Phys 114
Seminar 8

Sols

Problem 1 Bayesian Stats.

(From earlier week... "leftover" ii)

Problem 1

Monty Hall Problem via Bayesian Stat's

Event A_i: car is behind door i

Event B_i: host opens door i

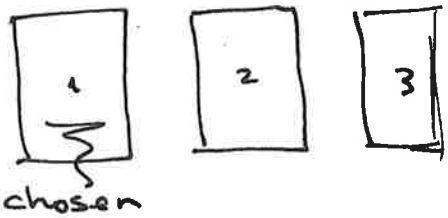
Definition: $P(E)$ means probability of event E

$P(E|E_g)$ means probability that given E_g occurs, E occurs

Known: Contestant chooses one of 3 doors

W.l.o.g. call it door 1

Host opens a door, call it j



Now, contestant would like know $P(A_1|B_j)$ ... likelihood car is behind chosen door, given host opened door j.

Calculations: Host's mentality is known ... ! host knows where car is!

$$P(B_2|A_1) = \frac{1}{2}$$

$$P(B_2|A_2) = 0$$

$$P(B_2|A_3) = 1$$

could also calculate $P(B_3|A_i)$ but these would be quite similar ... $P(B_3|A_1) = \frac{1}{2}$; $P(B_3|A_2) = 1$; $P(B_3|A_3) = 0$

$$P(A_1) = P(A_2) = P(A_3) = \frac{1}{3}$$

$P(B_1) = 0$

$P(B_2) = \sum_i P(B_2 \mid A_i) P(A_i)$

$P(B_2) = 1/2 \cdot 1/3 + 0 \cdot 1/3 + 1 \cdot 1/3 = \frac{1}{2}$

$P(B_3) = 1/2$

Ready to use Bayes' Theorem:

eg. $P(A_1 \mid B_2) = \frac{P(B_2 \mid A_1) P(A_1)}{P(B_2)}$

stick → A_1; given host opens door 2 → B_2

$= \frac{1/2 \cdot 1/3}{1/2} = \frac{1}{3}$

now $P(A_1 \mid B_3) = \frac{P(B_3 \mid A_1) P(A_1)}{P(B_3)} = \frac{1}{3}$

No matter whether host opens door 2 or 3,

Prob of sticking & winning is 1/3

Checking what we expect ...

$P(A_3 \mid B_2) = \frac{P(B_2 \mid A_3) P(A_3)}{P(B_2)}$

if switch to door 3 → A_3

$= \frac{1 \cdot 1/3}{1/2} = \frac{2}{3}$

so $P(A_2 \mid B_3) = \frac{P(B_3 \mid A_2) P(A_2)}{P(B_3)}$

if switch to door 2 → A_2

$= \frac{1 \cdot 1/3}{1/2} = \frac{2}{3}$

Prob of switching = 2/3

Second problem cont.

G+T 3.25

Accuracy refers to how many true positives and true negatives a test delivers.

$$A = P(+ \mid ill) \qquad \text{true positive}$$

and also $$A = P(- \mid well) \qquad \text{true negative}$$

Life doesn't have to be this way! A test could have different probs of true pos + true neg. But we are told to assume those are same.

It is true from probability by that

$$P(+ \mid ill) + P(- \mid ill) = 1$$

$$\therefore P(- \mid ill) = 1 - A$$

An ill person must get some result

Similarly

$$P(+ \mid well) + P(- \mid well) = 1$$

$$\therefore P(+ \mid well) = 1 - A$$

What a person wants to know is

$$P(ill \mid +)$$

Bayes Theorem:

$$P(ill \mid +) = \frac{P(+ \mid ill)\,P(ill)}{P(+)}$$

where $P(+) = P(+ \mid ill)P(ill) + P(+ \mid well)P(well)$

Thus,

$$P(\text{ill}\,|\,+) = \frac{A\,P(\text{ill})}{A\,P(\text{ill}) + (1-A)(1-P(\text{ill}))}$$

This is P(well)

Let $P(\text{ill}) = \epsilon$

Then $$P(\text{ill}\,|\,+) = \frac{A\epsilon}{A\epsilon + 1 - A - \epsilon + A\epsilon}$$

$$P(\text{ill}\,|\,+) = \frac{A\epsilon}{2A\epsilon + 1 - A - \epsilon} \quad (1)$$

