

## HW 3

2.24 (a)

$$\begin{aligned}
\Omega\left(N, \frac{N}{2}\right) &= \frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!} \\
&\approx \frac{N^N E^{-N} \sqrt{2\pi N}}{\left(\left(\frac{N}{2}\right)^{(N/2)} E^{-(N/2)} \sqrt{\pi N}\right) \left(\left(\frac{N}{2}\right)^{(N/2)} E^{-(N/2)} \sqrt{\pi N}\right)} \\
&\approx \frac{N^N E^{-N} \sqrt{2\pi N}}{\left(\frac{N}{2}\right)^N E^{-N} \pi N} \\
&\approx \frac{2^N \sqrt{2\pi N}}{\pi N} \\
&\approx \frac{2^{N+1}}{\sqrt{2\pi N}} \\
&\approx \frac{2^{N+\frac{1}{2}}}{\sqrt{2\pi}} \\
\Omega_{max} &\approx 2^N
\end{aligned}$$

(b)

$$x \equiv N \uparrow - \frac{N}{2}$$

$$N \uparrow = \frac{N}{2} + 2$$

$$N = N \uparrow + N \downarrow$$

$$N = \frac{N}{2} + x + N \downarrow$$

$$\frac{N}{2} = x + N \downarrow$$

$$N \downarrow = \frac{N}{2} - x$$

$$\Omega = \binom{N \downarrow + N \uparrow + 1}{N \downarrow} = \binom{\frac{N}{2} + x + \frac{N}{2} - x + 1}{\frac{N}{2} - x}$$

$$\begin{aligned}
\Omega &\approx \binom{N}{\frac{N}{2}-x} = \frac{N!}{(\frac{N}{2}-x)! (\frac{N}{2}+x)!} \\
&\approx \frac{N^N e^{-N} \sqrt{2\pi N}}{\left( \left( \frac{N}{2}-x \right)^{(\frac{N}{2}-x)} e^{-(\frac{N}{2}-x)} \sqrt{2\pi(\frac{N}{2}-x)} \right) \left( \left( \frac{N}{2}+x \right)^{(\frac{N}{2}+x)} e^{-(\frac{N}{2}+x)} \sqrt{2\pi(\frac{N}{2}+x)} \right)} \\
&\approx \frac{N^N \sqrt{2\pi N}}{\left( \left( \frac{N}{2}-x \right)^{(\frac{N}{2}-x)} \sqrt{2\pi(\frac{N}{2}-x)} \right) \left( \left( \frac{N}{2}+x \right)^{(\frac{N}{2}+x)} \sqrt{2\pi(\frac{N}{2}+x)} \right)} \\
&\approx \frac{N^N \sqrt{2\pi N}}{2\pi \sqrt{(\frac{N}{2})^2 - x^2} \left( \frac{N}{2}-x \right)^{(\frac{N}{2}-x)} \left( \frac{N}{2}+x \right)^{(\frac{N}{2}+x)}} \\
&\approx \frac{N^N \sqrt{2\pi N}}{2\pi \sqrt{(\frac{N}{2})^2 - x^2} \left( \frac{N}{2}-x \right)^{\frac{N}{2}} \left( \frac{N}{2}-x \right)^{-x} \left( \frac{N}{2}+x \right)^{\frac{N}{2}} \left( \frac{N}{2}+x \right)^x} \\
&\approx \frac{N^N \sqrt{2\pi N}}{2\pi \sqrt{(\frac{N}{2})^2 - x^2} \left( \left( \frac{N}{2} \right)^2 - x^2 \right)^{\frac{N}{2}} \left( \frac{N}{2}-x \right)^{-x} \left( \frac{N}{2}+x \right)^x} \\
&\approx \frac{N^N \sqrt{N}}{\sqrt{2\pi(\frac{N}{2})^2 - x^2} \left( \left( \frac{N}{2} \right)^2 - x^2 \right)^{\frac{N}{2}} \left( \frac{N}{2}-x \right)^{-x} \left( \frac{N}{2}+x \right)^x} \\
\Omega &\approx \frac{N^N}{\left( \left( \frac{N}{2} \right)^2 - x^2 \right)^{\frac{N}{2}} \left( \frac{N}{2}-x \right)^{-x} \left( \frac{N}{2}+x \right)^x} \\
\ln(\Omega) &\approx \ln \left( \frac{N^N}{\left( \left( \frac{N}{2} \right)^2 - x^2 \right)^{\frac{N}{2}} \left( \frac{N}{2}-x \right)^{-x} \left( \frac{N}{2}+x \right)^x} \right) \\
&\approx \ln(N^N) - \ln \left( \left( \left( \frac{N}{2} \right)^2 - x^2 \right)^{N/2} \right) - \ln \left( \left( \frac{N}{2}-x \right)^{-x} \right) - \ln \left( \left( \frac{N}{2}+x \right)^x \right) \\
&\approx N \ln(N) - \frac{N}{2} \ln \left( \left( \frac{N}{2} \right)^2 - x^2 \right) + x \ln \left( \frac{N}{2}-x \right) - x \ln \left( \frac{N}{2}+x \right)
\end{aligned}$$

