PChem Pset #2

1a. $$Q = \frac{1}{N!}\left(\frac{V}{\Lambda^3(T)}\right)^N$$

$4^?$

$$\ln Q = \ln\left(\frac{1}{N!}\left(\frac{V}{\Lambda^3(T)}\right)^N\right)$$

$$= \ln\left(\frac{1}{N!}\right) + N(\ln V - \ln \Lambda^3(T))$$

$$= \ln\left(\frac{1}{N!}\right) + N\left(\ln V - \ln\left(\left(\frac{h^2}{2\pi m k_B T}\right)^{\frac{3}{2}}\right)\right)$$

$$\ln Q = \ln\left(\frac{1}{N!}\right) + \underbrace{N\left(\ln V - \frac{3}{2}(2\ln(h)\right.}_{0 \text{ bc no } T \text{ dependance}} - \ln(2\pi m k_B T)))$$

b. $$\frac{3N}{2}\ln(2\pi m k_B T)$$

chain rule

$$\frac{\frac{3N}{2}\cdot \cancel{2\pi m k_B}}{\cancel{2\pi m k_B} T}$$

$$\frac{\partial \ln Q}{\partial T} = \frac{3N}{2T}$$

c. $$\frac{\partial \ln Q}{\partial V} = \frac{N}{V}$$ ← $N\ln V$ was the only term w/ V dependance

d. $$P = k_B T\left(\frac{\partial \ln Q}{\partial V}\right) = \frac{k_B T N}{V}$$ ✓

$$U = k_B T^2\left(\frac{\partial \ln Q}{\partial T}\right) = k_B T^2\left(\frac{3N}{2T}\right) = \frac{3}{2}N k_B T$$ ✓

$\frac{-1}{T^2}$

1, Pt.2, a $\quad T^{\frac{3}{2}} \exp\left(\frac{-\Delta}{k_B T}\right)$

Product rule

chain rule $\quad \underbrace{T^{\frac{3}{2}} \cdot \frac{\Delta}{k_B T^2}}$ $\exp\left(\frac{-\Delta}{k_B T}\right) + \frac{3}{2} T^{\frac{1}{2}} \exp\left(\frac{-\Delta}{k_B T}\right)$

$$\frac{\Delta}{k_B T^{\frac{1}{2}}} \exp\left(\frac{-\Delta}{k_B T}\right) + \frac{3}{2} T^{\frac{1}{2}} \exp\left(\frac{-\Delta}{k_B T}\right)$$

$$\frac{df}{dT} = \exp\left(\frac{-\Delta}{k_B T}\right)\left(\frac{\Delta}{k_B T^{\frac{1}{2}}} + \frac{3}{2} T^{\frac{1}{2}}\right)$$

1, Pt.2, ii $\quad \frac{d}{dT} \ln f(T) = \frac{f'(T)}{f(T)}$

$$= \frac{\exp\left(\frac{-\Delta}{k_B T}\right)\left(\frac{\Delta}{k_B T^{\frac{1}{2}}} + \frac{3}{2} T^{\frac{1}{2}}\right)}{T^{\frac{3}{2}} \exp\left(\frac{-\Delta}{k_B T}\right)}$$

$$= \frac{\frac{\Delta}{k_B T^{\frac{1}{2}}} + \frac{3}{2} T^{\frac{1}{2}}}{T^{\frac{3}{2}}}$$

$$= \frac{\Delta}{k_B T^{\frac{1}{2}}} \cdot T^{-\frac{3}{2}} + \frac{3}{2} T^{\frac{1}{2}} \cdot T^{-\frac{3}{2}}$$

$$= \frac{\Delta}{k_B T^2} + \frac{3}{2T}$$

2a i. $E_f = \frac{3}{2} N k_B T_f$

$E_i = \frac{3}{2} N k_B T_i$

$\Delta E_{sys} = E_f - E_i = \frac{3}{2} N k_B T_f - \frac{3}{2} N k_B T_i$

$\Delta E_{sys} = \frac{3}{2} N_{sys} k_B (T_{f_{sys}} - T_{i_{sys}})$

ii. $\Delta E_{sys} = -\Delta E_{env}$

$\frac{3}{2} N_{sys} k_B \Delta T_{sys} = -\frac{3}{2} N_{env} k_B \Delta T_{env}$

$-\frac{N_{sys}}{N_{env}} \Delta T_{sys} = \Delta T_{env}$

2b. $\frac{N_{sys}}{N_{env}} \Delta T_{sys} \geq 0.1$

$\frac{N_{sys}}{N_{env}} \geq \frac{0.1}{\Delta T_{sys}}$

$\frac{N_{env}}{N_{sys}} \geq \frac{\Delta T_{sys}}{0.1}$

For $\Delta T_{sys} = 100K$

$\frac{N_{env}}{N_{sys}} \geq \frac{100}{0.1} = 1000$

$$p = \frac{g_i \cdot Q_i^{5}}{Q_{total}}$$

2c. Based on the results from 2b, if the environment has 1000x # particles as the system, the environment will experience 1000x less of a temperature change. As the environment becomes even larger, it will experience even less of a temperature change. Therefore, boiling pasta in a large volume of water will lead to $\approx$ constant temperature because $N_{water} >> N_{pasta}$

