Segregation Kinetics of Particulate Solids Systems II

Particle Density–Size Interactions and Wall Effects

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Segregation in particulate mixtures is not observed in systems subjected to vertical sine wave motion when the particles differ only in density. However, a marked non-linear interaction is found between the variables of density and size where the spheres differ in both density and size. The influence of the over-all dimensions of the systems and the mode of agitation on the observed rates of unmixing has been studied and found to be a function of particle size.

PARTICULATE DENSITY has been studied by several workers (1–3) as a factor involved in the mixing of solids. It is also an important consideration in the segregation which accompanies most mixing operations. Pharmaceutically, mixtures of solid particles may contain components which vary widely in density and therefore can be expected to separate when subjected to agitation. Hardy and Gard (1) found that in mixtures of powders 100 mesh or finer surface energy prevented or retarded segregation; in some systems no separation was noted even with great differences in density of the components. Recent studies on the rate of mixing in horizontal drum mixers show the marked effect of a density differential between components (2, 3). In certain cases, a differential in density between particles resulted in a greater final degree of mixing than would be found otherwise. Much of the previously reported information is difficult to interpret since the results are obtained in systems where variables other than density are allowed to fluctuate. The present work is intended to give quantitative information on the extent and nature of the effect of density and interparticulate density differences on the segregation rate of idealized systems composed of spheres.

Volume of the mixer relative to the mean particle size is a factor which has received little consideration in the literature. It can be expected that interactions which occur between particle and container wall may influence the rate of mixing and also that of segregation. In the present studies we are limited to small containers, and the spheres used are relatively large. The wall effects which occur have been studied as a function of the size of the cylinder, depth of fill

in the cylinder, mode of agitation, and size of the spheres. Results indicate that the observed wall effects should not alter significantly the relationships between particulate variables and segregation rate or the interpretation of the data.

EXPERIMENTAL

Materials.—Chrome steel balls of the grade and type commonly employed in manufacture of commercial ball bearings were used. Glass spheres were of the common type used as laboratory boiling beads but were selected for uniformity of size and spheroidicity. Cylinders of 0.75- and 1.00-in. internal diameter were made of brass tubing and fitted with plungers for the removal of samples.

Procedures.—Systems consisting of binary mixtures of balls which varied as to size, density, or both were subjected to vertical sine wave motion of 1025 ± 5 c.p.m. frequency and an amplitude of 0.100 in. Studies were carried out in both 0.75- and 1.00-in. diameter cylinders with general procedure, particle size analysis, calculation of standard deviation, and computation of confidence limits carried out as previously reported (4). Additional studies were done with a variation in the mode of agitation. A 0.75-in. internal diameter brass cylinder was split longitudinally and arranged to allow movement of one side relative to the other which was held fixed. The resulting squeeze-type motion was adjusted to a frequency of 1025 ± 5 c.p.m. and an amplitude of 0.035 in. Horizontal motion of the movable half of the cylinder was approximately sine wave. However, since many of the systems studied in the present work contained spheres which were of different density and size, this fact should be considered in the interpretation of the computed standard deviations. Equivalence of the systems was maintained by using equal weights of spheres where densities were equal but differed in size, and equal volumes were taken in cases where the components varied in density. The standard deviation, on the basis of weight, of a completely unmixed system of this type and of a system in any other state of separation, is a function of the density differential between components and the state of mixedness. Since the effect of density difference on standard deviation is a constant factor in any given system and because the function $(S_\infty - S)$ is plotted as the logarithm, there is no net effect on the computed rate constant. For this reason, rate constants for monodensity systems can be compared directly with those where the components vary in density.