i.

$$\begin{aligned}
\frac{N}{2} \ln \left( \left( \frac{N}{2} \right)^2 - x^2 \right) &= \frac{N}{2} \ln \left( \left( \frac{N}{2} \right)^2 \left( 1 - \left( \frac{2x}{N} \right)^2 \right) \right) \\
&= \frac{N}{2} \ln \left( \left( \frac{N}{2} \right)^2 \right) + \frac{N}{2} \ln \left( 1 - \left( \frac{2x}{N} \right)^2 \right) \\
&= N \ln \left( \frac{N}{2} \right) - \frac{N}{2} \left( \frac{2x}{N} \right)^2 \\
&= N \ln(N) - N \ln(2) - \frac{2x^2}{N}
\end{aligned}$$

ii.

$$\begin{aligned}
x \ln \left( \frac{N}{2} - x \right) &= x \ln \left( \frac{N}{2} \left( 1 - \frac{2x}{N} \right) \right) \\
&= x \ln \left( \frac{N}{2} \right) + x \ln \left( 1 - \frac{2x}{N} \right) \\
&= x \ln \left( \frac{N}{2} \right) - x \left( \frac{2x}{N} \right) \\
&= x \ln \left( \frac{N}{2} \right) - \frac{2x^2}{N}
\end{aligned}$$

iii.

$$\begin{aligned}
x \ln \left( \frac{N}{2} + x \right) &= x \ln \left( \frac{N}{2} \left( 1 + \frac{2x}{N} \right) \right) \\
&= x \ln \left( \frac{N}{2} \right) + x \ln \left( 1 + \frac{2x}{N} \right) \\
&= x \ln \left( \frac{N}{2} \right) + x \left( \frac{2x}{N} \right) \\
&= x \ln \left( \frac{N}{2} \right) + \frac{2x^2}{N}
\end{aligned}$$

$$\ln(\Omega) \approx N \ln(N) - \left( N \ln(N) - N \ln(2) - \frac{2x^2}{N} \right) + \left( x \ln \left( \frac{N}{2} \right) - \frac{2x^2}{N} \right) - \left( x \ln \left( \frac{N}{2} \right) + \frac{2x^2}{N} \right)$$

$$\ln(\Omega) \approx N \ln(2) - \frac{2x^2}{N}$$

$$\Omega \approx 2^N e^{-\frac{2x^2}{N}}$$

$$\Omega \approx 2^N \quad (\Omega_{max}, x = 0)$$

(c) Width measured when value falls to  $\frac{1}{e}$  of max value.

$$\begin{aligned}\frac{\Omega_{max}}{e} &= \Omega_{max} e^{-\frac{2x^2}{N}} \\ e^{-1} &= e^{-\frac{2x^2}{N}} \\ 1 &= \frac{2x^2}{N} \\ x^2 &= \frac{N}{2} \\ x &= \sqrt{\frac{N}{2}}\end{aligned}$$

Total width  $w = 2x = 2\sqrt{\frac{N}{2}} = \sqrt{2N}$ .