Suppose $P(\text{ill}\,|\,+) = 0.50$

$\epsilon = 0.01 \Rightarrow$ $$0.50 = \frac{0.01}{0.02 + \frac{0.99}{A} - 1}$$

$$\Rightarrow \underline{A = 0.99\ldots\ 99\%}$$

Suppose $P(\text{ill}\,|\,+) = 0.50$, $\epsilon = 0.001$

$$\Rightarrow A = 0.999\ldots\ 99.9\%$$

In general

Given $P(\text{ill}\,|\,+) = 0.50 = 1/2$

Can solve Eq. (1) & get $\boxed{A = 1 - \epsilon}$

*

2) Grand Canonicals & fluids in ideal gas

G+T Problem 6.44

a) WTS that $\mathcal{Z}_G = \sum_{N=0}^{\infty} \frac{(z Z_1)^N}{N!} = e^{z Z_1}$

for ideal gas. z is the <u>activity</u> ... $z = e^{\beta\mu}$

solution $\rightarrow$ $\mathcal{Z}_G = \sum_s e^{-\beta(E_s - \mu N_s)}$

Using $E_s = E_s(N_s)$ we rewrite as

$$\mathcal{Z}_G = \sum_{N=0}^{\infty} \sum_{E_s(N)}' e^{-\beta E_s(N)} e^{\beta\mu N}$$

$\sum'$: sum over all states s with N particles

Thus

$$\mathcal{Z}_G = \sum_{N=0}^{\infty} e^{\beta\mu N} \underbrace{\sum_{E_s(N)} e^{-\beta E_s(N)}}_{\equiv \mathcal{Z}(T,V,N)}$$

Thus $\mathcal{Z}_G = \sum_{N=0}^{\infty} z^N \frac{\mathcal{Z}(T,V,1)^N}{N!}$ (for semiclassical ideal gas $\mathcal{Z}(T,V,N) = \frac{\mathcal{Z}(T,V,1)^N}{N!}$)

This series is an exponential $\Rightarrow$ $\mathcal{Z}_G = e^{z Z_1}$ QED

b) WTS $\bar{N} = z Z_1$

and $P_N = \frac{z_N Z(T,V,N)}{Z_G} = \frac{(z Z_1)^N}{N! Z_G} = \frac{\bar{N}^N}{N!} e^{-\bar{N}}$

Solution: $\bar{N} = \frac{1}{Z_G} \sum_{N=0}^{\infty} N \frac{(z Z_1)^N}{N!}$

But since $Z_G = e^{z Z_1} = \sum_{N=0}^{\infty} \frac{(z Z_1)^N}{N!}$,

$$\bar{N} = z Z_1 \cdot \frac{\frac{\partial}{\partial (z Z_1)} \sum_{N=0}^{\infty} \frac{(z Z_1)^N}{N!}}{Z_G}$$

$$= z Z_1 \frac{\partial}{\partial z Z_1} \ln Z_G$$

$$= z Z_1 \frac{\partial}{\partial (z Z_1)} \ln e^{z Z_1}$$

$$= z Z_1 \underbrace{\frac{\partial}{\partial (z Z_1)} z Z_1}_{1 \text{ ie}} = z Z_1 \quad \text{QED}$$

Now $P_N \overset{\text{obvious}}{=} e^{\beta \mu N} Z(T,V,N) / Z_G$

$$= \frac{z^N Z_1^N}{N!} \Big/ Z_G$$

$$\overset{\text{from above}}{=} \frac{\bar{N}^N}{N!} \Big/ e^{\bar{N}} = \frac{\bar{N}^N}{N!} e^{-\bar{N}} \quad \text{QED}$$

c) N-dependence of $\overline{(N-\bar{N})^2}$?

First of all, they must mean $\bar{N}$ dependence ☺

Anyway, it is variance of Poisson distⁿ with mean $\bar{N}$. This is, interestingly, equal to its mean!

$$\overline{(N-\bar{N})^2} \equiv \bar{N}$$

Solution by Luke Barbano

3.

GRT 6.19

Relation between the energy and pressure equations of state for a non-relativistic ideal gas.

The mean energy is given by

$$E = \int_0^\infty \epsilon \bar{n}(\epsilon) g(\epsilon)\, d\epsilon$$

where, for non-relativistic particles, the number of microstates in the interval $\epsilon + d\epsilon$ is given by

$$g(\epsilon)\, d\epsilon = n_s \frac{V}{4\pi^2\hbar^3} (2m)^{3/2} \epsilon^{1/2}\, d\epsilon$$

The mean number of particles in a single microstate $\vec{k}$ is given by

$$\bar{n}_k = \left(e^{\beta(\epsilon_k - \mu)} \pm 1 \right)^{-1}$$

So

$$* \quad E = n_s \frac{V}{4\pi^2\hbar^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{3/2}\, d\epsilon}{\left(e^{\beta(\epsilon-\mu)} \pm 1\right)}$$

