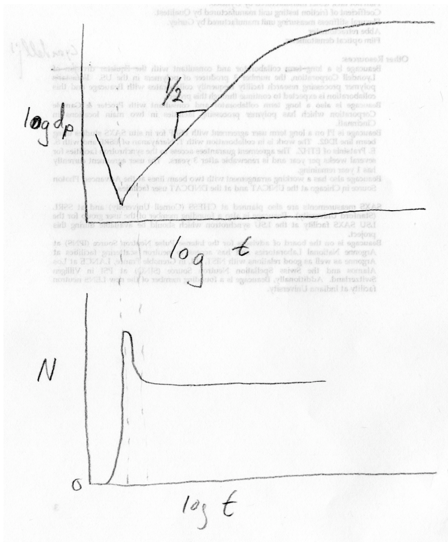
Quiz 2 Nanopowders 070206

The growth of nano-particles can be observed using in situ Small-Angle X-ray Scattering (SAXS) or by sampling from the growth media and performing TEM or gas absorption. These techniques can yield the Sauter Mean Diameter, $d_p = \langle V \rangle / \langle S \rangle$. The following two plots show d_p versus time and the number density of particles versus time.



1) Explain, in the plots, where you expect the particle growth to follow **homogenous nucleation** growth laws and where you expect the behavior to follow **surface growth laws**. **Write an approximate equation** that reflects the growth where the slope is ½ as indicated in the first plot. What type of growth agrees with this equation?

2) Make a sketch of a particle of radius r and with a diffusion boundary layer thickness of δ including the bulk concentration C_b, concentration at the interface C_i and concentration in equilibrium with the particle of size r, C_r. Write Fick's first law for the region within the boundary layer and integrate this between $x = (r+\delta)$ and $x = r$ (assuming constant flux, J, and diffusion coefficient, D.)

3) By substitution the following equation can be obtained:

$$\frac{dr}{dt} = \frac{V_m \frac{D}{r}\left(1 + \frac{r}{\delta}\right)\left(C_b - C_r\right)}{1 + \frac{D\left(1 + \frac{r}{\delta}\right)}{k_d r}} \qquad (1)$$

where k_d is the rate constant for deposition (reaction rate), V_m is the molar volume of a monomer and D is the diffusion coefficient (transport rate). Obtain a simplified growth law (r as a function of t) that can be obtained from (1) under diffusion limited surface growth.

4) Obtain a simplified rate law (r as a function of t) that can be obtained from (1) for deposition rate limited growth.

5) Particle nucleation and growth lead to polydisperse size distributions. Give a function that would be useful to describe a typical particle size distribution. Why is this function better than other distributions such as the Gaussian distribution?

ANSWERS: Quiz 2 Nanopowders 070206

1) Homogeneous nucleation occurs during the rise in number density. Surface growth occurs when N plateaus in time and the log d_p curve shows a ½ slope in log time. In this region we observe $\log(d_p) \sim 1/2 \log(t)$ or $d_p \sim t^{1/2}$. This corresponds to diffusion limited surface growth.

2)

$$J = 4\pi x^2 D \frac{dC}{dx}$$

Fick's 1st Law

$$J \int_r^{r+\delta} \frac{dx}{x^2} = 4\pi D \int_{C_i}^{C_b} dC$$

$$J\left(\frac{1}{r} - \frac{1}{(r+\delta)}\right) = 4\pi D (C_b - C_i)$$

$$J\left((r+\delta) - r\right) = 4\pi D\, r (r+\delta)(C_b - C_i)$$

$$J = \frac{4\pi D\, r (r+\delta)(C_b - C_i)}{\delta}$$

3) For diffusion limited growth $D \ll rk_d$ and $r/\delta \ll 1$.

$$\frac{dr}{dt} = \frac{V_m \frac{D}{r}\left(1+\cancelto{0}{r/\delta}\right)(C_b - C_r)}{1 + \cancelto{0}{\frac{D(1+r/\delta)}{k_d r}}}$$

$$\sim \frac{V_m D (C_b - C_r)}{r}$$

$$\int_{r_0}^{r} r\,dr \sim V_m D (C_b - C_r) \int_0^t dt$$

$$r^2 - r_0^2 = V_m D (C_b - C_r)\, t$$

$$r^2 = V_m D (C_b - C_r)\, t + r_0^2$$

$$r \sim t^{1/2}$$

4) For deposition rate limited growth $D >> rk_d$ and $r/\delta >> 1$

$$\frac{dr}{dt} = \frac{V_m \cancel{\frac{D}{r}} \left(\cancel{1}^{\,0} + \frac{r}{\delta}\right)(C_b - C_r)}{\underbrace{\cancel{1}}_{0} + \underbrace{\frac{D\,(1+r/\delta)}{k_d\, r}}_{0}}$$

$$= V_m k_d (C_b - C_r)$$

$$\int_{r_0}^{r} dr = V_m k_d (C_b - C_r) \int_0^t dt$$

$$r - r_0 = V_m k_d (C_b - C_r)\, t$$

$$r = V_m k_d (C_b - C_r)\, t + r_0$$

5) The log-normal distribution is useful to describe typical particle size distributions.

$$\left(\frac{dN}{dr}\right) = \frac{N_{00}}{\left(2\pi r^2 (\ln \sigma_g)^2\right)^{1/2}} \exp\left[\frac{-(\ln r - \langle \ln r_g \rangle)^2}{2 (\ln \sigma_g)^2}\right]$$

σ_g = geometric standard deviation

r_g = geometric mean

$= \sqrt[n]{r_1 \cdot r_2 \cdots r_n}$

This distribution is better than the Gaussian since it shows a skewed distribution towards larger sizes that is similar to the result of growth from small size particles to larger size particles.