ln \frac{\zeta'_{CO}(T)V}{N_{CO}} - \ln \frac{\zeta'_{H_2O}(T)V}{N_{H_2O}}$$

$$N_{CO_2} = \frac{\zeta'_{CO_2}(T)\zeta'_{H_2}(T)N_{CO}N_{H_2O}}{\zeta'_{CO}(T)\zeta'_{H_2O}(T)N_{H_2}} \quad . \tag{1}$$

This is independant of volume. Thus the number of the different species do not change, and the relative concentrations remain the same. □

8.2 Partial Pressure

Reif §8.14: Consider the following chemical reaction between ideal gases:

$$\sum_{i=1}^{m} b_i B_i = 0$$

Let the temperature be T, the total pressure be p. Denote the partial pressure of the ith species by p_i. Show that the law of mass action can be put into the form

$$p_1^{b_1} p_2^{b_2} \cdots p_m^{b_m} = K_p(T) \tag{2}$$

where the constant $K_p(T)$ depends only on T.

The law of mass action can be written

$$N_1^{b_1} N_2^{b_2} \cdots N_m^{b_m} = K_N(T, V) = \zeta_1^{b_1} \zeta_2^{b_2} \cdots \zeta_m^{b_m}$$

We've already seen that we can rewrite $\zeta_i(T, V) = V\zeta_i'(T)$, thus we have

$$\left(\frac{N_1}{V_1}\right)^{b_1} \left(\frac{N_2}{V_2}\right)^{b_2} \cdots \left(\frac{N_m}{V_m}\right)^{b_m} = \zeta'^{b_1}_1 \zeta'^{b_2}_2 \cdots \zeta'^{b_m}_m$$

The ideal gas law gives us $\frac{N_1}{V_1} = \frac{p}{kT}$ hence

$$p_1^{b_1} p_2^{b_2} \cdots p_m^{b_m} = K_p(T)$$

where $K_p(T) = \prod_{i=1}^{m} (kT\zeta_i'(T))^{b_i}$. □

8.3 Paramagnet

(a) This problem is similar to a random walk but instead of steps to the right and left we have spins that are up and down. Let $s_\pm =\#$ of particles with $s_i = \pm\frac{1}{2}$.

Then

$$\Omega(s_+) = \binom{N}{s_+} = \frac{N!}{s_+!s_-!} \approx \frac{N^N}{s_+^{s_+} s_-^{s_-}}\sqrt{\frac{N}{2\pi s_+ s_-}} \qquad \text{using Stirling's approximations.}$$

Since $s_+ + s_- = N$ and $E = \mu_B H(s_- - s_+)$ we have $s_\pm = \frac{N}{2} \mp a$ where $a \equiv \frac{E}{2\mu_B H}$. If we drop the square root term of th term of the stirling approximation we get

$$\Omega(E) = N^N \left(\frac{N}{2} + a\right)^{-(\frac{N}{2}+a)} \left(\frac{N}{2} - a\right)^{-(\frac{N}{2}-a)}$$

for integer values of $N/2 + a$. Defining δE to coarse grain such that $\mu_B H \ll \delta E \ll N\mu_B H$ this gives us

$$\Omega(E) = N^N \left(\frac{N}{2} + a\right)^{-(\frac{N}{2}+a)} \left(\frac{N}{2} - a\right)^{-(\frac{N}{2}-a)} \frac{\delta E}{2\mu_B H}$$

(b)

$$\begin{aligned}
\ln\Omega &= N\ln N - \left(\frac{N}{2} + a\right)\ln\left(\frac{N}{2} + a\right) - \left(\frac{N}{2} - a\right)\ln\left(\frac{N}{2} - a\right) \\
\beta &= \frac{\partial \ln\Omega}{\partial E} = -\frac{\partial a}{\partial E}\left[1 + \ln\left(\frac{N}{2} + a\right) - 1 - \ln\left(\frac{N}{2} - a\right)\right] \\
&= \frac{1}{2\mu_B H}\ln\left(\frac{N\mu_B H - E}{N\mu_B H + E}\right) \\
\Rightarrow T &= \frac{2\mu_B H}{k}\left[\ln\left(\frac{N\mu_B H - E}{N\mu_B H + E}\right)\right]^{-1}
\end{aligned}$$

(c) Let $b \equiv \frac{\mu_B H}{kT}$, we then have

$$e^{2b} = \frac{N\mu_B H - E}{N\mu_B H + E} \qquad \Rightarrow \qquad \boxed{E = \frac{N\mu_B H(1 - e^{2b})}{1 + e^{2b}} = -N\mu_B H\tanh b}$$

We also have

$$\begin{aligned}
S = k\ln\Omega &= k\left[N\ln N - \left(\frac{N}{2} - \frac{N}{2}\tanh b\right)\ln\left(\frac{N}{2} - \frac{N}{2}\tanh b\right)\right. \\
&\quad \left. - \left(\frac{N}{2} + \frac{N}{2}\tanh b\right)\ln\left(\frac{N}{2} + \frac{N}{2}\tanh b\right)\right]
\end{aligned}$$