The multiplicity Ω is given by the Landau potential in eq 6.86

$$\Omega = \sum_k \Omega_k = \mp kT \sum_k \ln\left(1 \pm e^{-\beta(\epsilon_k - \mu)}\right)$$

Since ϵ_k is very small, adjacent energy levels are very close together and the summation can be rewritten as an integral where the summation argument must be multiplied by the density of states $g(\epsilon)$ in energy space. So,

$$\Omega = \mp kT \int_0^\infty g(\epsilon) \ln\left(1 \pm e^{-\beta(\epsilon-\mu)}\right) d\epsilon$$

Given our previous definition of $g(\epsilon)$,

$$\Omega = \mp kT \frac{n_s V}{4\pi^2\hbar^3} (2m)^{3/2} \int_0^\infty \epsilon^{1/2} \ln\left(1 \pm e^{-\beta(\epsilon-\mu)}\right) d\epsilon$$

Let $u = \ln\left(1 \pm e^{-\beta(\epsilon-\mu)}\right)$ and $dv = \epsilon^{1/2} d\epsilon$, so $\int u\, dv = uv - \int v\, du$

continued...

$$\int_0^\infty \epsilon^{1/2} \ln\left(1 \pm e^{-\beta(\epsilon-\mu)}\right) d\epsilon = \left. \tfrac{2}{3} \epsilon^{3/2} \ln\left(1 \pm e^{-\beta(\epsilon-\mu)}\right) \right|_0^\infty - \int_0^\infty \frac{\tfrac{2}{3}\epsilon^{3/2}(-\beta) e^{-\beta(\epsilon-\mu)}}{1 \pm e^{-\beta(\epsilon-\mu)}}\, d\epsilon$$

Evaluate $\tfrac{2}{3}\epsilon^{3/2} \ln\left(1 \pm e^{-\beta(\epsilon-\mu)}\right)^{-1}$ at ∞

$\tfrac{2}{3}(\infty^{3/2}) / \ln(1+0) \rightarrow$ undefined

Use l'hopital's rule, so

$$\lim_{\epsilon\to\infty} \tfrac{2}{3}\epsilon^{3/2} \ln\left(1 \pm e^{-\beta(\epsilon-\mu)}\right) \xrightarrow{LH} \lim_{\epsilon\to\infty} \frac{-\beta\epsilon^{1/2} e^{-\beta(\epsilon-\mu)}}{1 \pm e^{-\beta(\epsilon-\mu)}}$$

$$= \frac{-\beta\epsilon^{1/2}}{e^{\beta(\epsilon-\mu)} \pm 1} \approx \frac{-\beta\epsilon^{1/2}}{e^{\beta(\epsilon-\mu)}} \rightarrow \infty/\infty$$

L'hopital again!

$$\xrightarrow{LH} \tfrac{1}{2}(-\beta)\epsilon^{-1/2}(-\beta) e^{-\beta(\epsilon-\mu)} = \frac{\tfrac{1}{2}\beta^2}{\epsilon^{1/2} e^{\beta(\epsilon-\mu)}}$$

$$\rightarrow \frac{\tfrac{1}{2}\beta^2}{\infty(\infty)} = 0$$

As $\epsilon \to 0$,

$$\lim_{\epsilon\to 0} \tfrac{2}{3}\epsilon^{3/2} \ln\left(1 \pm e^{-\beta(\epsilon-\mu)}\right) = (0)\ln\left(1 \pm e^{\beta\mu}\right) = 0$$

So, the UV term goes away entirely, so:

$$\int_0^\infty \epsilon^{1/2} \ln\left(1 \pm e^{-\beta(\epsilon-\mu)}\right) d\epsilon = \tfrac{2}{3}\beta \int_0^\infty \frac{\epsilon^{3/2}}{e^{\beta(\epsilon-\mu)} \pm 1}\, d\epsilon$$

$$\Omega = \mp kT\, n_s \frac{V}{4\pi^2\hbar^3} (2m)^{3/2} \tfrac{2}{3}\beta \int_0^\infty \frac{\epsilon^{3/2}}{\left(e^{\beta(\epsilon-\mu)} \pm 1\right)}\, d\epsilon$$

$$* \quad \Omega = -\tfrac{2}{3}\left[\pm n_s \frac{V}{4\pi^2\hbar^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{3/2}\, d\epsilon}{e^{\beta(\epsilon-\mu)} \pm 1} \right]$$

Since $E = n_s \frac{V}{4\pi^2\hbar^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{3/2}\, d\epsilon}{e^{\beta(\epsilon-\mu)} \pm 1}$

$$\Omega = -\tfrac{2}{3} E$$

Since $\Omega = PV$,

$$\boxed{PV = -\tfrac{2}{3} E} \quad \checkmark$$

Amy's Addendum to Prob 3

WTS "Surface term" $UV\Big|_{\epsilon=0}^{\epsilon=\infty} = 0$

Here $U = \mp \ln\left[1 \pm e^{-\beta(\epsilon-\mu)}\right]$; $V = \frac{2}{3}\epsilon^{3/2}$

