## PHCEU 5125 Equation Sheet, Exam 3

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## Micromeritics:

$\mathrm{N}=$ $\qquad$
$\mathrm{d}_{\mathrm{vn}}=$ mean diameter based on volume-mean number (see table p. 426), cm
$\rho=$ density of the powder, $\mathrm{g} / \mathrm{cm}^{3}$
Surface area of sphere $=\pi \mathrm{d}^{2}$
Volume of sphere $=\pi d^{3} / 6$
Surface area $=\alpha_{s} \mathrm{~d}_{\mathrm{p}}{ }^{2}=\pi \mathrm{d}_{\mathrm{s}}{ }^{2} \quad \alpha_{\mathrm{s}} / \alpha_{\mathrm{v}}=6$ for a sphere
Volume $=\alpha_{v} \mathrm{~d}_{\mathrm{p}}{ }^{3}=\pi \mathrm{d}_{\mathrm{v}}{ }^{3} / 6$
$\mathrm{S}_{\mathrm{v}}=\underline{\text { surface area of particles }}=\underline{\alpha}_{\underline{s}}$
volume of particles $\quad \alpha_{\mathrm{v}} \mathrm{d}$
$\mathrm{S}_{\mathrm{w}}=\underline{\text { surface area per unit volume }}=\underline{\mathrm{S}}_{\mathrm{v}-} \quad \rho=$ true density
density $\rho$
$=\frac{\alpha_{s}}{\rho \alpha_{v} d^{\prime}}=\frac{\alpha_{s}}{\rho \alpha_{v} d_{v s}} \quad \begin{aligned} & \text { d now defined as } d_{v s} \text { for this case; } \\ & d_{v s}=\text { volume-surface diameter characteristic }\end{aligned}$ of specific surface

For a sphere, $\mathrm{S}_{\mathrm{w}}=\frac{6}{\rho \mathrm{~d}_{\mathrm{vs}}} \quad$ since $\alpha_{\mathrm{s}} / \alpha_{\mathrm{v}}=6$
$\epsilon=\underline{\mathrm{V}}_{\text {bulk }} \underline{\mathrm{V}}_{\text {bulk }}-\mathrm{V}_{\text {particles }} \quad$ (often expressed as a percent, so multiply by 100)
$\mathrm{V}_{\text {bulk }}-\mathrm{V}_{\text {particles }}=$ void volume
Bulk density $=\rho_{\text {bulk }}=$ weight/ $\mathrm{V}_{\text {bulk }}$
True density $=\rho=$ weight/ $V_{\text {particles }}$
Bulkiness $=1 /($ bulk density $)=\mathrm{V}_{\text {bulk }} /$ weight

$$
\begin{aligned}
\tan \phi=\mu & =\mathrm{h} / \mathrm{r} \\
\mu & =\text { coefficient of friction } \\
\mathrm{h} & =\text { height of powder cone } \\
\mathrm{r} & =\text { radius of powder cone }
\end{aligned}
$$

## Rheology:

Shearing stress, F:

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\(F=\quad \underline{F}=\eta \underline{d v} \quad \eta=\) viscosity (dynes sec/ \(/ \mathrm{cm}^{2}\) or poise)
    \(\overline{\mathrm{A}} \quad \mathrm{dr} \quad \mathrm{dv} / \mathrm{dr}=\) rate of shear \(=\mathrm{G}\left(\sec ^{-1}\right)\)
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viscosity: $\quad \begin{array}{r}\eta=\underline{F} \\ \hline\end{array}$
fluidity: $\quad \phi=1 / \eta$

Kinematic viscosity $=\eta / \rho \quad$ in stokes where 1 stoke $=1$ poise $/\left(\mathrm{g} / \mathrm{cm}^{3}\right)$.
$\eta=\mathrm{Ae}^{\mathrm{E}_{\mathrm{v}} / R T}$
$\eta=$ viscosity (usually in centipoise)
A = constant
$\mathrm{E}_{\mathrm{v}}=$ activation energy required to initiate flow between the molecules ( $\mathrm{cal} / \mathrm{mol}$ )
$\mathrm{R}=$ gas constant $\left(1.987 \mathrm{cal} /{ }^{\circ} \mathrm{Kmol}\right)$
T = temp in Kelvins
$\eta_{\mathrm{rel}}=\underset{\eta_{1}}{\eta_{2}}=\underset{\rho_{2}}{\rho_{2} t_{2}}$
$\rho_{1}$ and $\rho_{2}=$ densities of liquids 1 and $2\left(\mathrm{~g} / \mathrm{cm}^{3}\right)$
$t_{1}$ and $t_{2}=$ flow times of liquids 1 and $2(\mathrm{sec})$
$\eta_{1}$ and $\eta_{2}=$ viscosities of liquids 1 and 2 (centipoise)
$1 / \eta=V_{1} / \eta_{1}+V_{2} / \eta_{2}$
$\mathrm{V}_{1}, \mathrm{~V}_{2}=$ volume fractions of pure solutions 1 and 2
$\eta_{1}, \eta_{2}=$ viscosities of solutions 1 and 2

$$
\begin{gathered}
\mathrm{U}=\frac{(\mathrm{F}-\mathrm{f})}{\mathrm{G}} \quad \begin{array}{r}
\text { where } \mathrm{F}=\text { shearing stress, or } \mathrm{F}^{\prime} / \mathrm{A}\left(\mathrm{dynes}^{2} / \mathrm{cm}^{2}\right) \\
\mathrm{f}=\text { yield value }\left(\text { dynes } / \mathrm{cm}^{2}\right) \\
\mathrm{G}=\text { rate of shear }\left(\mathrm{sec}^{-1}\right)
\end{array}
\end{gathered}
$$