(d)

$$\begin{aligned}P &= \frac{\Omega}{\Omega_{max}} = \frac{\Omega_{max} e^{-\frac{2x^2}{N}}}{\Omega_{max}} = e^{-\frac{2x^2}{N}} \\ P_{501000} &= e^{-\frac{2(1000)^2}{1000000}} = 0.135\end{aligned}$$

501000 heads is probable

$$P_{510000} = e^{-\frac{2(10000)^2}{1000000}} = 1.38 \times 10^{-87}$$

510000 heads is improbable

2.25 (a)  $N$  = Total Steps,  $n$  = Steps away from starting position

$$\Omega \approx \frac{N!}{n!(N-n)!}$$

$$\Omega_{max} \approx 2^N$$

$$P = \frac{\Omega}{\Omega_{max}} = \frac{N!}{n!(N-n)!} \frac{1}{2^N}$$

Highest probability state is when  $n = 0$ , so ending up at the same place. It is also probable that you will end up in a spot that is within the width of the peak, so  $\pm \sqrt{\frac{N}{2}}$  steps away from the starting position.

(b)  $\max \Delta x = \pm \sqrt{\frac{10000}{2}} \approx \pm 71$ .

It is likely that you will end up within  $\pm 71$  steps from the starting point.

(c) Mean free path:

$$\begin{aligned}\ell &= \frac{1}{4\pi r^2} \frac{V}{N_{mol}} \\ \bar{v} &= \sqrt{\frac{3kT}{m}}\end{aligned}$$

Typical values for air at STP:  $\ell = 1.5 \times 10^{-7}m$  and  $\bar{v} = 500m/s$ .

$$N = \frac{\bar{v}t}{\ell}$$

$$\begin{aligned}\Delta x &\approx x_{width}\ell = \sqrt{\frac{N}{2}}\ell = \sqrt{\frac{\bar{v}t}{2}}\ell \\ &\approx \sqrt{\frac{\bar{v}t\ell}{2}} \\ \Delta x &\approx \sqrt{\frac{(500)(1)(1.5 \times 10^{-7})}{2}} = 0.0061m\end{aligned}$$

$\Delta x$  depends on  $\sqrt{t}$  so for an increasing  $\Delta x$  the time it takes will grow at an exponential rate.

$\Delta x$  also has a dependence on  $\sqrt[4]{T}$  so for increases in temperature  $\Delta x$  does not appreciably change.

2.29

$$\begin{aligned}\Omega_{most} &= 6.87 \times 10^{114} \\ \Omega_{least} &= 2.77 \times 10^{81} \\ S_{most} &= \ln(\Omega_{most}) = \ln(6.87 \times 10^{114}) = 264.4 \\ S_{least} &= \ln(\Omega_{least}) = \ln(2.77 \times 10^{81}) = 187.5 \\ \Omega_{total} &= 9.26 \times 10^{115} \\ S_{total} &= \ln(\Omega_{total}) = \ln(9.26 \times 10^{115}) = 267\end{aligned}$$