3a. $Q = 5$ * Plots at the end of PDF

$P_m = 1$

The number of thermally accessible microstates does not depend on temperature

b. $Q = 3 + 2e^{-\Delta/k_B T}$

At low T, only the three lower energy states w/ energy $E = 0$ are accessible. As temperature increases, the two higher energy states become more accessible, reaching a max probability at 0.37 at 1000K, => # of thermally accessible microstates increases w/ T

3c. $Q = 2 + \exp(-\beta\Delta_1) + \exp(-\beta(\Delta_1 + \Delta_2)) + \exp(\beta(\Delta_1 + \Delta_2 + \Delta_3))$

At low T, only the lowest-energy states are the only accessible state. The probability of the lowest-energy states quickly drops off as T increases and the other three microstates become accessable. The microstates become accessible in the order of E_2, E_3, E_4. At all T, E_1 is the most probable state $\Rightarrow$.

4a. $\ln Q = \ln\left(\frac{1}{N!}\right) + N\left(\ln(V - Nb) - \frac{3}{2}\left(2\ln(h) - \ln(2\pi m k_B T)\right)\right) + \frac{N^2 a}{V k_B T}$

$$\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = \frac{3N \cdot 2\pi m k_B}{2 \cdot 2\pi m k_B T} - \frac{N^2 a}{V k_B T^2}$$

$$= \frac{3N}{2T} - \frac{N^2 a}{V k_B T^2}$$

$$\Rightarrow U = \frac{3}{2} N k_B T - \frac{N^2 a}{V}$$

b. $\left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2} N k_B$

c. $P = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$

$$N \ln(V - nb) + \frac{N^2 a}{V k_B T}$$

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N} = \frac{N}{V - nb} - \frac{N^2 a}{V^2 k_B T}$$

$$P = \frac{k_B T N}{V - nb} - \frac{\cancel{k_B T} N^2 a}{V^2 \cancel{k_B T}}$$

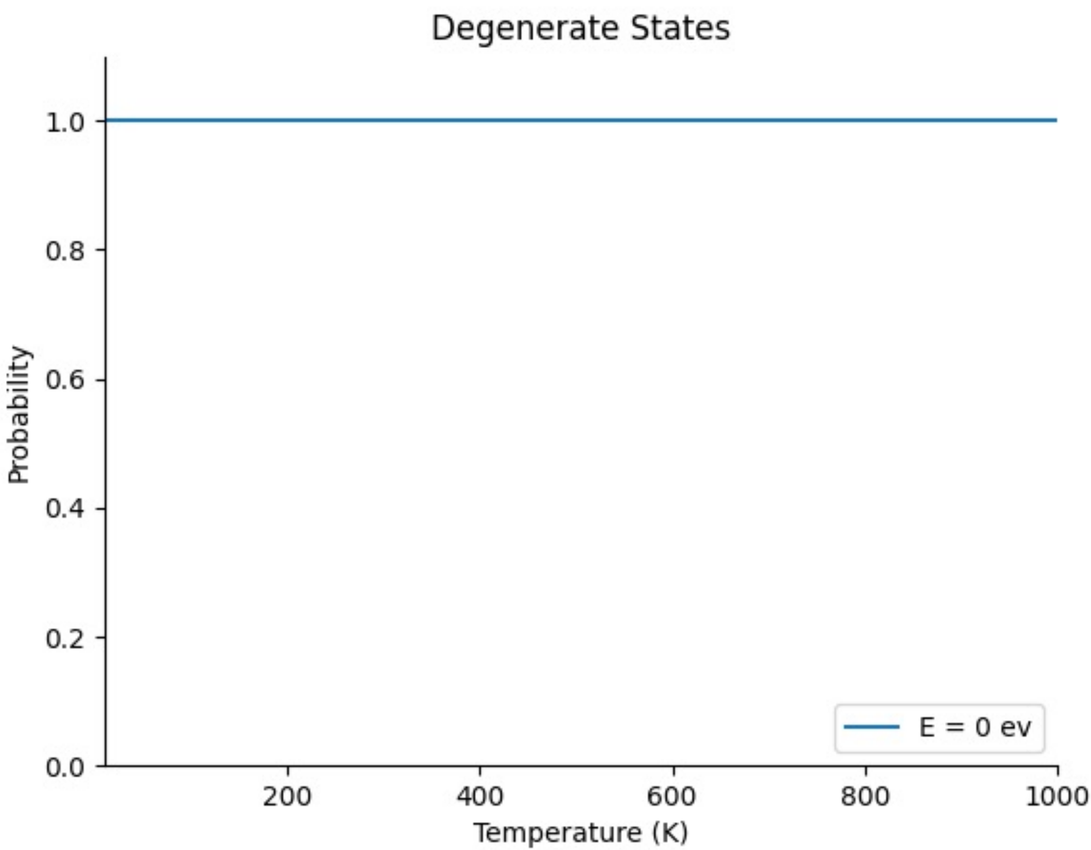
$$P = \frac{N k_B T}{V - Nb} - \frac{N^2 a}{V^2}$$

