QMB Homework 4.

Question 1.

a. When it reaches equilibrium $\Delta G = \Delta G^{\circ} + RT \ln K_{eq} = 0$.

$\therefore \Delta G^{\circ} = -RT \ln K_{eq} = -8.31432 \times (273.15 + 37) \ln 130{,}000$

$\therefore \Delta G^{\circ} = -30365 \text{ J/mol} = -30.4 \text{ kJ/mol}$.

b. $\Delta G = \Delta G^{\circ} + RT \ln Q$

$$Q = \frac{[Pi][ADP]}{[ATP][H_2O]} = \frac{1 \times 10^{-3} \text{ mol/L} \times 100 \times 10^{-6} \text{ mol/L}}{10 \times 10^{-3} \text{ mol/L} \times 55.56 \text{ mol/L}} = 1.8 \times 10^{-7}$$

$\Delta G = \Delta G^{\circ} + RT \ln Q = -30.4 \text{ kJ/mol} + 8.314 \times (310.15) \times \ln 1.8 \times 10^{-7}$.

$\Delta G = -70458 \text{ J/mol} \approx -70.5 \text{ kJ/mol}$.

① For 1 mole of ATP, it will produce 70.5 kJ Energy.

② For an individual ATP, it will produe. $\frac{70.5 \text{ kJ}}{6.02 \times 10^{23}} = 11703 \times 10^{-23} \text{ J}$

$$1 \, k_B T = 1 \cdot \frac{RT}{N_A} = \frac{8.314 \times 310}{6.02 \times 10^{23}} \text{ J}.$$

$$\therefore E = \frac{70458}{6.02 \times 10^{23}} \cdot \frac{6.02 \times 10^{23}}{8.314 \times 310} = 27.3 \, k_B T.$$

c. $$Q = \frac{[Pi][ADP]}{[ATP][H_2O]} = \frac{2 \text{ mM} \times 1 \text{ mM}}{2 \text{ mM} \times 55.56 \text{ M}} = \frac{1 \times 10^{-3}}{55.56} = 1.8 \times 10^{-5}$$

$\Delta G = \Delta G^{\circ} + RT \ln Q = -58568 \text{ J/mol} \approx -59 \text{ kJ/mol}$.

$$E = \frac{|\Delta G|}{N_A} \times \frac{N_A}{RT} = \frac{58568}{8.314 \times 310} = 22.7 \, k_B T$$

While $1 \, k_B T = 4 \text{ pN} \cdot \text{nm}$.

$\therefore E = 90.8 \text{ pN} \cdot \text{nm}$.

d. $E = 100 \text{ pN} \cdot \text{nm} \approx 25 \, k_B T$ / $\sim 25 \, k_B T \times N_A$ J/mol

$= 25 RT$ J/mol.

$\downarrow$

$\Delta G = -25RT = -25 \times 8.314 \times 310 = -64433.5 \text{ J/mol} \approx -64 \text{ kJ/mol}$

$\downarrow$

$\Delta G \approx \Delta G$ (calculated in "c" and "b"). So they are consistent.

Question 2.

$$x \begin{cases} \xrightarrow{x > K_1} Y_1 \\ \xrightarrow{x > K_2} Y_2 \end{cases} ; \quad \begin{cases} \dfrac{dx}{dt} = \beta - \alpha x \\ t=0 \text{ 時 } x=0 \end{cases} \Rightarrow x(t) = \frac{\beta}{\alpha}(1-e^{-\alpha t}).$$

$$x(t) = \frac{\beta}{\alpha}(1-e^{-\alpha t}).$$

$$x(t_1) = \frac{\beta}{\alpha}(1-e^{-\alpha t_1}) = K_1 \Rightarrow t_1 = \frac{1}{\alpha}\ln\left(\frac{\frac{\beta}{\alpha}}{\frac{\beta}{\alpha}-K_1}\right)$$

$$x(t_2) = \frac{\beta}{\alpha}(1-e^{-\alpha t_2}) = K_2 \Rightarrow t_2 = \frac{1}{\alpha}\ln\left(\frac{\frac{\beta}{\alpha}}{\frac{\beta}{\alpha}-K_2}\right)$$

$$\frac{dY_1}{dt} = \beta_{Y_1} - \alpha Y_1 \Rightarrow Y_1(t) = \frac{\beta_{Y_1}}{\alpha}(1-e^{-\alpha t}).$$

$$Y_1(t_{1/2}) = \frac{\beta_{Y_1}}{\alpha} \times \frac{1}{2} \Rightarrow t_{1/2} = \frac{\ln 2}{\alpha}$$

$$\therefore t_{Y_1} = t_{1/2} + t_1 = \frac{\ln 2}{\alpha} + \frac{1}{\alpha}\ln\left(\frac{\frac{\beta}{\alpha}}{\frac{\beta}{\alpha}-K_1}\right).$$