Thus, as $\epsilon \to 0$

UV approaches $\mp \ln\left[1 \pm e^{\beta\mu}\right] \frac{2}{3} \epsilon^{3/2}$ with $\epsilon \to 0$

Thus $UV\Big|_{\epsilon=0} = 0$

Now as $\epsilon \to \infty$ ... have $\beta\epsilon \equiv E_1$ for larger numbers:

$$UV \to \mp \ln\left[1 \pm e^{\beta\mu} e^{-E_1}\right] \frac{2}{3} E_1^{3/2} \frac{1}{\beta^{3/2}}$$

Thus $UV \propto \ln\left[1 \pm e^{\beta\mu} e^{-E_1}\right] E_1^{3/2}$

lets let $x = e^{-E_1}$. Then $UV \propto \ln\left[1 \pm e^{\beta\mu} x\right] (-\log x)^{3/2}$

Thus $\ln[1 \pm \delta] \approx \pm\delta \Rightarrow$

$$UV \propto x(-\log x)^{3/2}$$

Hence $UV\Big|^{E\to\infty}_{\Rightarrow x\to 0} \propto -x(\log x)^{3/2} \equiv 0$

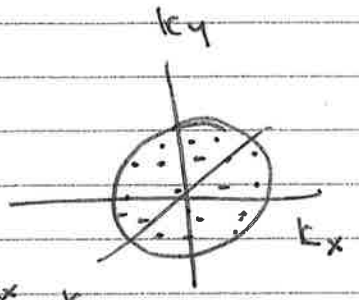
$\lim_{x\to 0}$

Aside

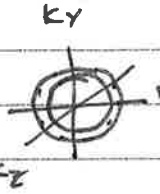
How to find $g(\epsilon)$?

Recall, $\Gamma(k) = \frac{4\pi k^3/3}{(\pi/L)^3}$ is # of states up to wave number k

only take 1st octant of k-space... $\frac{1}{8}$ where $k_x, k_y, k_z > 0$



And $g(k)\,dk = \frac{L}{2\pi}^3 k^2 dk = \frac{V k^2 dk}{2\pi^2}$ is volume of k-space shell of width dk



Now, what is $g(\epsilon)$? We need two ideas:

① Conservation of probability

$$g(\epsilon)\,d\epsilon \equiv g(k)\,dk$$

② "Dispersion relation" tells us what the relationship is btwn ϵ & k.

eg. massive particle: $\epsilon = \frac{\hbar^2 k^2}{2m}$; $k = \sqrt{2m\epsilon/\hbar^2}$

eg. photon: $\epsilon = \hbar c k$; $k = \epsilon/\hbar c$

Thus $g(\epsilon) = g(k)\frac{dk}{d\epsilon}$

$$g(\epsilon) = \frac{V}{2\pi^2}\left(\frac{2m\epsilon}{\hbar^2}\right)\cdot\sqrt{\frac{m}{2\epsilon\hbar^2}}$$

or for matter particles

$$g(\epsilon) = \frac{V}{4\pi^2\hbar^3}(2m)^{3/2}\epsilon^{1/2} \checkmark$$

Note: If there are n_s internal states ..... we multiply this $g(\epsilon)$ by n_s !

4: Production of Ammonia

4: Chemical reactions: production of Ammonia

The commercial production of ammonia from nitrogen and hydrogen is an example of a reaction that occurs the gaseous state:

$$N_2 + 3H_2 \leftrightarrow 2NH_3$$

a) Write down the equilibrium constant, K, in terms of the partial pressures of the nitrogen, hydrogen, and ammonia. (You may take $p^o = 1$ atm.)
b) Using the data tables at the back of Schroder (on our website under "Resources" link) please confirm that at $T = 298K$, $K = 5.9 \times 10^5$.
c) Please draw a quantitatively accurate plot of $logK$ vs. $1/T$. From this plot or in some other way, find K when $T = 773K$. (This is 500^oC which is apparently a good temperature at which to run this reaction, using a catalyst to speed it up.)
d) Will you drive the equilibrium toward more ammonia, or more nitrogen and hydrogen, if you increase T?
e) Same question, if you increase the pressure?