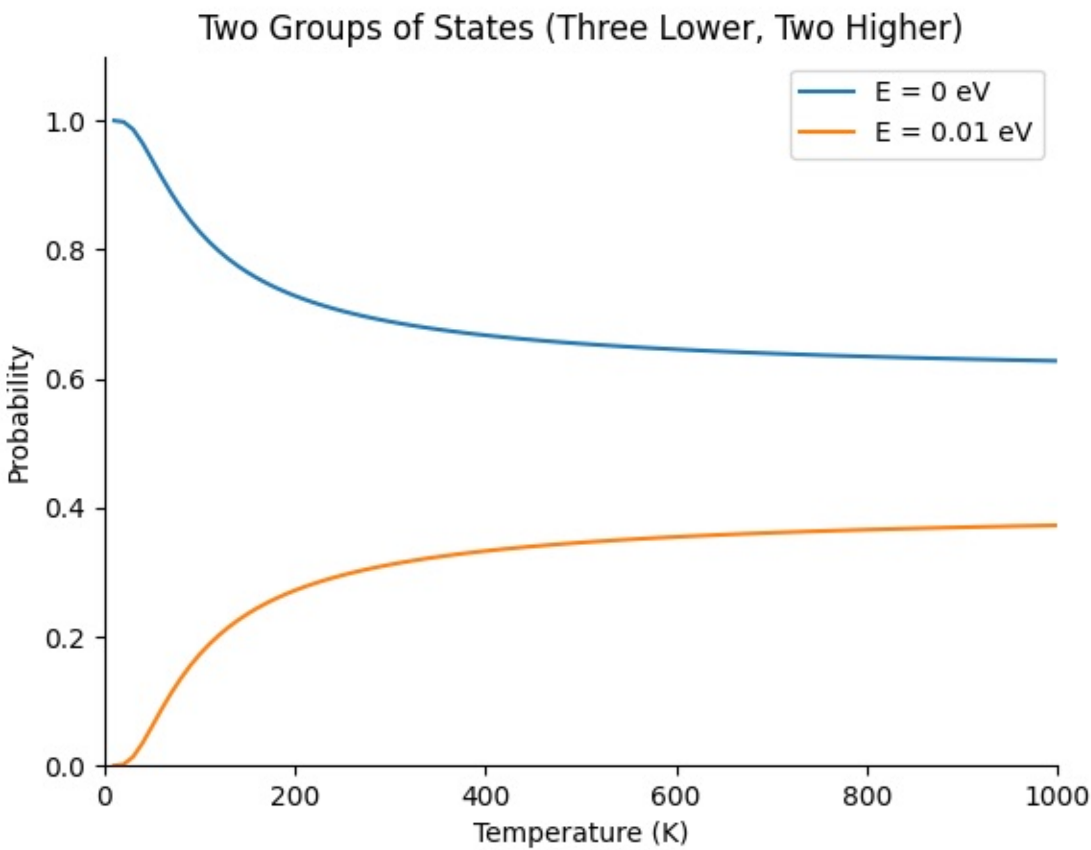
5a. Done in python, screenshots appended to this pdf file