2.34

$$\begin{aligned}S &= k \ln(\Omega) \\ &= Nk \left[ \ln \left( \frac{V}{N} \left( \frac{4n\pi U}{3Nh^3} \right)^{\frac{3}{2}} \right) + \frac{5}{2} \right] \quad DoF = 3 \\ Q &= \Delta U + W \quad \Delta U = 0 \\ &= W = \int_{V_i}^{V_f} PdV \quad P = \frac{NkT}{V} \\ &= NkT \int_{V_i}^{V_f} \frac{dV}{V} = NkT \ln \left( \frac{V_f}{V_i} \right) \\ S &= Nk \left[ \ln \left( \frac{V}{N} \left( \frac{4n\pi U}{3Nh^3} \right)^{\frac{3}{2}} + \frac{5}{2} \right) \right] \\ &= Nk \left[ \ln(V) \ln \left( \frac{1}{N} \left( \frac{4n\pi U}{3Nh^3} \right)^{\frac{3}{2}} \right) + \frac{5}{2} \right]\end{aligned}$$

$$\ln \left( \frac{1}{N} \left( \frac{4n\pi U}{3Nh^3} \right)^{\frac{3}{2}} \right) + \frac{5}{2} \text{ is constant}$$

$$\begin{aligned} \Delta S &= Nk \ln(V_f) - Nk \ln(V_i) = Nk \ln \left( \frac{V_f}{V_i} \right) \\ &= Nk \ln \left( \frac{V_f}{V_i} \right) \frac{T}{T} = \frac{NkT \ln \left( \frac{V_f}{V_i} \right)}{T} \\ \Delta S &= \frac{Q}{T} \end{aligned}$$

2.36

$$\begin{aligned} S &\approx Nk \\ N_{book} &= \frac{1000}{12} \times 6.022 \times 10^{22} = 5.02 \times 10^{25} \\ S_{book} &= 5.02 \times 10^{25} \times 1.38 \times 10^{-23} = 693 JK^{-1} \\ N_{moose} &= \frac{400 \times 10^3}{18} \times 6.022 \times 10^{22} = 1.34 \times 10^{28} \\ S_{moose} &= 1.34 \times 10^{28} \times 1.38 \times 10^{-23} = 1.84 \times 10^5 JK^{-1} \\ N_{sun} &= \frac{2 \times 10^{33}}{12} \times 6.022 \times 10^{22} = 1.2 \times 10^{57} \\ S_{sun} &= 1.2 \times 10^{57} \times 1.38 \times 10^{-23} = 1.66 \times 10^{34} JK^{-1} \end{aligned}$$

3.1

$$\begin{aligned} \frac{1}{T} &= \frac{\partial S}{\partial U} \\ T &= \frac{\partial U}{\partial S} = \frac{\Delta U}{\Delta S} = \frac{\epsilon \Delta q}{\Delta S} \\ \epsilon &= 0.1 eV = 1.6 \times 10^{-20} J \end{aligned}$$

(a)  $q_a = 1$

$$\begin{aligned} T_A &= \frac{\epsilon(2-0)}{S_A(2) - S_A(0)} = \frac{2\epsilon}{k(10.7-0)} = 0.187 \frac{\epsilon}{k} \\ &= 0.187 \left( \frac{1.6 \times 10^{-20}}{1.38 \times 10^{-23}} \right) = 216.7 K \end{aligned}$$

$$\begin{aligned} T_B &= \frac{\epsilon(100-98)}{S_B(100) - S_B(98)} = \frac{2\epsilon}{k(187.53 - 185.33)} = 0.909 \frac{\epsilon}{k} \\ &= 0.909 \left( \frac{1.6 \times 10^{-20}}{1.38 \times 10^{-23}} \right) = 1054 K \end{aligned}$$

