Exam Colloid Science, November 9, 2017.

Answers

$$1\text{A)}\ \ \Delta G = 6d^2\gamma - \frac{d^3}{v_m}\left|\Delta\mu\right| \quad \Rightarrow d^* = \frac{4\gamma v_m}{\left|\Delta\mu\right|}$$

$$\Rightarrow \Delta G = 6d^2\gamma[1-\frac{2d}{3d^*}] \ \ \Rightarrow \Delta G^*(d=d^*) = \frac{1}{3}A^*\gamma$$

B) Bulk volume formation lowers the Gibbs energy.

C) This result holds for any shape.

2 A) Equilibrium: $\rho_+\rho_- = \rho_{\text{salt}}^2$; Neutrality: $z\rho_{\text{colloid}} + \rho_- = \rho_+$.

B) From these two conditions we obtain a quadratic in $\rho\_$ with the solution

$$\frac{\rho_-}{\rho_{\text{salt}}} = -y + \sqrt{1+y^2} \ \ ; \ y = \frac{z\rho_{\text{colloid}}}{2\rho_{\text{salt}}}$$

C) Since $-y+\sqrt{1+y^2} < 1$, it follows that $\rho_- < \rho_{\text{salt}}$. The colloids release sodium counter-ions, part of which migrate to the reservoir. To maintain neutrality, each counter-ion must be accompanied by a chloride ion ('salt expulsion') so the chloride concentration in *L* is lower than in *R*.

D) De-ionize the reservoir; then $y \gg 1$ and $\rho_- \approx 0$; all chloride has been expelled to the large reservoir with the very low, constant salt concentration.

3A) Option 1: employ the random walk of uncorrelated steps. Option 2: use the Einstein argument " for chemists'.

B) No- time must be very much larger than the momentum relaxation time.

C) The ion cloud will only affect the (friction factor in the) diffusion constant; that will slow down the random walk – but will not change the randomness of that walk.

Answers to the questions on *Colloidal Analysis Techniques*

4. a. $$\kappa^{-1} = \sqrt{\frac{\varepsilon_0 \varepsilon_r k_B T}{e^2 \sum_i n_i z_i^2}} = \sqrt{\frac{\left(9\times10^{-12}\ \mathrm{CV^{-1}m^{-1}}\right)(78)\left(1.38\times10^{-23}\ \mathrm{J/K}\right)(300\,\mathrm{K})}{\left(1.6\times10^{-19}\ \mathrm{C}\right)^2\left[\left(\frac{10^{-3}\,\mathrm{mol}}{10^{-3}\,\mathrm{m^3}}\cdot1^2\right)+\left(\frac{10^{-3}\,\mathrm{mol}}{10^{-3}\,\mathrm{m^3}}\cdot1^2\right)\right]\frac{6.0\times10^{23}}{\mathrm{mol}}}} = 10\,\mathrm{nm}$$

$$\kappa a = \frac{100\,\mathrm{nm}}{10\,\mathrm{nm}} = 10$$

b. Even though κa>100 is not fulfilled, the high-κa limit seems closer than the low-κa limit.

$$\zeta = \frac{\eta}{\varepsilon_0 \varepsilon_r} u = \frac{0.0009\,\mathrm{Pa\cdot s}}{\left(9\times10^{-12}\ \mathrm{CV^{-1}m^{-1}}\right)(78)} \cdot \frac{100\cdot10^{-6}\,\mathrm{m/s}}{30\,\mathrm{V}/0.01\,\mathrm{m}} = 0.043\,\mathrm{V}$$

The zeta potential gives the electric potential at or in the vicinity of the surface of the colloidal particle, an essential quantity when it comes to charge stabilization.

c. On the 0.05 s time scale, the particles diffuse a root mean square distance given by:

$$\sqrt{\left\langle x^2 \right\rangle} = \sqrt{2Dt} = \sqrt{2\frac{kT}{6\pi\eta a}t} = \sqrt{2\frac{\left(1.38\times10^{-23}\ \mathrm{J/K}\right)(300\,\mathrm{K})}{6\pi(0.0009\,\mathrm{Pas})\left(100\cdot10^{-9}\,\mathrm{m}\right)}(0.05\,\mathrm{s})} = 0.49\cdot10^{-6}\,\mathrm{m}$$

The field strength E required for electrophoretic motion across the same distance is given by:

$$E = \frac{0.49\cdot10^{-6}\,\mathrm{m}}{ut} = \frac{0.49\cdot10^{-6}\,\mathrm{m}}{\left(\frac{100\cdot10^{-6}\,\mathrm{m/s}}{30\,\mathrm{V}/0.01\,\mathrm{m}}\right)(0.05\,\mathrm{s})} = 300\,\mathrm{V/m} = 0.3\,\mathrm{V/cm}$$

At the field strength of 30 V/cm, electrophoretic motion dominates on the 0.05 s time scale. The lesser the relative contribution to electrophoretic motion, the less reliable the zeta potential determination.