For the Same Reason:

$$t_{Y_2} = t_{1/2} + t_2 = \frac{\ln 2}{\alpha} + \frac{1}{\alpha}\ln\left(\frac{\frac{\beta}{\alpha}}{\frac{\beta}{\alpha}-K_2}\right).$$

Question 3

(a). $E(x) = \frac{1}{2}kx^2$; $E(v) = \frac{1}{2}mv^2$.

$$Z = \int_{-\infty}^{+\infty} e^{-\frac{\frac{1}{2}kx^2}{k_BT}} \cdot dx \quad ; \quad Z = \int_{-\infty}^{+\infty} e^{-\frac{\frac{1}{2}mv^2}{k_BT}} dv.$$

$$Z = \int_{-\infty}^{+\infty} e^{-\left(\frac{k}{2k_BT}\right)x^2} dx.$$

$$Z = \sqrt{\frac{2\pi k_BT}{k}} \quad ; \quad Z = \sqrt{\frac{2\pi k_BT}{m}}$$

(b). $$p(x) = \frac{1}{Z} \cdot e^{-\frac{\frac{1}{2}kx^2}{k_BT}}$$

$$\left\langle \frac{1}{2}kx^2 \right\rangle = \int_{-\infty}^{+\infty} p(x) \cdot \left(\frac{1}{2}kx^2\right) dx = \int_{-\infty}^{+\infty} \frac{1}{2}kx^2 \cdot \frac{1}{Z} e^{-\frac{\frac{1}{2}kx^2}{k_BT}} dx$$

$$= \frac{k}{2Z} \cdot \int_{-\infty}^{+\infty} x^2 \cdot e^{-\left(\frac{k}{2k_BT}\right)x^2} dx.$$

$$= \frac{k}{2Z} \cdot \frac{\sqrt{\pi}}{2\left(\frac{k}{2k_BT}\right)^{\frac{3}{2}}} = \frac{\cancel{k}\cancel{\sqrt{\pi}}}{4 \cdot \cancel{\sqrt{\pi}}\cancel{\sqrt{\frac{2k_BT}{k}}} \cdot \cancel{\sqrt{\frac{k}{2k_BT}}} \cdot \left(\frac{\cancel{k}}{2k_BT}\right)}$$

$$= \frac{1}{2} k_BT.$$

(c). $Z = \sqrt{\frac{2\pi k_BT}{m}}$. $\quad p(v) = \frac{1}{Z} e^{-\frac{\frac{1}{2}mv^2}{k_BT}}$

$$\left\langle \frac{1}{2}mv^2 \right\rangle = \frac{1}{2}k_BT.$$

The integrals do not change and I did get the same result $\frac{1}{2}k_BT = \langle \frac{1}{2}mv^2 \rangle$

Question 4.

$$\Delta G^{o} = -RT\ln K.$$

$$\Delta G^{o\prime} = E_0 - RT\ln K, \quad E_0 = +11.9\,kJ/mol.$$

$$\Delta G^{o\prime} = -RT\ln K' \Rightarrow \ln K' = \ln K - \frac{E_0}{RT}$$

$$\therefore K' = e^{\ln K - \frac{E_0}{RT}} = \frac{K}{e^{\frac{E_0}{RT}}}$$

$$\therefore K' = \frac{5\times10^{9}}{e^{\frac{11.9\times10^{3}}{8.314\times310}}} = 4.94\times10^{7} \simeq 5\times10^{7}\,M^{-1}$$

Question 5. G_0. G_N.

a) Δ Zipped $\longrightarrow$ N: Unzipped. $\Delta G = N\,\delta G$.

$$P(N) = \frac{e^{-\frac{G_N}{k_BT}}}{Z} \qquad P(0) = \frac{e^{-\frac{G_0}{k_BT}}}{Z}$$

$$\frac{P(N)}{P(0)} = \frac{e^{-\frac{G_N}{k_BT}}}{e^{-\frac{G_0}{k_BT}}} = e^{-\frac{G_N-G_0}{k_BT}} = e^{-\frac{\Delta G}{k_BT}}$$

$$\frac{P(N)}{P(0)} = e^{-\frac{N\cdot\delta G}{k_BT}}$$

b). $\delta G_1 = 3k_BT$, $T = 298K$.

$$\frac{P(N=2)}{P(0)} = e^{-\frac{2\times3k_BT}{k_BT}} = e^{-6} \approx 0.25\%.$$

$$\frac{P(N=5)}{P(0)} = e^{-\frac{5\times3k_BT}{k_BT}} = e^{-15} \approx 3.06\times10^{-5}\,\%.$$

Since it has little probability to be unzipped, I think DNA double helix is very stable against thermal unzipping.