TABLE I.—SEGREGATION RATE CONSTANTS IN
BINARY SYSTEMS OF GLASS SPHERES

Sphere Diameters,[a] mm.	$\dfrac{V_l - V_s}{V_s}$	k (Min.$^{-1}$) 95% C.L.
3–6	7.00	0.100 ± 0.015
3–5	3.63	0.050 ± 0.011
3–4	1.37	0.014 ± 0.003
4–6	2.38	0.033 ± 0.009
5–6	0.73	0.012 ± 0.001

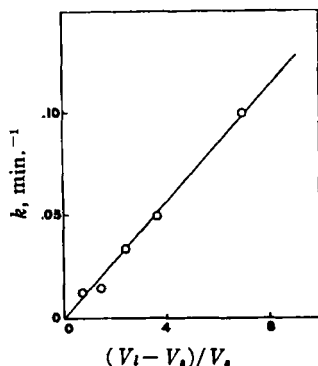[a] Equal weights of both components were used (28.5 Gm.).

Fig. 1.—First-order rate constant, k, *versus* the ratio of the difference in particulate volumes, $(V_l - V_s)$, to the particulate volume of the smaller component, V_s. Glass balls were used in all runs at a 1:1 ratio (w/w) of the two components. The solid line represents the least-square regression.

RESULTS AND DISCUSSION

Density Effects.—Earlier work (4) has shown that systems of steel balls segregate as a function of the ratio of their particulate volumes. Plots of apparent rate constants *versus* particulate volume ratios resulted in straight lines for systems where the large balls were held constant and the size of the smaller component varied and also where the reverse was true. As noted previously, the slopes of these lines were similar and passed through the point (1,0).

Rate constants are presented in Table I for systems of glass balls occupying the same volume within the 0.75-in. cylinder and subjected to the same vertical agitation as the steel balls studied previously—1025-c.p.m. frequency, 0.100-in. amplitude. The rate constants have been plotted in Fig. 1 against $(V_l - V_s)/V_s$, where V_l and V_s are the particulate volumes of the large and small spheres, respectively. The function corresponds to the particulate volume ratio, V_r, minus 1. This method of plotting results in a straight line as before (4) but transposes the line so that it passes through the origin rather than the point (1,0). The least-square slope of this line through the origin was 0.014. The composite data reported previously for systems of steel spheres yield a least-square slope of 0.017. Confidence limits of the points from which the slopes were determined indicate that no significance can be given to the observed difference. These results for systems whose densities were in the ratio of 3.14 (7.79 density for steel, 2.48 density for glass) suggest that density is not an important factor in segregation where it is the same for all particles in the system.

In an attempt to obtain data on systems of higher density, experiments were carried out with lead shot.

Here no segregation could be detected in mixtures with particulate volume ratios as high as 111. It is apparent from these results that a factor or factors other than size and density must be taken into account. In this case, it is likely that elasticity plays an important role.

The coefficient of restitution, C, is defined as $(V_4 - V_3)/(V_2 - V_1)$, where two bodies moving in a straight line with velocities V_1 and V_2, respectively, collide and after impact move with velocities V_3 and V_4. As a rough indication of C, balls of the material to be studied were dropped onto a glass plate and the height to which they bounced was noted. The ratio of the initial height to the bounce height gave a measure of the elasticity as we were concerned with it. No attempt was made to use a plate of the same material as the ball since plates of the same composition and hardness could not be obtained. The chrome steel balls gave a bounce height ratio of 0.95, glass balls 0.87, and lead shot 0.05. While these results are quite approximate and not done for a degree of accuracy, they correlate well with the aforementioned segregation rates.

Segregation was anticipated in binary systems in which components of the same particle size differed in density. A decrease in free energy would occur with a displacement of lighter balls to the top of the cylinder with a resultant drop in the center of gravity. This was not the case experimentally. Lead shot and glass balls of the same diameter (0.110 in.) showed no unmixing when subjected to vertical sine wave motion for a prolonged period (1 to 5 hours) of time. This could have been due possibly to the low elasticity of the lead. A system of glass balls (0.118 in.) and steel balls (0.094 in.), where elasticity should not be a critical factor was also agitated for several hours; again no segregation could be detected. It should be emphasized that these results have been found for a specific mode of vibration only (sine wave at 1025 c.p.m. and amplitude 0.100 in.) and may not hold where void space created by shaking is greater, or where other modes of vibration become dominant.

