PHCEU 5125 Equation Sheet, Exam 3

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Micromeritics:

 $N = \frac{6}{\pi d_{vn}^{3} \rho}$ d_{vn} = mean diameter based on volume-mean number (see table p. 426), cm ρ = density of the powder, g/cm³ Surface area of sphere = πd^2 Volume of sphere = $\pi d^3/6$ $\alpha_{\rm s}/\alpha_{\rm v} = 6$ for a sphere Surface area = $\alpha_s d_p^2 = \pi d_s^2$ Volume = $\alpha_v d_p^3 = \pi d_v^3/6$ $S_v = \frac{\text{surface area of particles}}{\text{volume of particles}} = \frac{\alpha_s}{\alpha_v d}$ $S_w = \frac{\text{surface area per unit volume}}{\text{density}} = \frac{S_v}{\rho}$ ρ = true density density $= \underline{\alpha_{s}}_{\rho\alpha_{v}d} = \underline{\alpha_{s}}_{\rho\alpha_{v}d_{vs}}$ d now defined as d_{vs} for this case; d_{vs} = volume-surface diameter characteristic of specific surface For a sphere, $S_w = \frac{6}{\rho d_{vs}}$ since $\alpha_s / \alpha_v = 6$

 $C = \frac{V_{bulk} - V_{particles}}{V_{bulk}}$ (often expressed as a percent, so multiply by 100)

 V_{bulk} - $V_{\text{particles}}$ = void volume

 $\begin{array}{l} Bulk \; density = \rho_{bulk} = weight/ \; V_{bulk} \\ True \; density = \rho = weight/ \; V_{particles} \\ Bulkiness = 1/(bulk \; density) = V_{bulk}/weight \end{array}$

 $tan \phi = \mu = h/r$ $\mu = coefficient of friction$ h = height of powder coner = radius of powder cone

Rheology:

Shearing stress, F:

$$F = \begin{bmatrix} F' \\ A \end{bmatrix} = \eta \frac{dv}{dr}$$

$$\eta = viscosity (dynes sec/cm2 or poise)$$

$$dv/dr = rate of shear = G (sec-1)$$

$$fluidity: \qquad \phi = 1/\eta$$
Kinematic viscosity = η/ρ
in stokes where 1 stoke = 1 poise/(g/cm³).

 $\eta = A e^{\frac{1}{E_v/RT}}$

 η = viscosity (usually in centipoise)

A = constant

 E_v = activation energy required to initiate flow between the molecules (cal/mol)

R = gas constant (1.987 cal/°Kmol)

T = temp in Kelvins

$$\begin{array}{rl} \eta_{rel} = & \underline{\eta}_1 &= \underline{\rho}_1 \underline{t}_1 \\ & \eta_2 & \rho_2 t_2 \end{array}$$

 ρ_1 and ρ_2 = densities of liquids 1 and 2 (g/cm³) t₁ and t₂ = flow times of liquids 1 and 2 (sec) η_1 and η_2 = viscosities of liquids 1 and 2 (centipoise)

$$1/\eta = V_1/\eta_1 + V_2/\eta_2$$

 V_1 , V_2 = volume fractions of pure solutions 1 and 2 η_1 , η_2 = viscosities of solutions 1 and 2

$$U = \frac{(F-f)}{G}$$

where
$$F =$$
 shearing stress, or F'/A (dynes/cm²)
f = yield value (dynes/cm²)
G = rate of shear (sec⁻¹)

(Units of U are poise, or dynes sec/cm²)

 $F^N = \eta' G$

 η ' represents a viscosity coefficient

$$\mathbf{B} = \frac{\mathbf{U}_1 - \mathbf{U}_2}{\ln(\mathbf{t}_2/\mathbf{t}_1)}$$

 U_1 and U_2 = plastic viscosities of the 2 down curves after shearing at a constant rate for t_1 and t_2 , respectively.

$$M = \underbrace{U_1 - U_2}_{\ln (v_2/v_1)}$$

Flow of a liquid:
 $F = \text{shear stress}$
 $G = \text{shear rate}$

Elasticity of the solid (from Hooke's Law, equation of a spring): $E = F/\gamma$ E = elastic modulus (dyne/cm²)F = stress (dyne/cm²)

 γ = strain (dimensionless)

Coarse dispersions:

$$\Delta G = \gamma_{SL} \Delta A = G_{\text{final}} - G_{\text{initial}} = \gamma_{SL} (A_{\text{final}} - A_{\text{initial}})$$