(b)  $q_a = 60$

$$\begin{aligned} T_A &= \frac{\epsilon(61 - 59)}{S_A(61) - S_A(59)} = \frac{2\epsilon}{k(160.9 - 157.35)} = 0.56 \frac{\epsilon}{k} \\ &= 0.56 \left( \frac{1.6 \times 10^{-20}}{1.38 \times 10^{-23}} \right) = 649K \end{aligned}$$

$$\begin{aligned} T_B &= \frac{\epsilon(41 - 39)}{S_B(41) - S_B(39)} = \frac{2\epsilon}{k(107.0 - 103.5)} = 0.56 \frac{\epsilon}{k} \\ &= 0.56 \left( \frac{1.6 \times 10^{-20}}{1.38 \times 10^{-23}} \right) = 649K \end{aligned}$$

$$T_A = T_B$$

3.2

$$\begin{aligned} \frac{1}{T} &= \frac{\partial S}{\partial U} \Rightarrow T = \frac{\partial U}{\partial S} \\ T_A &= \frac{\partial U_A}{\partial S_A} \quad T_B = \frac{\partial U_B}{\partial S_B} \quad T_C = \frac{\partial U_C}{\partial S_C} \end{aligned}$$

$$\begin{aligned} T_A &= T_B \\ \frac{\partial U_A}{\partial S_A} &= \frac{\partial U_B}{\partial S_B} \\ T_B &= T_C \\ \frac{\partial U_B}{\partial S_B} &= \frac{\partial U_C}{\partial S_C} \Rightarrow \frac{\partial U_A}{\partial S_A} = \frac{\partial U_C}{\partial S_C} \Rightarrow T_A = T_C \end{aligned}$$

3.3 The two objects will exchange thermal energy until the slopes of their entropy vs energy graphs are equal.

3.5

$$\begin{aligned} \frac{1}{T} &= \frac{\partial S}{\partial U} \quad \Omega = \left( \frac{Ne}{q} \right)^q \\ U &= q\epsilon \Rightarrow q = \frac{U}{\epsilon} \\ \omega &= \left( \frac{Ne\epsilon}{U} \right)^{\frac{U}{\epsilon}} \end{aligned}$$

$$\begin{aligned}
S &= k \ln(\Omega) = k \ln \left[ \left( \frac{Ne\epsilon}{U} \right)^{\frac{U}{\epsilon}} \right] \\
&= \frac{Uk}{\epsilon} \ln \left( \frac{Ne\epsilon}{U} \right) \\
&= \frac{Uk}{\epsilon} (\ln(N\epsilon) + \ln(e) - \ln(U)) \\
\frac{1}{T} &= \frac{\partial S}{\partial U} = \frac{\partial}{\partial U} \left[ \frac{Uk}{\epsilon} (\ln(N\epsilon) + 1 - \ln(U)) \right] \\
&= \frac{\partial}{\partial U} \left[ \frac{Uk}{\epsilon} \ln(N\epsilon) + \frac{Uk}{\epsilon} - \frac{Uk}{\epsilon} \ln(U) \right] \\
&= \frac{k}{\epsilon} \ln(N\epsilon) + \frac{k}{\epsilon} - \left( \frac{k}{\epsilon} \ln(U) + \frac{Uk}{U\epsilon} \right) \\
\frac{1}{T} &= \frac{k}{\epsilon} (\ln(N\epsilon) - \ln(U)) \\
\frac{\epsilon}{kT} &= \ln(N\epsilon) - \ln(U) \\
e^{\ln(U)} &= e^{(\ln(N\epsilon) - \frac{\epsilon}{kT})} \\
U &= N\epsilon e^{-\frac{\epsilon}{kT}}
\end{aligned}$$

3.10 (a) Heat of formation for water  $L_{H_2O(\ell)} = 334 Jg^{-1}$

$$Q = mL = (30)(334) = 10020 J$$

$$\Delta S_A = \frac{Q}{T} = \frac{10020}{273} = 36.7 JK^{-1}$$

(b)

$$c_{H_2O(\ell)} = 4.181 Jg^{-1}K^{-1}$$

$$\Delta S_B = C_V \int_{T_i}^{T_f} \frac{1}{T} dT$$

$$C_V = mc$$

$$\Delta S_B = mc \int_{T_i}^{T_f} \frac{1}{T} dT$$

$$= mc \ln \left( \frac{T_f}{T_i} \right)$$

$$= (30)(4.181) \ln \left( \frac{298}{273} \right) = 11 JK^{-1}$$

$$\Delta S_{water} = \Delta S_A + \Delta S_B = 36.7 + 11 = 47.7 JK^{-1}$$



(c)