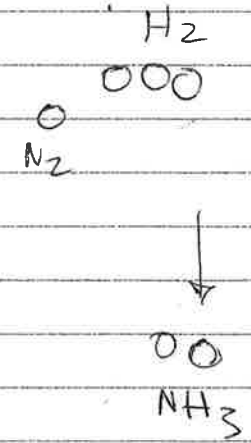
a) $$K = \prod_{j=1}^{p+q} \left(\frac{P_j}{P^o}\right)^{\nu_j}$$

p products
q reactants

So here $N_2 + 3H_2 \leftrightarrow 2NH_3$ ...

$\nu_1 = -1$ $\nu_2 = -3$ $\nu_3 = +2$

$$K = \frac{P_{NH_3}^2 P^{o\,2}}{P_{N_2} P_{H_2}^3}$$



b) Also could write

$$\ln K = -\frac{\Delta_r G^\circ}{RT}$$

Look at Schroder data ....

$$\Delta_r G^\circ = 2\underbrace{\Delta G^\circ_{NH_3}}_{=16.45\,kJ} - \underbrace{\Delta G^\circ_{N_2}}_{0} - \underbrace{3G^\circ_{H_2}}_{0}$$

$$\therefore \quad \Delta_r G^\circ = -32.9 \times 10^3\ J \quad \text{and}$$

$$\ln K = -\frac{-32.9\times10^3\ J}{8.315\ \frac{J}{mol\,K}\cdot 298\,K} = 13.2775$$

$$\Rightarrow \quad K = 5.8\times10^5 \quad \text{close enuff ☺}$$

c)

Try this ...

$$\frac{d\ln K}{dT} = \frac{\Delta_r H^\circ}{RT^2} \Rightarrow \frac{d\ln K}{d(1/T)} = -\frac{\Delta_r H^\circ}{R}$$

This is van t'Hoff equ ...

say graph of $\ln K$ vs. $1/T$ is straight line with slope $-\Delta_r H^\circ/R$.

Again from Schroeder's table:

$$\Delta_r H^\circ = \underbrace{2(-46.11)}_{NH_3\ \text{contribn}}\ kJ = -92.2\ kJ$$

Thus, with $R = 8.315 \frac{J}{mol\,K}$ ... 4-3

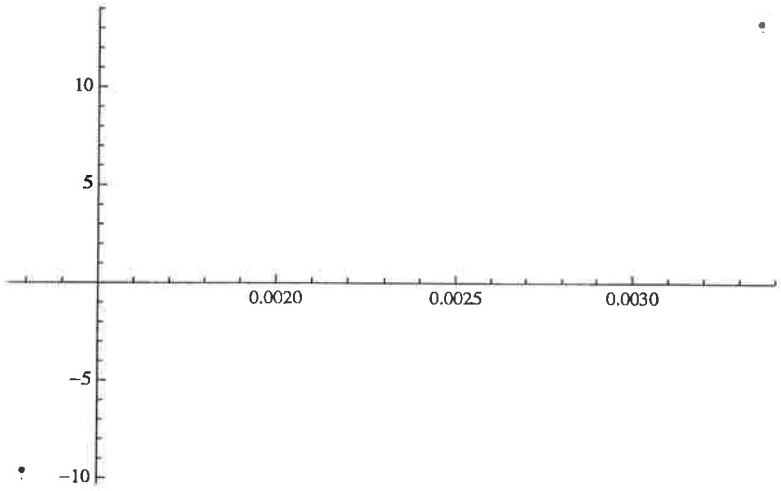
$$\ln k = +11.09 \times 10^3 \left(\frac{1}{T}\right) + \ln k_o$$

or ... $\ln k(773) - \ln k(298) = +11.09 \times 10^3 \left(\frac{1}{773} - \frac{1}{298}\right)$

$= -9.587$ see fitted slope below ☺

$\Rightarrow K(773) = 6.86 \times 10^{-5}$ wow! really different + less.

```
lnKdata = {{1 / 298.0, 13.2775}, {1 / 773.0, -9.587}}
{{0.0033557, 13.2775}, {0.00129366, -9.587}}
Aplot = ListPlot[lnKdata]
```




```
LinearModelFit[lnKdata, x, x]
FittedModel[ -23.9315 + 11088.3 x ]
```

d) Le Chatelier's principle: If you heat up an exothermic rxn, you slow it down. You make less NH_3. (Duh... that's what part c) just showed.)

e) Le Chatelier again: If you increase pressure, rxn will try & make a lower pressure. Thus, since ∃ 4 gas molecules LHS + 2 on RHS, you make more NH_3.