Which reduces to

$$S = k\left[N\ln N - \frac{Ne^b}{e^b+e^{-b}}\ln\left(\frac{Ne^b}{e^b+e^{-b}}\right)\right] - \frac{Ne^{-b}}{e^b+e^{-b}}\ln\left(\frac{Ne^{-b}}{e^b+e^{-b}}\right)$$

since $1-\tanh b = \frac{2e^{-b}}{e^b+e^{-b}}$ and $1+\tanh b = \frac{2e^b}{e^b+e^{-b}}$.

$$\begin{aligned} S &= kN\left[\frac{e^b}{e^b+e^{-b}}\ln\left(\frac{e^b+e^{-b}}{e^b}\right)\frac{e^{-b}}{e^b+e^{-b}}\ln\left(\frac{e^b+e^{-b}}{e^{-b}}\right)\right] \\ &= kN\left[\ln(e^b+e^{-b}) - \frac{e^b\ln e^b + e^{-b}\ln e^{-b}}{e^b-e^{-b}}\right] \\ &= kN\left[\ln(2\cosh b) - \frac{be^b-be^{-b}}{e^b+e^{-b}}\right] \end{aligned}$$

$$\boxed{S = kN\left[\ln\left(2\cosh\frac{\mu_B H}{kT}\right) - \frac{\mu_B H}{kT}\tanh\frac{\mu_B H}{kT}\right]}$$

This gives us a Helmholtz free energy

$$F = E - TS = -N\mu_B H\tanh\frac{\mu_B H}{kT} - NkT\left[\ln\left(2\cosh\frac{\mu_B H}{kT}\right) - \frac{\mu_B H}{kT}\tanh\frac{\mu_B H}{kT}\right]$$

$$\boxed{F = -NkT\ln\left(2\cosh\frac{\mu_B H}{kT}\right)}$$

(d) The canonical partition function is given by

$$\boxed{Z = \prod_{i=1}^{N} e^{-\beta\mu_B H} + e^{\beta\mu_B H} = \left(2\cosh\frac{\mu_B H}{kT}\right)^N}$$

(e) From the partition function we can calculate

$$E = -\frac{\partial \ln Z}{\partial\beta} = -N\mu_B H\tanh\frac{\mu_B H}{kT}\ ,$$

$$S = k(\ln Z + \beta E) = Nk\left[\ln(2\cosh\beta\mu_B H) - \beta\mu_B H\tanh\frac{\mu_B H}{kT}\right]\ ,$$

$$F = -kT\ln Z = -NkT\ln\left(2\cosh\frac{\mu_B H}{kT}\right)\ ,$$

as above. □

8.4 Quantum Harmonic Oscillator

(a) We have

$$Z_n(T) = e^{-\beta E_n} = e^{-\frac{\hbar\omega}{kT}\left(\frac{1}{2}+n\right)}$$

(b)

$$\begin{aligned}
\Xi(\mu, T) &= \sum_n Z_n e^{\beta\mu n} = e^{-\frac{\hbar\omega}{2kT}} \sum_n e^{\frac{n}{kT}(\mu-\hbar\omega)} \\
&= \frac{e^{-\hbar\omega/2kT}}{1 - e^{(\mu-\hbar\omega)/kT}} = \frac{e^{-\mu/2kT}}{2\sinh[(\hbar\omega-\mu)/2kT]}
\end{aligned}$$

(c) For the energy we have

$$\begin{aligned}
\bar{E} &= -\left(\frac{\partial \ln \Xi}{\partial \beta}\right)_{\mu,V} = -\frac{\partial}{\partial \beta}\left[-\frac{\beta\mu}{2} - \ln 2 - \ln(\sinh(\beta(\hbar\omega-\mu)/2))\right] \\
&= \frac{\hbar\omega}{2}\coth[(\hbar\omega-\mu)/2kT]
\end{aligned}$$

For the entropy we have

$$\begin{aligned}
S &= \frac{\partial}{\partial T}[kT\ln\Xi] = \frac{\partial}{\partial T}\left[-\frac{\mu}{2} - kT\ln(2\sinh[(\hbar\omega-\mu)/2kT]\right] \\
&= -k\ln\left[2\sinh\left(\frac{\hbar\omega}{2kT}\right)\right] - \frac{\hbar\omega}{2kT}\coth\left[\frac{\hbar\omega}{2kT}\right]
\end{aligned}$$

(d) Using the normal canonical parition function given in the problem we see,

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = \frac{\partial}{\partial \beta}\ln[\sinh(\beta\hbar\omega/2)] = \frac{\hbar\omega}{2}\coth(\beta\hbar\omega/2)$$

and

$$S = k\ln Z - \beta\bar{E} = -k\ln(2\sinh(\beta\hbar\omega/2)) - \frac{\hbar\omega}{2kT}\coth(\hbar\omega/2kT)$$

Thus we see we must have $\mu = 0$ for the oscillation quanta.

