

6. This question is about storing vaccines

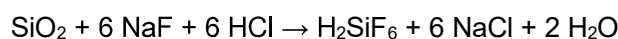
Because of degradation of components, vaccines need to be refrigerated, which increases their cost and makes distribution difficult. A recently developed process called “ensilication” can drastically improve the vaccines’ stability. Ensilicated vaccine components can be stored at room temperature and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



The ensilication process begins with the hydrolysis of ethyl orthosilicate, $\text{Si}(\text{OCH}_2\text{CH}_3)_4$, to form orthosilicic acid, $\text{Si}(\text{OH})_4$, (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).



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



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

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

and

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

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

(c) Calculate the molar enthalpy change, ΔH^\ominus , and molar entropy change, ΔS^\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 $\Gamma = 0.170713 \text{ nm } \mu\text{s}^{-1}$. 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

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

- (e)** Calculate the values of the slope a and intercept b , given that $c = 1.54289$ at $t = 1 \mu\text{s}$ and $c = 1.51937$ at $t = 2 \mu\text{s}$.
If you do not get an answer, use $a = 0.00250 \text{ nm}^{-1} \mu\text{s}^{-1}$ and $b = 0.12500 \text{ nm}^{-1}$ in subsequent calculations.
- (f)** Hence calculate the radii r_1 and r_2 . Consider first solving for $x_1 = r_1^{-1}$ and $x_2 = r_2^{-1}$.