Problem 5

Absorption onto a surface

Suppose a surface has M distinguishable sites, each of which can absorb at most one indistinguishable gas molecule. Say that an absorbed gas molecule has an energy of $-\epsilon$ compared with an unabsorbed molecule. The molecules have chemical potential μ both in the gas phase and on the surface. (This is what it means for the gas phase to be in equilibrium with the absorbed phase.)

a) Show that $\mathcal{Z}(T, V, \mu) = (1 + e^{\beta(\epsilon+\mu)})^M$

b) Find the equilibrium fraction, f, of sites that have absorbed molecules. In other words, if N_o molecules are absorbed, then $f = N_o/M$.

c) By equating μ with the chemical potential of an ideal gas at pressure P and temperature T, show that

$$f = \frac{P}{P + P_o(T)}$$

and find an expression for $P_o(T)$. *Hint: P_o will also depend on ϵ, the mass of the gas particles, and constants of nature.*

Absorption Onto a Surface

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(a) Show that $Z(T, V, \mu) = (1 + e^{\beta(\epsilon+\mu)})^M$

Well, while the gas molecules are indistinguishable, the surface is distinguishable, so we can use B & B 21.25,

$$Z_N = (Z_1)^N$$

Since there are two states, 0 and $-\epsilon$, the probability for one would be

$$\begin{aligned} Z_1 &= \sum_S e^{-\beta(E_S - \mu N_s)} \\ &= 1 + e^{-\beta(-\epsilon-\mu)} \\ &= 1 + e^{\beta(\epsilon+\mu)} \\ Z_M &= (1 + e^{\beta(\epsilon+\mu)})^M \end{aligned}$$

This is perfectly correct, but see next page for alternative soln...

The solution for 1a) found Z_1 for one surface site:

The circled site could have 1 molecule : prob $\sim e^{\beta(\mu-\epsilon)}$

or 0 molecule : prob $\sim e^{0}$

Thus $Z_1 = 1 + e^{\beta(\epsilon+\mu)}$; $Z_N = (Z_1)^N$ ✓

Alternatively

$$Z_G(T,V,N) = \sum_{N=0}^{M} e^{\beta\mu N} e^{\beta N\epsilon} g(N)$$

$g(N)$: # microstates with N particles in M distinguishable locations ... giving energy $-N\epsilon$

$$g(N) = \frac{M!}{N!(M-N)!}$$

like N indistinq. balls in M distinq. boxes

Thus ... $$Z = \sum_{N=0}^{M} e^{\beta(\epsilon+\mu)N} \frac{M!}{N!(M-n)!} = (1+e^{\beta(\epsilon+\mu)})^M$$

Just a binomial expansion

(b) $f = \frac{\bar{N}}{M}$

To find f we can use formula that is in reading & also subject of problem (9) ∴

$$\bar{N} = \frac{kT}{Z_G}\frac{\partial Z_G}{\partial \mu}$$. Use Z_G from part (a) ⇒

$$\frac{\bar{N}}{M} = f = \frac{e^{\beta(\epsilon+\mu)}}{(1+e^{\beta(\epsilon+\mu)})}$$

This makes sense b/c it follows Gibb's dist & says fraction of all sites occupied is just probability that any single site is occupied.

c) Suppose that gas is at pressure P.

$PV = NkT$

for ideal gas $\mu = kT \ln\left(\frac{N}{V}\lambda_{th}^3\right)$

$= kT \ln\left(\frac{P}{kT}\lambda_{th}^3\right)$ $\quad \lambda_{th} = \sqrt{\frac{h^2}{2\pi m kT}}$

$= \ln\left(\frac{P}{kT}\lambda_{th}^3\right)^{kT}$

$\therefore f = \dfrac{\left(\frac{P}{kT}\lambda_{th}^3\right)^{\beta kT} e^{\beta\epsilon}}{1 + \left(\frac{P}{kT}\lambda_{th}^3\right)^{\beta kT} e^{\beta\epsilon}}$

$= \dfrac{P}{P + kT e^{-\beta\epsilon} \lambda_{th}^{-3}}$

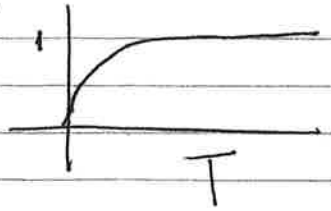
$f = \dfrac{P}{P + kT\left(\frac{2\pi m kT}{h^3}\right)^3 e^{-\beta\epsilon}}$

where $P_s(T) = T^{5/2} \dfrac{k e^{-\beta\epsilon}}{h^3} (2\pi m k)^{3/2}$

$P_0(T) = kT^{5/2}\left(\dfrac{2\pi m k}{h^2}\right)^3 e^{-\beta\epsilon}$

As $T \to 0$, $P_0 \to 0$ so $f \to 1$

as $T \to \infty$ $P_0 \to \infty$ so $f \to 0$



"Langmuir Isotherm"

Problem 6 → Chem pot'l + eqn. of state of ideal gas

i) G+T Prob 6.21

Problem 6.21. The chemical potential.

