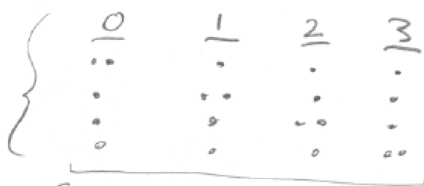
# ME 3007
# HW 2 Solutions

**1.**

From distinguishability section:

$$W_{fer} = \prod_{i=0}^{3} \frac{g_i!}{N_{a,i}!\,(g_i - N_{a,i})!}$$

Because these are fermions, can be distributed




Since particles are indisting, and g is the same for all energy levels, these are interchangeable

For $g = 2$:

$$W = \prod_{i=0}^{3} \frac{2!}{N_{a,i}!\,(2 - N_{a,i})!} = \left(\underset{i=0}{\frac{2!}{2!\,(2-2)!}} \cdot \underbrace{\underset{i=1}{\frac{2!}{1!\,(2-1)!}} \cdot \underset{i=2}{\frac{2!}{1!\,(2-1)!}} \cdot \underset{i=3}{\frac{2!}{1!\,(2-1)!}}}_{\text{3 identical}}\right)$$

$$W = 1 \cdot 2 \cdot 2 \cdot 2 = \underline{8}$$

For $g = 5$:

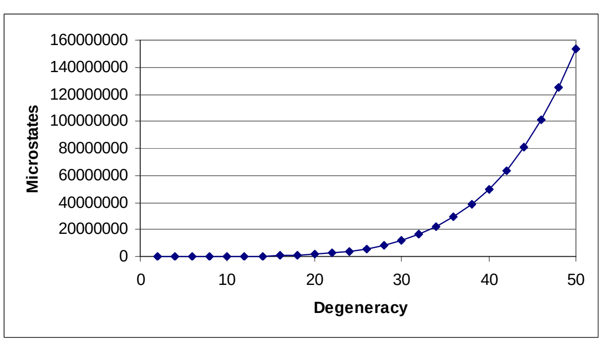
$$W = \left(\frac{5!}{2!\,(5-2)!} \cdot \left(\frac{5!}{1!\,(5-1)!}\right)^3\right) = 1250$$

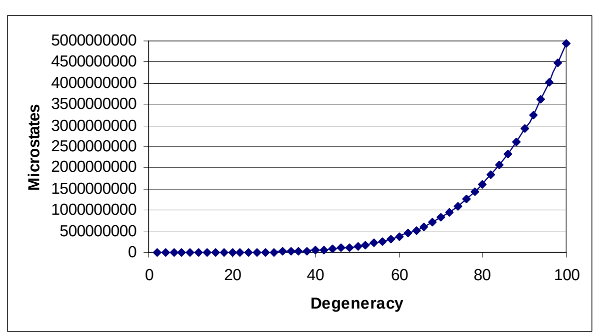
For $g = 10$:

$$W = \left(\frac{10!}{2!\,(10-2)!} \cdot \left(\frac{10!}{1!\,(10-1)!}\right)^3\right) = 45{,}000$$

For $g = 50$:

$$W = \left(\frac{50!}{2!\,(50-2)!} \cdot \left(\frac{50!}{1!\,(50-1)!}\right)^3\right) = 153{,}125{,}000$$



**2.**

Partition Function: $\ln Z = a\,T^4\,V$ . I did not specify which ensemble theory to use, so any of canonical, microcanonical, or grand canonical is acceptable. However, since Z is a function of T and V, you might deduce that you should use the canonical ensemble.

<u>For microcanonical:</u>

$$U = \frac{Nk_BT^2}{Z}\left(\frac{\partial Z}{\partial T}\right)_{N,V} = \frac{Nk_BT^2}{\exp(aT^4V)}\left(4aT^3V\exp(aT^4V)\right) = \underline{\underline{4Nk_BaVT^5}}$$

$$S = \frac{U}{T} + k_BN\ln Z = 4Nk_BaVT^4 + Nk_BaVT^4 = \underline{\underline{5Nk_BaVT^4}}$$

(Note: This assumes a distinguishable system. If it is indistinguishable, $S = 5Nk_BaVT^4 + Nk_B$ .)

$$P = k_BT\left(\frac{\partial \ln Z}{\partial V}\right)_{N,U} = k_BTaT^4 = \underline{\underline{ak_BT^5}}$$

(However, here I've had to assume that constant U = constant T, which is not necessarily true.)

