HW 3 Solutions

2.25 a) I will end where I started.
b) See blog for long explanation.

Distribution of ending positions for $N$ steps:

$$f(Nx) \propto e^{-\frac{x^2}{2N^2}}$$

$x$: excess of forward steps over $N/2$ steps.

$2xL = \text{net distance traveled}$

$2x$: excess of forward steps over $N$ steps.

Half width of the distribution:

$$\text{FWHM} = \sqrt{\frac{\pi}{2}} \cdot \frac{g_{\text{max}}}{g} \Rightarrow \text{FWHM} = \sqrt{2N} \cdot L$$

$N = 10^4 \Rightarrow$ half width = 140 steps.

Chances of getting farther than $\approx 10^2$ (100-500) steps is negligible.

2.30 a) $S = \frac{k_B}{N} \ln \frac{2^{4N}}{\sqrt{3}N} = \frac{k_B}{N} \ln 2^{4N} - \ln \sqrt{3}N \approx 3 \cdot 10^{-23}$

$N = 10^{23} \Rightarrow 2.8 \cdot 10^{-23} \approx 28$
b) Most likely incorrect

\[ \frac{S}{k_B} = \ln \frac{2^{4N}}{4N} = 2.8 \times 10^{-23} - 55.5 \]

The difference is only 27.9 units which is negligible compared to the total value. Time scales are irrelevant for such a large system.

c) The partition reduces \( S \) in 27 units out of 3.10

\[ \Rightarrow 1 \text{ part in } \sim 10^{22} \text{ !} \]

This violation of the second law is insignificant.

2.33 \( \text{Ar} \), \( T = 300 \text{ K}, \ P = 1 \text{ atm} \)

\[ \frac{V}{N} = \frac{kT}{P} = \frac{1.38 \times 10^{-23} \text{ J/K}}{300 \text{ K}} \cdot \frac{3 \text{ atm}}{10^5 \text{ N/m}^2} = 4.14 \times 10^{-26} \text{ m}^3 \]

\[ \frac{U}{N} = \frac{3}{2} kT = 6.21 \times 10^{-21} \text{ J} \]

1 mol \( \text{Ar} \) \( \Rightarrow \) 40 g

1 molecule \( \frac{0.040 \text{ kg/mol}}{N_A \text{ mol}^{-1}} = 6.69 \times 10^{-26} \text{ kg/mol} \)

\[ \frac{V}{N \left( \frac{27 \text{ mV}}{3 \text{ N} \cdot \text{m}^2} \right)^{3/2}} = 1.02 \times 10^{-7} \text{ (no units)} \]
\[ S \text{ (1 mol)} = S = R \left[ \ln \left( 1.02 \times 10^7 \right) + \frac{5}{2} \right] = 155.5 \text{ J/K} \]

The mass of 44 \text{ u} \left( \frac{44}{4} \right)^{3/2} = 31.6 \text{ } \Rightarrow \text{ factor difference in molar entropy}

The mass matters, because between He and Ar

The momentum hypersphere \( r = \frac{m^{3/2}}{2\pi m} \), larger with larger mass \( \Rightarrow \) more multiplicity.

\[ \frac{5}{2} = \ln \left[ \frac{N}{V} e^{\frac{5}{2}} \left( \frac{4\pi m U}{3N\hbar^2} \right)^{3/2} \right] \]

This is negative if the argument of \( \ln \) is \( < 1 \)

\[ 1 = \frac{V}{N} e^{\frac{5}{2}} \left( \frac{4\pi m U}{3N\hbar^2} \right) \]

\[ U = \frac{3}{2} \frac{Nk_B T}{m} \]

\[ T = \left( \frac{N}{V} \right)^{2/3} \frac{\hbar^2}{2\pi c^3 m \kappa} \frac{N}{V} \text{ from room } T \text{ and atmospheric } P \]

\[ \frac{N}{V} = \frac{P_0}{kT_0} = \frac{10^5 P_a}{k T_0} \]

\[ T \approx 0.01 \text{ K} \text{ below this } T \text{ quantum effects matter} \]
24. a) NaCl in crystal has much less multiplicity than in soup (configurational entropy increases).

b) Mixing entropy of salt increases.

also the proteins are denaturalized at high T, unfolding occurs, which again increases configurational entropy.

c) Breaking many different ways of breaking, only 1 way of being full

d) many more ways for sand to be in any order than for sand to be in a "castle" order

e) Many ways the tree can be cut down

d) Entropy of environment increases because the energy (due to heat) increases.

\[
T_A = \frac{\Delta U_A}{\Delta S_A} = \frac{2E - 0E}{10.7 \text{ kJ/mol}} = 0.19 \frac{E}{k_B} = 220 \text{ K} \quad (E = 0.1 \text{ eV})
\]

\[
T_B = \frac{\Delta U_B}{\Delta S_B} = \frac{100E - 98E}{187.5 \text{ kJ/mol} - 185.9 \text{ kJ/mol}} = 0.91 \frac{E}{k_B} = 1660 \text{ K}
\]
Solid B is much hotter when it has all energy

\[ T_A = \frac{61E-59E}{160.9 k_B - 157.4 k_B} = 660K \]

\[ T_B = \frac{41E-39E}{(167.2-163.5) k_B} = 660K \]

Energy will transfer from B to A until:

\[ \frac{\partial S_A}{\partial U_A} \bigg|_{U_{AF}} = \frac{\partial S_B}{\partial U_B} \bigg|_{U_{BF}} \]

A transfer of energy from B to A will make A gain more \( S \) than B loses.

\( \Rightarrow \) spontaneous
3.10) Ice cube melting

a) \( \Delta S = \frac{Q}{T} - \frac{mL}{T} = \frac{30 \times 333.3/3}{273.15} = 36.6 \text{ J/K} \)

b) \( \Delta S = \int_{T_i}^{T_f} \frac{C dt}{T} = C \ln \frac{T_f}{T_i} = 11.0 \text{ J/K} \)

c) heat loss by kitchen = heat gained by ice/water
\( \Delta S = \frac{Q}{T} = \frac{mL + MC \Delta T}{T} = \frac{-30 \times 333 - 30 \times 4.18 \times 25}{298} \) = -44.1 J/K

d) \( \Delta S_{total} = 36.6 \text{ J/K} + 11.0 \text{ J/K} - 44.1 \text{ J/K} = 3.5 \text{ J/K} \)

Tiny increase! but irreversible process anyway