(Units of $U$ are poise, or dynes $\mathrm{sec} / \mathrm{cm}^{2}$ )
$F^{N}=\eta^{\prime} G \quad \quad \eta^{\prime}$ represents a viscosity coefficient

$$
\mathrm{B}=\frac{\mathrm{U}_{1}}{\ln } \frac{-\mathrm{U}_{2}}{\left(\mathrm{t}_{2} / \mathrm{t}_{1}\right)}
$$

$\mathrm{U}_{1}$ and $\mathrm{U}_{2}=$ plastic viscosities of the 2 down curves after shearing at a constant rate for $\mathrm{t}_{1}$ and $\mathrm{t}_{2}$, respectively.

$$
\mathrm{M}=\underline{\mathrm{U}}_{1}-\underline{\mathrm{U}}_{2}
$$

$$
\ln \left(v_{2} / v_{1}\right)
$$

Flow of a liquid: $\quad \eta=F / G$

$$
\mathrm{F}=\text { shear stress }
$$

$$
\mathrm{G}=\text { shear rate }
$$

Elasticity of the solid (from Hooke's Law, equation of a spring): $\quad E=F / \gamma$

$$
\begin{aligned}
& \mathrm{E}=\text { elastic modulus }\left(\text { dyne } / \mathrm{cm}^{2}\right) \\
& \mathrm{F}=\text { stress }\left(\text { dyne } / \mathrm{cm}^{2}\right) \\
& \gamma=\text { strain }(\text { dimensionless })
\end{aligned}
$$

## Coarse dispersions:

$\Delta \mathrm{G}=\gamma_{\mathrm{SL}} \Delta \mathrm{A}=\mathrm{G}_{\text {final }}-\mathrm{G}_{\text {initial }}=\gamma_{\mathrm{SL}}\left(\mathrm{A}_{\text {final }}-\mathrm{A}_{\text {initial }}\right)$
$\gamma_{\mathrm{SL}}=$ the interfacial tension between solid and liquid, measured in dynes $/ \mathrm{cm}$
$\Delta G=\operatorname{surface}$ free energy $(\Delta G) \mathrm{erg} / \mathrm{cm}^{2} \quad\left(\mathrm{erg}=\mathrm{g} \mathrm{cm}^{2} / \mathrm{sec}^{2}\right)$
$\Delta \mathrm{A}=$ change in surface area, $\mathrm{cm}^{2}$

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

$\mathrm{v}=$ velocity of sedimentation $(\mathrm{cm} / \mathrm{sec})$; also known as rate of settling
$d=$ diameter of particle (cm)
$\rho_{\mathrm{s}}, \rho_{\mathrm{o}}=$ densities of dispersed phase and dispersion medium, respectively $\left(\mathrm{g} / \mathrm{cm}^{3}\right)$
$\mathrm{g}=$ acceleration of gravity ( $981 \mathrm{~cm} / \mathrm{sec}^{2}$ )
$\eta_{\mathrm{o}}=$ viscosity of dispersion medium in poise
$\mathrm{v}^{\prime}=\mathrm{v} \in^{\mathrm{n}}$
$\mathrm{v}^{\prime}=$
$\mathrm{v}^{\prime}=$ rate of fall at the interface ( $\mathrm{cm} / \mathrm{sec}$ )
$\mathrm{v}=$ velocity of sedimentation from Stokes' Law
$\epsilon=$ initial porosity of the system
$\mathrm{n}=\mathrm{a}$ measure of the "hindering" of the system (a constant for each system)

$$
\begin{array}{|c|}
\hline \mathrm{F}=\mathrm{V}_{\mathrm{u}} / \mathrm{V}_{\mathrm{o}} \\
\mathrm{~V}_{\mathrm{u}}=\text { final, or ultimate volume of sediment }
\end{array}
$$

$\mathrm{V}_{\mathrm{o}}=$ original volume of the suspension
$\mathrm{F}_{\infty}=\mathrm{V}_{\infty} / \mathrm{V}_{\mathrm{o}}$
$\beta=\mathrm{F} / \mathrm{F}_{\infty}=\mathrm{V}_{\mathrm{u}} / \mathrm{V}_{\infty}$
$\beta=\underline{\text { ultimate sediment volume of flocculated suspension }}$ ultimate sediment volume of deflocculated suspension

