

第十次作业

10.1 假设 s 随温度的变化关系为 $s = s_0 e^{-\frac{\Delta\varepsilon}{RT}}$, 其中 $\Delta\varepsilon$ 为 monomer 在状态 b 与状态 a 下的能量差。

$s_0 = 0.1$, $\Delta\varepsilon = -5.7 \text{ kJ/mol}$, polymer 长度 $N = 10$ 。考虑 all-or-none transition 与

noncooperative transition: (a) 画出平衡常数 ($K = \frac{\langle b \rangle}{\langle a \rangle}$) 与体系平均能量 ($\langle E \rangle = N \langle b \rangle \Delta\varepsilon$) 随温度的变化曲线; (b) 计算相变的焓变 ΔH_{cal} (即体系在极高温与极低温的能量差); (c) 计算转变的 van't Hoff 焓 $\Delta H_{van't} (= RT^2 \frac{d \ln K}{dT})$; (d) 比较 ΔH_{cal} 与 $\Delta H_{van't}$ (实验上经常通过此比较判断转变是否协同)

解: (a) 由 $s = s_0 e^{-\frac{\Delta\varepsilon}{RT}}$ 得 $\Delta\varepsilon = -RT \ln \frac{s}{s_0}$, 因此 $\langle E \rangle = N \langle b \rangle \Delta\varepsilon = -N \langle b \rangle RT \ln \frac{s}{s_0}$, 现在分情况讨论:

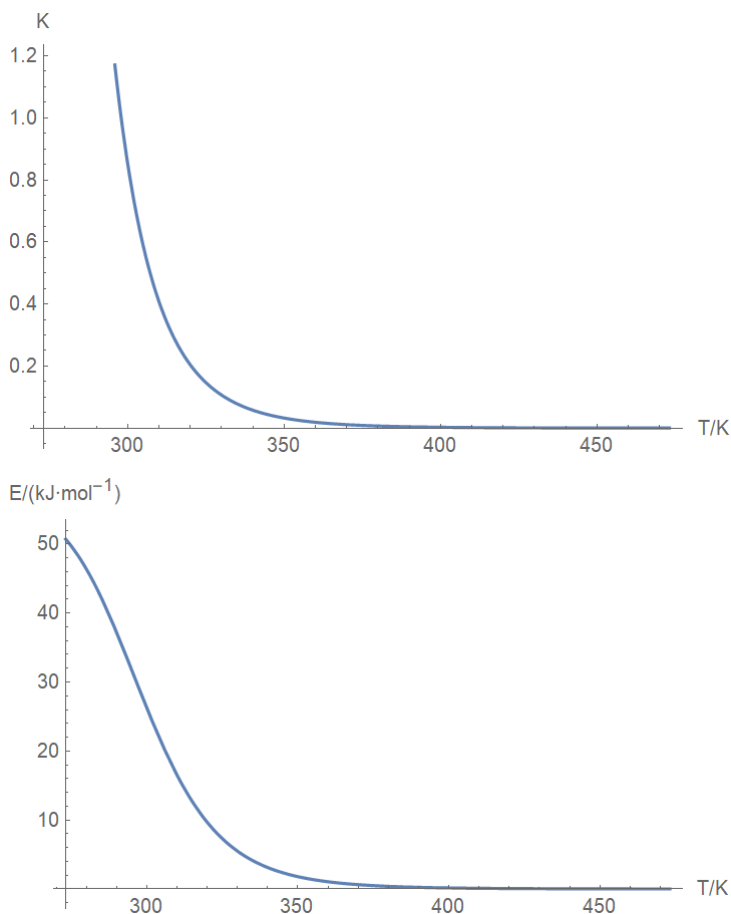
(i) 若转变过程为 all-or-none transition, 则由于 $\langle b \rangle = \frac{s^N}{1+s^N}$, $\langle a \rangle = \frac{1}{1+s^N}$, 因此平衡常数为:

$$K = \frac{\langle b \rangle}{\langle a \rangle} = s^N = s_0^N e^{-\frac{N\Delta\varepsilon}{RT}} = (0.1)^{10} e^{-\frac{10 \times (-5.7 \text{ kJ/mol})}{8.314 \text{ J/(mol}\cdot\text{K)} \times T}} = 10^{-10} e^{\frac{6.86 \times 10^3 \text{ K}}{T}}$$