<u>For canonical:</u>

$$U = k_BT^2\left(\frac{\partial \ln Z}{\partial T}\right)_{N,V} = k_BT^2\,4aT^3V = \underline{\underline{4k_BaVT^5}}$$

$$S = k_B\ln Z + \frac{U}{T} = k_BaVT^4 + 4k_BaVT^4 = \underline{\underline{5k_BaVT^4}}$$

$$P = k_BT\left(\frac{\partial \ln Z}{\partial V}\right)_{N,T} = k_BTaT^4 = \underline{\underline{ak_BT^5}}$$

**3.**

$\bar{V} = 1020\ \mathrm{m/s}$, $T = 27°C$, He, $u = ?$

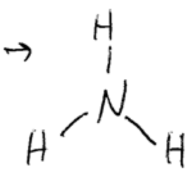
Use the NIST Webbook (or another source) to find that the mass of a He atom is $6.65\times10^{-27}$ kg. The internal energy is due only to the kinetic energy, so

$$e_k = \frac{1}{2}m\bar{V}^2 = 3.46\times10^{-21}\ \mathrm{J}$$

Avogadro's # gives us the energy per kmol:

$$u = N_A e_k = (6.02\times10^{26})(3.46\times10^{-21}) = \boxed{2.082\times10^6\ \frac{\mathrm{J}}{\mathrm{kmol}} \text{ or } 2082\ \frac{\mathrm{kJ}}{\mathrm{kmol}}}$$

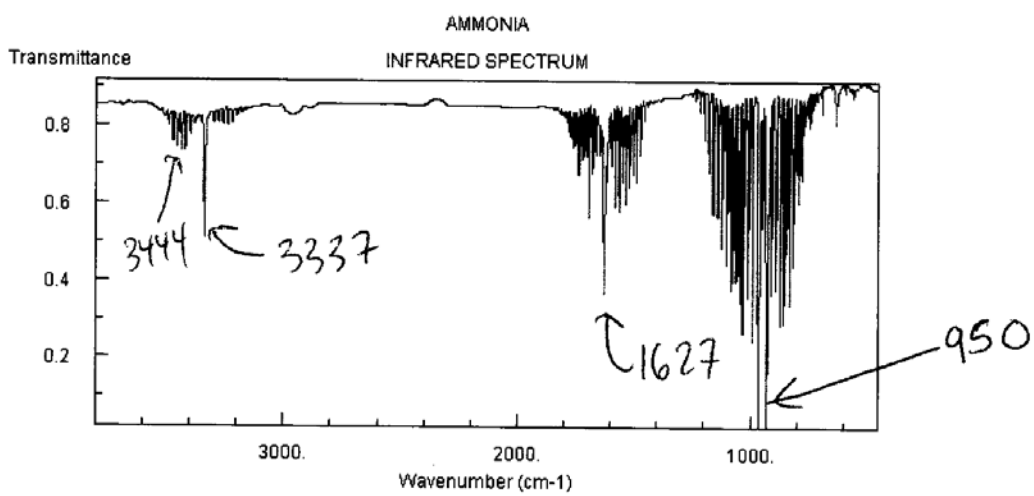
**4.**

a) $NH_3 \rightarrow$ 

b) 4 molecules → 12 DoF

3 Translational
3 Rotational
6 Vibrational

c) You can guess at the peaks from the spectroscopic data, or see in the "Energy Levels" section that they have already been found for you.

c) 


| Temperature | | 300 | 300 | 600 | 600 | 2000 | 2000 |
|---|---|---|---|---|---|---|---|
| Wave number | Degeneracy | u | E(u) | u | E(u) | u | E(u) |
| 950 | 1 | 4.55617 | 0.222665 | 2.27808 | 0.66023 | 0.6834 | 0.96197 |
| 1627 | 2 | 7.80303 | 0.049785 | 3.90152 | 0.64095 | 1.1705 | 1.7865 |
| 3337 | 1 | 16.0041 | 2.87E-05 | 8.00207 | 0.02145 | 2.4006 | 0.63186 |
| 3444 | 2 | 16.5173 | 3.66E-05 | 8.25865 | 0.03535 | 2.4776 | 1.22812 |
| | | | | | | | |
| Total DoF | 6 | | 0.272515 | | 1.35798 | | 4.60845 |

Sums

$$u = 1.4387894 \times \frac{\text{Wave \#}}{T}$$

$$E(u) = \frac{u^2 e^u}{(e^u - 1)^2} \times \text{degen.}$$

$C_p = 4R + R \times$ Sum from Spectrographic data, $R = 8.314$

$C_p = 35.52$ @ 300 K, 44.546 @ 600 K, 71.57 @ 2000 K d)

| | < 1400 | > 1400 |
|---|---|---|
| A | 19.99563 | 52.02427 |
| B | 49.77119 | 18.48801 |
| C | -15.37599 | -3.765128 |
| D | 1.921168 | 0.248541 |
| E | 0.189174 | -12.45799 |

$$C_p = A + BT + CT^2 + DT^3 + \frac{E}{T^2}$$

$C_p = 35.7$ @ 300K, 45.26 @ 600K, 72.8 @ 2000K

∴ excellent agreement