Fractional release (F) of drug from a gel at time $t: F=M_{t} / M_{0}=k t^{n}$
$\mathrm{M}_{\mathrm{t}}=$ amount of drug released at time t ( g or other)
$\mathrm{Mo}=$ initial amount of drug ( g or other)
$\mathrm{k}=$ rate constant $\left(\mathrm{min}^{-\mathrm{n}}\right)$
$\mathrm{t}=$ time (min)
$\mathrm{n}=$ diffusional exponent (unitless)
Drug diffusivity, D , in the gel matrix:

$$
\begin{array}{cc}
\ln \mathrm{D}=\ln \mathrm{D}_{\mathrm{o}}-\mathrm{K}_{\mathrm{f}}\left(\frac{1}{\mathrm{H}}-1\right) \\
& \begin{array}{l}
\mathrm{D}_{\mathrm{o}}=\text { diffusivity of solute in water }\left(\mathrm{cm}^{2} / \mathrm{sec}\right) \\
\mathrm{K}_{\mathrm{f}}=\text { constant }\left(\mathrm{cm}^{2} / \mathrm{sec}\right) \\
\mathrm{H}=\text { matrix hydration (unitless), } \\
\\
\end{array} \quad \begin{array}{l}
\text { eq. swollen gel wt }- \text { dry gel wt }
\end{array} \\
& \text { eq. swollen gel wt. }
\end{array}
$$

Thermal degradation with respect to rigidity:

$$
\begin{gathered}
\frac{1}{\mathrm{f}}-\frac{1}{\mathrm{f}_{\mathrm{o}}}=\mathrm{k}_{\mathrm{f}} \mathrm{t} \\
\begin{array}{l}
\text { where } \mathrm{f}, \mathrm{f}_{\mathrm{o}}=\text { rigidity index at time } \mathrm{t}, \text { or time zero }\left(\mathrm{g}^{-1}\right) \\
\mathrm{k}_{\mathrm{f}}=\text { rate constant }\left(\mathrm{g}^{-1} \mathrm{hr}^{-1}\right) \\
\mathrm{t}=\text { heating time in hours }
\end{array}
\end{gathered}
$$

$$
\begin{array}{|ll}
\mathrm{k}_{\mathrm{f}}=\mathrm{Ae}^{-\mathrm{Ea} / \mathrm{RT}} \quad \begin{array}{l}
\mathrm{A}=\text { Arrhenius constant } \\
\mathrm{Ea}=\text { energy of activation } \\
\mathrm{R}=\text { gas constant; } \mathrm{T}=\text { temp }(\mathrm{K})
\end{array}
\end{array}
$$

## Kinetics

1. The following table summarizes the results for 0,1 st and 2 nd order reactions:
$\begin{array}{ccccc}n & \text { rate equation } & \mathrm{t}_{1 / 2} & \mathrm{t}_{90} & \mathrm{t}_{95} \\ 0 & c=a-k_{0} \mathrm{t} & \mathrm{t}_{1 / 2}=\frac{0.5 a}{k_{0}} & \mathrm{t}_{90}=\frac{0.1 a}{k_{0}} & \mathrm{t}_{95}=\frac{0.05 a}{k_{0}}\end{array}$
$1 \quad \ln c=\ln a-k_{1} \mathrm{t} \quad \mathrm{t}_{1 / 2}=\frac{0.693}{k_{1}} \quad \mathrm{t}_{90}=\frac{0.105}{k_{1}} \quad \mathrm{t}_{95}=\frac{0.051}{k_{1}}$
$2 \quad \frac{a-c}{a c}=k_{2} \mathrm{t} \quad \mathrm{t}_{1 / 2}=\frac{1}{a k_{2}} \quad \mathrm{t}_{90}=\frac{1}{9 a k_{2}} \quad \mathrm{t}_{95}=\frac{1}{19 a k_{2}}$
2. For pseudo zero order degradation of suspension: $k_{0}=k_{1} S$
3. Reversible reactions:

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

4. The Arrhenius equation: $\quad k(\mathrm{~T})=A \exp \left(-E_{a} / \mathrm{RT}\right)$

$$
E_{a} \text { is activation energy }(\mathrm{kcal} / \mathrm{mole})
$$

5. The $\mathrm{Q}_{10}$ value:

$$
\mathrm{Q}_{10}=\frac{k(\mathrm{~T}+10)}{k(\mathrm{~T})}
$$

6. Shelf life estimation: $\mathrm{t}_{90}$ and $\mathrm{Q}_{10}$.

$$
\mathrm{t}_{90}\left(\mathrm{~T}_{2}\right)=\frac{\mathrm{t}_{90}\left(\mathrm{~T}_{1}\right)}{\left(\mathrm{Q}_{10}\right)^{\Delta \mathrm{T} / 10}} \quad\left(\Delta \mathrm{~T}=\mathrm{T}_{2}-\mathrm{T}_{1}\right)
$$

7. Rate constant due to catalysis

$$
\frac{k_{c}(\mathrm{~T})}{k_{s}(\mathrm{~T})}=\exp \left[-\frac{\Delta E_{a}}{\mathrm{RT}}\right]
$$

8. Specific acid-base catalysis: $\quad k_{\mathrm{obs}}=k_{\mathrm{s}}+k_{\mathrm{H}}\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]+k_{\mathrm{OH}}\left[\mathrm{OH}^{-}\right]$