体系平均能量的表达式为:

$$\langle E \rangle = -N \frac{s^N}{1+s^N} \Delta\varepsilon = -N \frac{s_0^N e^{-\frac{N\Delta\varepsilon}{RT}}}{1+s_0^N e^{-\frac{N\Delta\varepsilon}{RT}}} \Delta\varepsilon = -\frac{N s_0^N \Delta\varepsilon}{e^{\frac{N\Delta\varepsilon}{RT}} + s_0^N} = -\frac{10 \times (0.1)^{10} \times (-5.7 \text{ kJ/mol})}{e^{\frac{10 \times (-5.7 \text{ kJ/mol})}{8.314 \text{ J/(mol}\cdot\text{K)} \times T}} + (0.1)^{10}} = \frac{5.7 \times 10^{-9}}{e^{-\frac{6.86 \times 10^3 \text{ K}}{T}} + 10^{-10}} \text{ kJ/mol}$$

由此可作出随温度变化的图像:



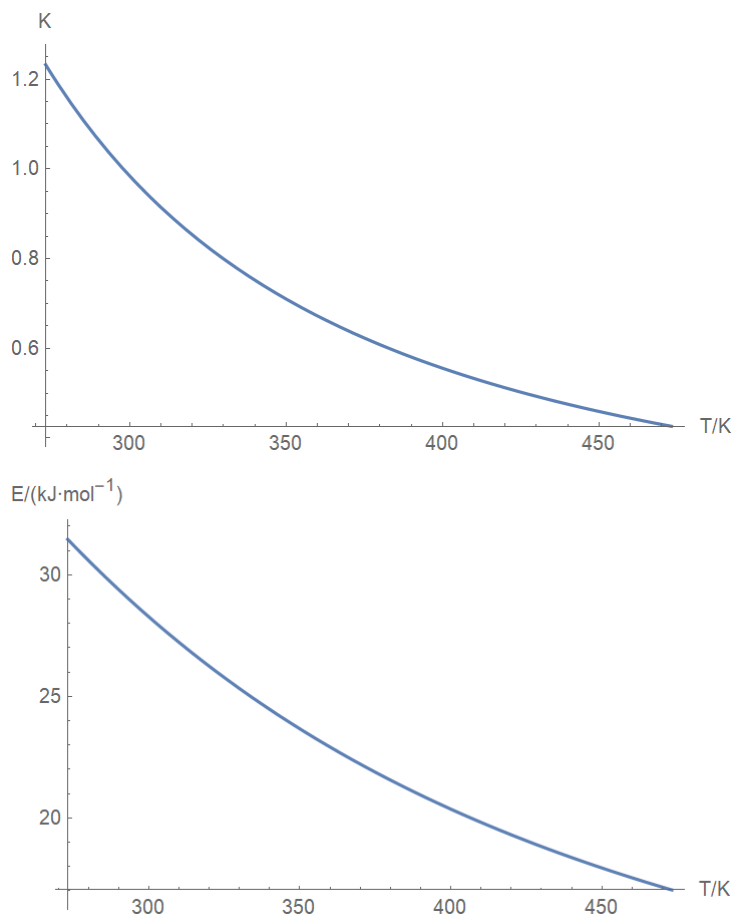
(ii) 若转变过程为 noncooperative transition, 则由于 $\langle b \rangle = \frac{s}{1+s}$, $\langle a \rangle = \frac{1}{1+s}$, 因此平衡常数为:

$$K = \frac{\langle b \rangle}{\langle a \rangle} = s = s_0 e^{-\frac{\Delta\varepsilon}{RT}} = 0.1 e^{-\frac{-5.7 \text{ kJ/mol}}{8.314 \text{ J/(mol}\cdot\text{K)} \times T}} = 0.1 e^{\frac{6.86 \times 10^2 \text{ K}}{T}}$$

体系平均能量的表达式为：

$$\langle E \rangle = -N \frac{s}{1+s} \Delta \varepsilon = -N \frac{s_0 e^{-\frac{\Delta \varepsilon}{RT}}}{1 + s_0 e^{-\frac{\Delta \varepsilon}{RT}}} \Delta \varepsilon = -\frac{N s_0 \Delta \varepsilon}{e^{\frac{\Delta \varepsilon}{RT}} + s_0} = -\frac{10 \times 0.1 \times (-5.7 \text{ kJ/mol})}{e^{\frac{-5.7 \text{ kJ/mol}}{8.314 \text{ J/(mol·K)}}} + 0.1} = \frac{5.7}{e^{-\frac{6.86 \times 10^2 \text{ K}}{T}} + 0.1} \text{ kJ/mol}$$