□

8.5 Equilibrium Fluctuations

(a) The grand canonical parition function is

$$\Xi = \sum_r e^{-\beta(E_r - \mu N)} \quad \Rightarrow \quad \left(\frac{\partial \Xi}{\partial \mu}\right)_{V,T} = \beta \bar{N} \Xi \quad \Rightarrow \quad \bar{N} = kT \left(\frac{\partial \ln \Xi}{\partial \mu}\right)_{V,T}$$

We also have

$$\left(\frac{\partial^2 \Xi}{\partial \mu^2}\right)_{V,T} = \beta^2 \sum (N^2+1) e^{-\beta(E_r - \mu N)} = \beta^2 \xi (1 + \overline{N^2}$$

Noting that

$$\left(\frac{\partial^2 \ln \Xi}{\partial \mu^2}\right)_{V,T} = \frac{1}{\Xi}\left(\frac{\partial^2 \Xi}{\partial \mu^2}\right)_{V,T} - \frac{1}{\Xi^2}\left(\frac{\partial \Xi}{\partial \mu}\right)_{V,T}^2 = \frac{1}{\Xi}\left(\frac{\partial^2 \Xi}{\partial \mu^2}\right)_{V,T} - \frac{\bar{N}^2}{(kT)^2}$$

Solving for $\overline{N^2}$ we see

$$\overline{N^2} = \frac{(kT)^2}{\Xi}\left(\frac{\partial^2 \Xi}{\partial \mu^2}\right)_{V,T} - 1 \approx (kT)^2 \left(\frac{\partial^2 \ln \Xi}{\partial \mu^2}\right)_{V,T} + \bar{N}^2 = kT \left(\frac{\partial \bar{N}}{\partial \mu}\right)_{V,T} + \bar{N}^2$$

which gives us

$$\boxed{\operatorname{var} N = kT \left(\frac{\partial \bar{N}}{\partial \mu}\right)_{V,T}}$$

(b) The isothermal compressibility can be expressed as

$$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P} = -\frac{1}{v}\frac{\partial v}{\partial P}$$

where $v = V/N$ is the volume per particle.

From the maxwell relation for F, we have

$$\begin{aligned} -\left(\frac{\partial P}{\partial N}\right)_{T,V} &= \left(\frac{\partial \mu}{\partial V}\right)_{T,N} \\ -\frac{v}{N}\left(\frac{\partial P}{\partial v}\right)_T &= -\frac{1}{N}\left(\frac{\partial \mu}{\partial v}\right)_T \end{aligned}$$

since $dN = -\frac{N}{v}dv$.

This gives us

$$\left(\frac{\partial P}{\partial \mu}\right)_T = \left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial \mu}{\partial v}\right)_T^{-1} = \frac{1}{v}$$

Taking another derivative with respect to μ we see

$$\left(\frac{\partial^2 P}{\partial \mu^2}\right)_{T,N} = \frac{\partial}{\partial \mu}\frac{1}{v} = \frac{1}{Nv^2}\left(\frac{\partial V}{\partial \mu}\right)_{T,N} = \frac{1}{Vv}\left(\frac{\partial N}{\partial P}\right)_{T,V} = -\frac{1}{Vv^2}\frac{V}{v}\left(\frac{\partial v}{\partial P}\right)_{T} = -\frac{1}{v^3}\frac{\partial v}{\partial P}$$

$$\left(\frac{\partial^2 P}{\partial \mu^2}\right)_{T,N} = \frac{1}{v^2}\kappa_T$$

Noting that $PV = kT \ln \Xi$ and using the second last equation in part (a) we see

$$\boxed{\operatorname{var} N = kTV\left(\frac{\partial^2 P}{\partial \mu^2}\right)_{T,N} = \frac{kTV\kappa_T}{v^2} = \frac{kT\bar{N}^2\kappa_T}{V}}$$

□

8.6 Grand Canonical Ensemble

(a) The grand canonical ensemble for an ideal gas where V, T, and N can vary is given as

$$\Xi = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N$$

where

$$Z_n = \frac{1}{N!}V^N\left[\frac{2\pi m}{h^2\beta}\right]^{3N/2}$$

is the canonical partition function.

This gives

$$\Xi = \sum_{N=0}^{\infty}\frac{1}{N!}\left(Ve^{\beta\mu}\left[\frac{2\pi m}{h^2\beta}\right]^{3/2}\right)$$

Recognizing this as a Taylor series for an exponential we see

$$\boxed{\Xi = \exp\left[Ve^{\beta\mu}\left(\frac{2\pi m}{h^2\beta}\right)^{3/2}\right]} \tag{3}$$

(b) We have

$$\begin{aligned} pV &= kT\ln\Xi = kTVe^{\beta\mu}\left(\frac{2\pi m}{h^2\beta}\right)^{3/2} \\ p &= kTe^{\mu/kT}\left(\frac{2\pi m}{h^2\beta}\right)^{3/2} \end{aligned}$$

Solving for the chemical potential μ, we see

$$\boxed{\mu = kT \ln\left[\frac{p}{kT}\left(\frac{h^2\beta}{2\pi m}\right)^{3/2}\right]}.$$

□