6. This question is about storing vaccines

Because of degradation of components, vaccines need to be refrigerated, which increases their cost and makes distribution difficult. A recently developed process called "ensilication" can drastically improve the vaccines' stability. Ensilicated vaccine components can be stored at room temperature and withstand heating up to 100 °C.

The ensilication process begins with the hydrolysis of ethyl orthosilicate, $Si(OCH_2CH_3)_4$, to form orthosilicic acid, $Si(OH)_4$, (process 1). This is added to a solution of the protein/antibody, which catalyses the decomposition of the acid into silica, SiO_2 (process 2).

(a) Write the chemical equations for processes 1 and 2.

At the end of the process a suspension of silica nanoparticles loaded with protein is formed. The protein can be released using a solution of NaF and HCl, which breaks up the silica (process 3).

$$SiO_2 + 6\ NaF + 6\ HCl \rightarrow H_2SiF_6 + 6\ NaCl + 2\ H_2O$$

(b) Calculate the standard enthalpy change of this reaction given the following data:

$NaOH + HCl \rightarrow NaCl + H_2O$ $\qquad \Delta H^{\ominus} = -56.7\ \text{kJ mol}^{-1}$

$SiO_2 + 6\ HF \rightarrow H_2SiF_6 + 2\ H_2O$ $\qquad \Delta H^{\ominus} = -100.3\ \text{kJ mol}^{-1}$

$NaOH + HF \rightarrow H_2O + NaF$ $\qquad \Delta H^{\ominus} = -61.5\ \text{kJ mol}^{-1}$

Process 2 is thermodynamically favoured but slow, which is why it requires a catalyst. The equilibrium constant for this reaction is

$$K_{\text{eq}} = 1/[\text{Si(OH)}_4]$$

and

$$\ln[\text{Si(OH)}_4] = -\frac{1680}{T} - 0.605$$

where $[Si(OH)_4]$ is the equilibrium concentration in mol dm^{-3}, and T is the temperature in K.

(c) Calculate the molar enthalpy change, $\Delta H^{\ominus}$, and molar entropy change, $\Delta S^{\ominus}$, for process 2.

Dynamic light scattering can be used to determine the size of the nanoparticles. Assume our solution contains spherical particles of only two types: ensilicated protein with radius r_1 and free protein with radius r_2. The intensity of the light scattered by these particles can be converted into an autocorrelation function, *c*.

$$c = \left(1 - \frac{\Gamma t}{r_1} + \frac{1}{2}\left(\frac{\Gamma t}{r_1}\right)^2\right) + A\left(1 - \frac{\Gamma t}{r_2} + \frac{1}{2}\left(\frac{\Gamma t}{r_2}\right)^2\right)$$

where A is a dimensionless constant, t is time in μs, r_1 and r_2 are the radii in nm and $\Gamma = 0.170713\ \mathrm{nm}\ \mu\mathrm{s}^{-1}$. Note: the following calculations are sensitive to rounding error. Work to the specified number of significant figures in **(d)−(f)**.

(d) Calculate the constant A, given that at $t = 0$, the autocorrelation function $c_0 = 1.56744$.

If you do not get an answer, use $A = 0.50000$ in subsequent calculations.

The equation for c can be rearranged into the form $f = a \times t - b$, where

$$f = \frac{c - c_0}{\Gamma t}, \qquad a = \frac{1}{2}\Gamma(r_1^{-2} + A\, r_2^{-2}), \qquad b = r_1^{-1} + A\, r_2^{-1}.$$

(e) Calculate the values of the slope a and intercept b, given that $c = 1.54289$ at $t = 1\ \mu s$ and $c = 1.51937$ at $t = 2\ \mu s$.

If you do not get an answer, use $a = 0.00250\ \mathrm{nm}^{-1}\mu\mathrm{s}^{-1}$ and $b = 0.12500\ \mathrm{nm}^{-1}$ in subsequent calculations.

(f) Hence calculate the radii r_1 and r_2. Consider first solving for $x_1 = r_1^{-1}$ and $x_2 = r_2^{-1}$.