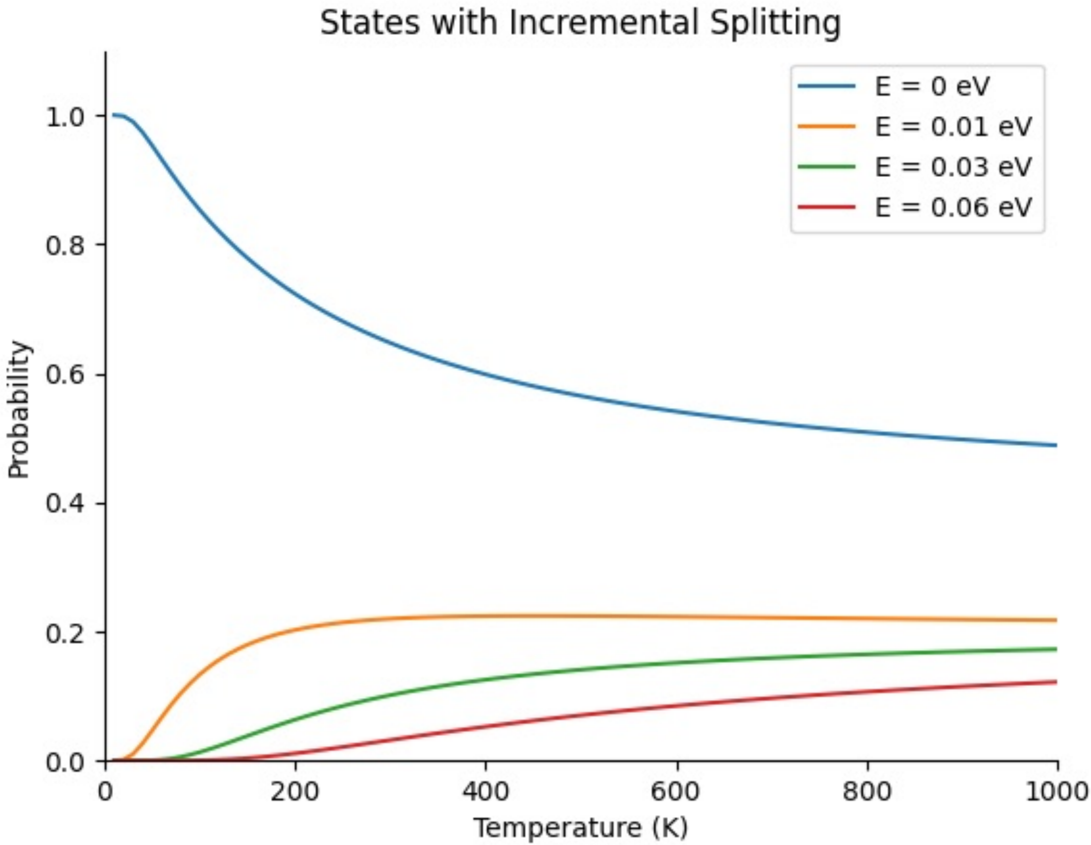
b. i. At $T = 300K$, $P = 1 bar$, the $\frac{\lambda}{d}$ % are all 1.5% or lower, meaning the interparticle distance is much larger than the de Broglie λ, suggesting that quantum effects are not significant.

At $T = 300K$, $P = 100$ bar, the $\frac{\lambda}{d}$ % is larger than at $P = 1$ bar for all elements. However, the interparticle distances are still much larger than the de Broglie wavelength, suggesting that quantum effects are not significant.

At $T = 3K$, $P = 100$ bar, the minimum $\frac{\lambda}{d}$ % is 54% and the maximum is 317%, which means the de Broglie wavelength is comparable to the average interparticle distance if not much larger, suggesting that quantum effects are significant.


Degenerate States
Probability
Temperature (K)
E = 0 ev
1.0
0.8
0.6
0.4
0.2
0.0
200
400
600
800
1000


Two Groups of States (Three Lower, Two Higher)
E = 0 eV
E = 0.01 eV
Probability
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
Temperature (K)


States with Incremental Splitting
E = 0 eV
E = 0.01 eV
E = 0.03 eV
E = 0.06 eV
Probability
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
Temperature (K)

5a) i. T = 300 K , P = 1 bar

	M_r (amu)	m (kg)	d (nm)	λ (nm)	λ/d (%)
He	4.002602	6.644319e-27	3.4594	0.0504	1.4569
Ne	20.179700	3.350918e-26	3.4594	0.0224	0.6475
Ar	39.948000	6.633521e-26	3.4594	0.0160	0.4625
Kr	83.798000	1.391498e-25	3.4594	0.0110	0.3180
Xe	131.293000	2.180171e-25	3.4594	0.0088	0.2544

5a) ii. T = 300 K , P = 100 bar

	M_r (amu)	m (kg)	d (nm)	λ (nm)	λ/d (%)
He	4.002602	6.644319e-27	0.745	0.050	6.711
Ne	20.179700	3.350918e-26	0.745	0.022	2.953
Ar	39.948000	6.633521e-26	0.745	0.016	2.148
Kr	83.798000	1.391498e-25	0.745	0.011	1.477
Xe	131.293000	2.180171e-25	0.745	0.009	1.208

5a) iii. T = 3 K , P = 100 bar

	M_r (amu)	m (kg)	d (nm)	λ (nm)	λ/d (%)
He	4.002602	6.646480e-27	0.161	0.504	313.043
Ne	20.179700	3.350918e-26	0.161	0.224	139.130
Ar	39.948000	6.633521e-26	0.161	0.160	99.379
Kr	83.798000	1.391498e-25	0.161	0.110	68.323
Xe	131.293000	2.180171e-25	0.161	0.088	54.658