5. a. Melting point T_m: equal chemical potential of H_2O in liquid (liq) and solid phases (assumption: solid phase is pure H_2O).

$$\mu_{\mathrm{H_2O,liq}}{}^0(T_m) + RT_m \ln a_{\mathrm{H_2O,liq}} = \mu_{\mathrm{H_2O,solid}}{}^0(T_m) \qquad \text{(A)}$$

and $$RT_m \ln a_{\mathrm{H_2O,liq}} = -\left[\mu_{\mathrm{H_2O,liquid}}{}^0(T_m) - \mu_{\mathrm{H_2O,solid}}{}^0(T_m)\right] = -\Delta\mu_{\mathrm{H_2O}}{}^0(T_m) \qquad \text{(B)}$$

Here, $\Delta\mu_{\mathrm{H_2O}}{}^0(T_m)$ is defined for melting; one could also define it for freezing, with consequences for the sign of several terms in the derivation, without affecting the final outcome.
Temperature dependence of the chemical potential:

$$RT_m \ln a_{\mathrm{H_2O,liq}} = \underbrace{\mu_{\mathrm{H_2O,solid}}{}^0(0\,^\circ\mathrm{C}) - \mu_{\mathrm{H_2O,liq}}{}^0(0\,^\circ\mathrm{C})}_{=\ 0\ \text{(equilibrium pure water and ice)}} + \underbrace{\int_{0\,^\circ\mathrm{C}}^{T_m}\left(-\frac{\partial\Delta\mu_{\mathrm{H_2O}}{}^0}{\partial T}\right)dT}_{+\Delta s_{\mathrm{H_2O}}{}^0\cdot(T_m - 0\,^\circ\mathrm{C})} \qquad \text{(C)} \quad \text{(D)}$$

We find $RT_m \ln a_{\mathrm{H_2O,liq}} = -\Pi v_{\mathrm{H_2O}}$ from:

$$\mu_{\mathrm{H_2O,liq}}{}^0(T_m,P) = \mu_{\mathrm{H_2O,liq}}{}^0(T_m,P) + RT_m \ln a_{\mathrm{H_2O,liq}} + \int_P^{P+\Pi}\underbrace{\left(\frac{\partial\Delta\mu_{\mathrm{H_2O}}}{\partial P}\right)}_{v_{\mathrm{H_2O}}}dP \qquad \text{(E)}$$

Combination of (C)-(E) yields: $$\Pi = -\left(\Delta_m s^0/v_1\right)(T_m - 0\,^\circ\mathrm{C}) \qquad \text{(F)}$$

b. $\Pi = -\frac{\Delta_m s^0}{v_1}\left(T_m - 0\,°\mathrm{C}\right) = -\frac{\left(22\ \mathrm{JK}^{-1}\mathrm{mol}^{-1}\right)}{18.0\times 10^{-6}\ \mathrm{m}^3\mathrm{mol}^{-1}}\left(-0.60\,°\mathrm{C}\right) = 7.3\times 10^5\ \mathrm{Pa}$

c. Osmotic pressure scales with the number concentration of thermally translating species. Aggregation decreases the number of dispersed species, resulting in lowered osmotic pressure.

6. The measurements are from the following publication: H. Liu, X.M. Xu, Sh.D. Guo, *LWT* 40, 946 (2007), “Rheological, texture and sensory properties of low-fat mayonnaise with different fat mimetics”.

a. The x-axis gives the shear rate. In the model of two parallel plates, the shear rate is the relative velocity of the two plates divided by the separating distance between them.

The y-axis gives the shear stress, the force per unit area applied to one of the plates with respect to the other plate in a direction in the plane of the moving plate.

b. At zero shear rate, the curves start at a positive shear stress (called the yield stress). This stress must be applied before the substance starts to flow. Apparently, there is a microstructure (formed by the densely packed oil emulsion droplets) that must first be partly broken.

At the maximal shear rate in the graph, the two curves are connected by several points, a time-dependent decrease in shear stress as shearing is prolonged at constant shear rate. The lower curve is measured finally, lower than the top curve because structure requires time to recover. If recovery at zero shear rate is complete, the observed effect is referred to as “thixotropy”.

c. A purely viscous substance (Newtonian) would lead to a linear dependence of shear stress on shear rate, going through the origin. The observations discussed under b thus indicate that the system is not simply viscous. Moreover, both G’ and G” are nonzero, as is the case for a viscoelastic substance (see for instance the derivation of the expressions for G’ and G” for a Maxwell element), whereas a purely viscous substance would have only a loss modulus (*G*”), not also a storage modulus (*G*’).