020411 Quiz 2 Nanopowders

1) **-Write** an expression describing steady state for the kinetics of growth of an n-mer cluster from an (n-1)-mer. (The equation has 5 terms and balances deposition with dissolution.)
-Explain why only one side of this equality has concentration of monomers as a factor.
-Define the terms in the equation.
-Which of the terms depends on n and what is their functionality with n?

2) Under the pseudo-steady-state assumption we obtained an expression for J, the growth rate of n-mers in terms of the ratios of the concentrations of n-mers to the equilibrium concentration of n-mers.
-Give this expression and define the terms.
-Why doesn' t this expression depend on the rate of dissolution? (This could be answered by writing an expression for k_n in terms of parameters in the equation.)

3) **-Write** an expression for the equilibrium concentration of n-mers as a function of "n", **and** an expression for the kinetically determined concentration under the pseudo-steady state assumption.
-What is the value of the kinetic concentration at n* where the concentration of monomers in equilibrium with an n-mer is 0 (as a function of c_n^e)?
-Describe the pseudo-steady state condition that leads to high populations of small nanoparticles.

4) Compare growth of a surface patch of size n' to growth of an n-mer cluster by giving:
- **n*** for both conditions (in terms of ψ, ψ', and φ);
- **ΔG*** in terms of φ and n* (n'*) for both conditions;
-**the relationship** between r* and r'*.

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1) $k_d^0 a_{n-1} c_{(n)} = k_n^0 a_n$

k_d describes the inclusion rate of a monomer at the interface so it must be multiplied by the concentration of monomers in equilibrium with the n-mer. k_n describes the dissolution rate of the n-mer and is not effected directly by concentration. a's are area of the cluster.

k_d does not depend on n, $k_d^0 c_{(\infty)} = k_\infty^0$, all others depend on n,

$$a_n = a n^{\frac{2}{3}};\ c_{(n)} = c_{(\infty)} \exp\left(\frac{2\psi}{3kTn^{\frac{1}{3}}}\right);\ k_n^0 = k_\infty^0 \left(\frac{n-1}{n}\right)^{\frac{2}{3}} \exp\left(\frac{2\psi}{3kTn^{\frac{1}{3}}}\right)$$

2) $J = C c_{n-1}^e a_{n-1} k_d \left(\frac{c_{n-1}}{c_{n-1}^e} - \frac{c_n}{c_n^e}\right)$

C is the total monomer species concentration in the system, c_n^e is the equilibrium n-mer concentration. The other terms are described in 1).

The rate of dissolution can be expressed as a function of k_d and the equilibrium concentrations,

$$\frac{C c_{n-1}^e}{c_n^e} = \frac{k_n a_n}{k_d a_{n-1}} \quad \textbf{or}\ k_n = \frac{C c_{n-1}^e k_d a_{n-1}}{a_n c_n^e}$$

3) $$c_n^e = \frac{\exp\left(\frac{-\Delta G_n}{kT}\right)}{v_0} = \frac{\exp\left(\frac{n\varphi_n - n^{\frac{2}{3}}\psi}{kT}\right)}{v_0}$$

$$c_n = \frac{c_n^e}{2}\left(1 - erf(x)\right) \text{ where } x = \left(\frac{3\Delta G^*}{kT}\right)^{\frac{1}{2}}\left(\left(\frac{n}{n^*}\right)^{\frac{1}{3}} - 1\right)$$

at x = 0 $c_n = c_n^e/2$

In the pseudo-steady state condition the net J for each nanoparticle size (n) is the same. (This only needs to be assumed over a narrow range of n and it can be achieved by holding the monomer concentration, C, constant during nucleation.

4) $$n'^* = \left(\frac{\psi'}{2\varphi}\right)^2;\ n^* = \left(\frac{2\psi}{3\varphi}\right)^3$$

$$\Delta G'^* = \varphi n'^*;\ \Delta G^* = \frac{\varphi n^*}{2}$$

$$r^* = 2r'^*$$