$$Q = Q_{ice} + Q_{water} = Q_{ice} + mc\Delta T$$

$$= 10020 + (30)(4.181)(25) = 13156J$$

$$\Delta S_{room} = \frac{-13156}{298} = -44.7 JK^{-1}$$

(d)

$$\Delta S_{univ} = \Delta S_{room} + \Delta S_{water} = -44.1 + 47.7 = 3.6 JK^{-1}$$

A positive entropy is expected since the reaction occurs spontaneously

3.11

$$T_1 = 55C = 328K \quad T_2 = 10C = 283K \quad V_1 = 50L \quad V_2 = 25L$$

$$T_f = \frac{T_1 V_1 + T_2 V_2}{V_1 + V_2}$$

$$= \frac{(328)(50) + (283)(25)}{50 + 25} = 313K$$

$$\Delta S = C_V \int_{T_i}^{T_f} \frac{1}{T} dT = C_v \ln \left( \frac{T_f}{T_i} \right) = mc \ln \left( \frac{T_f}{T_i} \right)$$

$$\Delta S_{hot} = (50000)(4.181) \ln \left( \frac{313}{328} \right) = -9786 JK^{-1}$$

$$\Delta S_{cold} = (25000)(4.181) \ln \left( \frac{313}{283} \right) = 10532 JK^{-1}$$

$$\Delta S_{univ} = \Delta S_{hot} + \Delta S_{cold} = -9786 + 10532 = 746 JK^{-1}$$

3.13 (a)

$$\Delta S = \frac{Q}{T} \quad Q = F_s T$$

$$F_s = 1000 W m^{-2} \quad t = 365 \times 8 \times 60 \times 60 = 10512000 s$$

$$Q = (1000)(10512000) = 1.0512 \times 10^{10}$$

$$\Delta S_{\oplus} = \frac{1.0512 \times 10^{10}}{300} = 3.5 \times 10^7 JK^{-1}$$

$$\Delta S_{\odot} = \frac{-1.0512 \times 10^{10}}{6000} = -1.75 \times 10^6 JK^{-1}$$

$$\Delta S_{univ} = \Delta S_{\oplus} + \Delta S_{\odot} = 3.5 \times 10^7 - 1.75 \times 10^6 = 3.325 JK^{-1}$$

(b) In order for the grass to grow it needs sunlight. The entropy that is gained in the 1 square meter of grass is many magnitudes higher than the entropy lost in the formation of complex hydrocarbons.

3.14

$$C_V = aT + bT^3 \quad a = 0.00135 \quad b = 2.48 \times 10^{-5}$$

$$S(T_f) - S(T_i) = \int_{T_i}^{T_f} \frac{C_V(T)}{T} dT$$

$$S(T_f) - S(0) = \int_0^{T_f} (a + bT^2) dT$$

$$S(T_f) = \left( aT + \frac{bT^3}{3} \right) \Big|_{T=0}^{T=T_f}$$

$$S(T_f) = aT_f + \frac{bT_f^3}{3}$$

$$S(1) = (0.00135)(1) + \frac{2.48 \times 10^{-5}}{3}(1)^3 = 1.36 \times 10^{-3} JK^{-1}$$

$$\frac{S(1)}{k} = \frac{1.36 \times 10^{-3}}{1.38 \times 10^{-23}} = 9.86 \times 10^{19}$$

$$S(10) = (0.00135)(10) + \frac{2.48 \times 10^{-5}}{3}(10)^3 = 2.18 \times 10^{-2} JK^{-1}$$

$$\frac{S(10)}{k} = \frac{2.18 \times 10^{-2}}{1.38 \times 10^{-23}} = 1.58 \times 10^{21}$$