(a) Estimate the chemical potential of one mole of an ideal monatomic classical gas at standard temperature and pressure and show that $\mu \ll 0$.

Solution. We use (6.115) with $\overline{N}/V = P/kT$ and $P \approx 1\times10^5\,\mathrm{N/m^2}$ and $T \approx 273\,\mathrm{K}$. Thus, $kT \approx (1.38\times 10^{-23}\,\mathrm{J/K})\,273\,\mathrm{K} = 3.77\times10^{-21}\,\mathrm{J}$. We consider an argon atom, which has a mass of $(39.95)(1.66\times10^{-27}) \approx 6.63\times10^{-26}\,\mathrm{kg}$. Thus, in SI units

$$\mu = kT\ln\Big[\frac{\overline{N}}{V}\Big(\frac{2\pi\hbar^2\beta}{m}\Big)^{3/2}\Big] \tag{S6.65a}$$

$$\approx 3.77\times10^{-21}\ln\Big[\frac{(1.013\times10^5)}{(3.77\times10^{-21})}\Big(\frac{2(3.14)(1.05\times10^{-34})^2}{(3.77\times10^{-21})(6.63\times10^{-26})}\Big)^{3/2}\Big] \tag{S6.65b}$$

$$\approx -6\times10^{-20}\,\mathrm{J}, \tag{S6.65c}$$

which is $\approx -60/3.77 \approx -16kT$. Thus, compared to kT, μ is large in magnitude and negative.

(b) Show that $\overline{N}$ can be expressed as [see (6.114)]

$$\overline{N} = \frac{V}{\lambda^3}e^{\beta\mu}, \tag{6.116}$$

and hence

$$\mu(T,V) = -kT\ln\frac{1}{\rho\lambda^3}, \tag{6.117}$$

where $\rho = \overline{N}/V$.

Solution. Equation (6.114) is

$$\overline{N}(T,V,\mu) = V\Big(\frac{m}{2\pi\hbar^2\beta}\Big)^{3/2}e^{\beta\mu}. \tag{6.114}$$

From (6.2) we have

$$\lambda = \Big(\frac{2\pi\hbar^2\beta}{m}\Big)^{1/2}. \tag{6.2}$$

Thus,

$$\overline{N}(T,V,\mu) = V\lambda^{-3}e^{\beta\mu} = \frac{V}{\lambda^3}e^{\beta\mu}. \tag{S6.66}$$

(c) In Section 6.1 we argued that the semiclassical limit $\lambda \ll \rho^{-1/3}$ [see (6.1)] implies that $\overline{n}_{\mathbf{k}} \ll 1$; that is, the mean number of particles in any single particle energy state is very small. Use the expression (6.117) for μ and (6.87) for $\overline{n}_{\mathbf{k}}$ to show that the condition $\overline{n}_{\mathbf{k}} \ll 1$ implies that $\lambda \ll \rho^{-1/3}$.

Solution. Equation (6.87) is

$$\overline{n}_{\mathbf{k}} = e^{-\beta(\epsilon_{\mathbf{k}}-\mu)} \tag{S6.67}$$

If $\overline{n}_{\mathbf{k}} \ll 1$, then $\beta\mu \ll 0$, which implies that $\ln(1/\rho\lambda^3) \gg 0$. Hence, $\rho\lambda^3 \ll 1$, $\lambda^3 \ll \rho^{-1}$, and $\lambda \ll \rho^{-1/3}$.

Prob 7 cont →

ii) G+T Prob 6.22

Problem 6.22. Show that $E = (3/2)NkT$ and $PV = NkT$ from the results of this section.

Solution. From (6.121) and (6.122) we have

$$\overline{P} = \frac{kT}{\lambda^3} e^{\beta\mu}, \tag{6.121}$$

and

$$\overline{N} = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{V,T} = \frac{V}{\lambda^3} e^{\beta\mu}. \tag{6.122}$$

The ratio of these two equations yields

$$\frac{\overline{P}}{\overline{N}} = \frac{kT}{V}, \tag{S6.68}$$

or $\overline{P}V = \overline{N}kT$ as expected. Because $\overline{E} = (3/2)\overline{P}V$, we have $\overline{E} = (3/2)\overline{N}kT$.

Problem 7

Ionization of H B+B Problem 22.6

B+B prob. 22.6 (with a side-stop at B+B prob. 22.5)

22.6 (a) Consider

$$H \rightleftharpoons p^+ + e^-.$$

To explain: why $\mu_H = \mu_p + \mu_e$

Answer: This is discussed in derivation and leads to $\sum_{j=1}^{p+q} \nu_j \mu_j = 0$ Here $\nu_H = -1$

$\nu_{p^+} = \nu_{e^-} = +1$

Thus $-\mu_H + \mu_p + \mu_e = 0$ ...