 γ_{SL} = the interfacial tension between solid and liquid, measured in dynes/cm

 ΔG = surface free energy (ΔG) erg/cm² (erg = g cm²/sec²)

 ΔA = change in surface area, cm²

$$\mathbf{v} = \underline{\mathbf{d}^2 \left(\rho_{\rm s} - \rho_{\rm o} \right) \mathbf{g}}{18\eta_{\rm o}}$$

v = velocity of sedimentation (cm/sec); also known as rate of settling

d = diameter of particle (cm)

 ρ_s , ρ_o = densities of dispersed phase and dispersion medium, respectively (g/cm³)

 $g = acceleration of gravity (981 cm/sec^2)$

 η_o = viscosity of dispersion medium in poise

$$v' = v \in {}^n$$

v' = rate of fall at the interface (cm/sec)

v = velocity of sedimentation from Stokes' Law

 \in = initial porosity of the system

n = a measure of the "hindering" of the system (a constant for each system)

$$F = V_u / V_o$$

 $\overline{V_u}$ = final, or ultimate volume of sediment

 $V_o =$ original volume of the suspension

$$F_{\infty} = V_{\infty} / V_{o}$$
$$\beta = F / F_{\infty} = V_{u} / V_{\infty}$$

 β = <u>ultimate sediment volume of flocculated suspension</u> ultimate sediment volume of deflocculated suspension

Fractional release (F) of drug from a gel at time t: $F = M_t/M_o = kt^n$ M_t = amount of drug released at time t (g or other) M_o = initial amount of drug (g or other) k = rate constant (min⁻ⁿ) t = time (min) n = diffusional exponent (unitless)

Drug diffusivity, D, in the gel matrix:

$$\ln D = \ln D_{o} - K_{f} \left(\frac{1}{H} - 1 \right)$$

$$D_{o} = diffusivity of solute in water (cm2/sec)K_{f} = constant (cm2/sec)H = matrix hydration (unitless),= eq. swollen gel wt - dry gel wteq. swollen gel wt.$$

Thermal degradation with respect to rigidity:

$$\frac{1}{f} - \frac{1}{f_o} = k_f t$$

where f, $f_0 = rigidity$ index at time t, or time zero (g^{-1}) $k_f = rate constant (g^{-1} hr^{-1})$ t = heating time in hours

 $k_{\rm f} = \overline{Ae^{-Ea/RT}}$

A = Arrhenius constant Ea = energy of activation R = gas constant; T = temp (K)

Kinetics

1. The following table summarizes the results for 0, 1st and 2nd order reactions:

n rate equation $t_{1/2}$ t_{90} t_{95} $c = a - k_0 t$ $t_{1/2} = \frac{0.5a}{k_0}$ $t_{90} = \frac{0.1a}{k_0}$ $t_{95} = \frac{0.05a}{k_0}$ $\ln c = \ln a - k_1 t$ $t_{1/2} = \frac{0.693}{k_1}$ $t_{90} = \frac{0.105}{k_1}$ $t_{95} = \frac{0.051}{k_1}$ $\frac{a - c}{ac} = k_2 t$ $t_{1/2} = \frac{1}{ak_2}$ $t_{90} = \frac{1}{9ak_2}$ $t_{95} = \frac{1}{19ak_2}$

2. For pseudo zero order degradation of suspension: $k_0 = k_1 S$

3. Reversible reactions:

$$\mathbf{K}_{\mathrm{eq}} = \frac{[\mathbf{B}]_{\mathrm{eq}}}{[\mathbf{A}]_{\mathrm{eq}}} = \frac{k_{\mathrm{f}}}{k_{\mathrm{r}}}$$

4. The Arrhenius equation: $k(T) = A \exp(-E_a / RT)$ E_a is activation energy (kcal/mole)

5. The Q₁₀ value:
$$Q_{10} = \frac{k(T+10)}{k(T)}$$

6. Shelf life estimation: t₉₀ and Q₁₀.

$$t_{90}(T_2) = \frac{t_{90}(T_1)}{(Q_{10})^{\Delta T/10}} \qquad (\Delta T = T_2 - T_1)$$

7. Rate constant due to catalysis

$$\frac{k_c(T)}{k_s(T)} = \exp[-\frac{\Delta E_a}{RT}]$$

8. Specific acid-base catalysis: $k_{obs} = k_s + k_H [H_3 O^+] + k_{OH} [OH^-]$