由此可作出随温度变化的图像：



(b) 若转变过程为all-or-none transition, 则相变的焓变为

$$\begin{aligned} \Delta H_{cal} &= \lim_{T \rightarrow +\infty} \langle E \rangle - \lim_{T \rightarrow 0 \text{ K}} \langle E \rangle = \lim_{T \rightarrow +\infty} \frac{5.7 \times 10^{-9}}{e^{-\frac{6.86 \times 10^3 \text{ K}}{T}} + 10^{-10}} \text{ kJ/mol} - \lim_{T \rightarrow 0 \text{ K}} \frac{5.7 \times 10^{-9}}{e^{-\frac{6.86 \times 10^3 \text{ K}}{T}} + 10^{-10}} \text{ kJ/mol} \\ &= 5.7 \times 10^{-9} \text{ kJ/mol} - 57 \text{ kJ/mol} \approx -57 \text{ kJ/mol} \end{aligned}$$

若转变过程为noncooperative transition, 则相变的焓变为

$$\begin{aligned} \Delta H_{cal} &= \lim_{T \rightarrow +\infty} \langle E \rangle - \lim_{T \rightarrow 0 \text{ K}} \langle E \rangle = \lim_{T \rightarrow +\infty} \frac{5.7}{e^{-\frac{6.86 \times 10^2 \text{ K}}{T}} + 0.1} \text{ kJ/mol} - \lim_{T \rightarrow 0 \text{ K}} \frac{5.7}{e^{-\frac{6.86 \times 10^2 \text{ K}}{T}} + 0.1} \text{ kJ/mol} \\ &= 5.2 \text{ kJ/mol} - 57 \text{ kJ/mol} \approx -51.8 \text{ kJ/mol} \end{aligned}$$

(c) 若转变过程为all-or-none transition, 则van't Hoff焓为

$$\begin{aligned} \Delta H_{van't} &= RT^2 \frac{d \ln K}{dT} = RT^2 \frac{d \ln (s_0^N e^{-\frac{N \Delta \varepsilon}{RT}})}{dT} = RT^2 \frac{d(N \ln s_0 - \frac{N \Delta \varepsilon}{RT})}{dT} \\ &= RT^2 \cdot \frac{N \Delta \varepsilon}{RT^2} = N \Delta \varepsilon = 10 \times (-5.7 \text{ kJ/mol}) = -57 \text{ kJ/mol} \end{aligned}$$

若转变过程为noncooperative transition, 则van't Hoff焓为

$$\begin{aligned} \Delta H_{van't} &= RT^2 \frac{d \ln K}{dT} = RT^2 \frac{d \ln (s_0 e^{-\frac{\Delta \varepsilon}{RT}})}{dT} = RT^2 \frac{d(\ln s_0 - \frac{\Delta \varepsilon}{RT})}{dT} \\ &= RT^2 \cdot \frac{\Delta \varepsilon}{RT^2} = \Delta \varepsilon = -5.7 \text{ kJ/mol} \end{aligned}$$

(d) 若转变过程为all-or-none transition, 则有 $\Delta H_{cal} \approx \Delta H_{van't} < 0$ (实际上两者相差的能量数量级约为 10^{-9} kJ/mol, 可认为两者相等); 若转变过程为noncooperative transition, 则有

$$\Delta H_{cal} < \Delta H_{van't} < 0$$

10.2 DNA的persistence length约为50 nm, 对于一个总长度为1.5 m的人类DNA, 估计其在平衡条件下的端点距离 $\sqrt{\langle h^2 \rangle}$

解: 该DNA在平衡条件下的端点距离为

$$\sqrt{\langle h^2 \rangle} = \sqrt{2L_p[L - L_p(1 - e^{-\frac{L}{L_p}})]} = \sqrt{2 \times 50 \times 10^{-9} \text{ m} \times [1.5 \text{ m} - 50 \times 10^{-9} \text{ m}(1 - e^{-\frac{1.5 \text{ m}}{50 \times 10^{-9} \text{ m}}})]} = 3.87 \times 10^{-4} \text{ m}$$