$\Rightarrow \mu_H = \mu_p + \mu_e$ QED ✓

(b) For H atoms, we can use

$$Z_1^H = \underbrace{\frac{V}{\lambda_{th}^3}}_{Z_{trans,H}} \underbrace{e^{(\beta R)}}_{Z_{int,H}} \quad \beta R = -\beta E_{gs}$$

Eq. 21.50 ... assumes $kT \ll R$

Also prob 22.5 asks us to show

$$\mu = -kT \ln \frac{Z_1}{N}.$$

This readily follows from $Z_N = \frac{Z_1^N}{N!}$, $F = -kT \ln Z_N$

$$= -kT\left[N \ln Z_1 - N \ln N + N\right]$$

$$= -NkT\left[\ln Z_1 - \ln N + 1\right]$$

and

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT\left(\ln Z_1 - \ln N + 1\right) + \frac{NkT}{N}$$

$$= -kT \ln \frac{Z_1}{N}$$ ✓

Thus, $\mu_H = \mu_p + \mu_e$ Using Z_{ig} for ideal gas

$$\Rightarrow -kT \ln \frac{Z_{ig}^H e^{\beta R}}{N_H} = -kT \ln \frac{Z_{ig}^p}{N_p} - kT \ln \frac{Z_{ig}^e}{N_e}$$

$$\Rightarrow e^{-\beta R} = \frac{Z_{ig}^H}{N_H} \frac{N_e N_p}{Z_{ig}^p Z_{ig}^e}$$

$$e^{-\beta R} = \frac{Z_{ig}^H}{n_H} \frac{n_e n_p}{Z_{ig}^p Z_{ig}^e} \frac{V}{} \qquad (1)$$

Now $Z_{ig} = \frac{V}{\lambda_m^3} = V \sqrt{\frac{2\pi m kT}{h^2}}^3$ so assuming $m_H \approx m_p$

Eq (1) becomes

$$e^{-\beta R} = \frac{n_e n_p}{n_H} \frac{h^3}{\sqrt{2\pi m_e kT}}$$

or $$\frac{n_e n_p}{n_H} = \frac{\sqrt{2\pi m_e kT}}{h^3} e^{-\beta R}$$ Saha Eq !

(b) Charge neutrality must give us $n_e = n_p$ bc H has zero net charge.. so an uncharged system of H, n_e, n_p has equal amounts of n_e with charge $-1e$ + n_p with charge $+1e$. Similarly, $n_H + n_p = n$ ... can't create or destroy a nucleon like proton.

Let $y = \frac{n_p}{n}$ be the degree of ionizn. Saha equ. is

$$\frac{n_e n_p}{n_H} = \lambda_{th,e}^{-3} e^{-\beta R} \qquad \text{Saha}$$

And we have $n_H = n - n_p$

$$n_e = n_p$$

Thus $$\frac{n_p n_p}{n - n_p} = \frac{e^{-\beta R}}{\lambda_{th,e}^3}$$

$$\Rightarrow \frac{y^2}{1-y} = \underbrace{\frac{e^{-\beta R}}{n \cdot \lambda_{th,e}^3}}_{\equiv A} \qquad \text{Eq. (22.108)}$$

Find this for atomic cloud at 1000K & $n = 10^{20}\ m^{-3}$?

We solve quadratic

$$y^2 = A(1-y)$$

$$y^2 - Ay - A = 0$$

For this cloud, $\lambda_{th} = 2.36 \times 10^{-9} m$

$$\Rightarrow A = 2.3 \times 10^{-63}$$

$$\Rightarrow y \cong 5 \times 10^{-32}$$

(c) $y \uparrow$ when $n \downarrow$. Why? I guess this is law of mass action. Ionizn rate $\propto n_H \propto n_p^2$

Recombination rate $\propto n_p n_e \propto$ so I guess that if we suddenly rescaled n, it would hit recomb rate harder than ionizn rate. So smaller $n \Rightarrow$ less recomb $\Rightarrow$ higher y

Problem 8

Condition of chemical equilibrium:
Please write the conditions * for equilibrium to exist:

* ie. what is true of

ν_i & μ_i

i) $e^+ + e^- \leftrightarrow 2\gamma$

$\mu_{e^+} + \mu_{e^-} = 0$ ← photons have $\mu_\gamma = 0$

ii) $CH_4 + 2O_2 \longleftrightarrow 2H_2O + CO_2$

$\mu_{CH_4} + 2\mu_{O_2} = 2\mu_{H_2O} + \mu_{CO_2}$