Combined Density and Size Effects.—Studies on density effects in systems with no size differential fail to give data relative to the combined effect of these two variables. Extrapolation of results to cases where both density and size differences exist would require an assumption that these variables are independent. Therefore, the apparent first-order rate constants for binary systems comprising equal volumes of various sized glass and steel balls were determined. The results, which are presented in Table II, fall into two groups on the basis of the more

TABLE II.—SEGREGATION RATE CONSTANTS IN
SYSTEMS OF GLASS AND STEEL SPHERES

Glass, mm.	Steel, 32nds of an in.	$\dfrac{V_l - V_s}{V_s}$	k, Min.$^{-1}$ 95% C.L.
6	3	15.64	0.621 ± 0.047
6	4	6.08	0.190 ± 0.050
6	5	2.64	0.071 ± 0.015
5	3	8.20	0.284 ± 0.063
3	8	8.51	0.087 ± 0.010
4	8	2.96	0.043 ± 0.004
5	8	1.04	0.021 ± 0.003
3	7	5.39	0.073 ± 0.025
3	6	3.04	0.065 ± 0.008
3	5	1.31	0.037 ± 0.008

dense component being either larger or smaller than the less dense component. Dimensions of the balls will be given in thirty-seconds of an inch and millimeters for the steel and glass balls, respectively, so that previously reported data (4) may be compared more easily with the present results. Figure 2 shows plots of the apparent rate constants *versus* $(V_l - V_s)/V_s$ for the two cases. It is apparent from this graph that a distinctly nonlinear interaction occurs between size and density. When the larger particles are more dense, the segregation rate falls off at higher particulate volume ratios, and the reverse is noted in the case of more dense–smaller systems. In general, the effect of density becomes more pronounced as the size difference increases.

The solid curves through the points in Fig. 2 were drawn from Eq. 1. Coefficients were determined by

$$k = B \left(\frac{V_l - V_s}{V_s} \right) + C \left(\frac{V_l - V_s}{V_s} \right)^2 \quad \text{(Eq. 1)}$$

the method of least squares for the curves passing through the origin. For the more dense–smaller curve, $B = 0.027$ and $C = 0.0008$; for the more dense–larger curve, $B = 0.022$ and $C = -0.0014$. While no theoretical significance should be attached to this equation, it is useful in analysis of the data. It is interesting that the linear coefficients, B, are higher in both cases than those in the monodensity systems. The reasonably close numerical correspondence of the coefficient of the square term, C, for the two curves is significant since this coefficient largely represents the influence of the density differential as it interacts with the difference in particle size. Obviously, the equation breaks down at higher particulate volume ratios than those studied and would require the addition of higher-order terms. Attempts to extend these studies to glass–lead systems were unsuccessful, presumably due to the low elasticity of the lead. No detectable segregation occurred regardless of particulate size ratio.

Particle–Wall Interactions.—A study designed to yield fundamental information on the behavior of mixtures of solid particles must necessarily allow control or evaluation of the interactions between
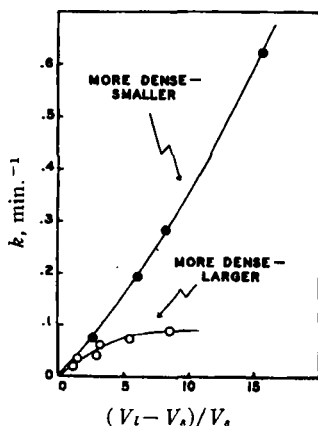
TABLE III.—SEGREGATION RATE CONSTANTS IN BINARY SYSTEMS OF STEEL SPHERES

Particle Diam., 32nds of an in.	Cylinder Diam., in.	Fill Wt., Gm.	$\dfrac{V_l - V_s}{V_s}$	k (Min.$^{-1}$) 95% C.L.
3–5	1.00	304	3.63	0.031 ± 0.006
3–6	1.00	304	7.00	0.124 ± 0.027
3–7	1.00	304	11.18	0.283 ± 0.038
3–8	1.00	304	17.96	0.401 ± 0.067
3–5	1.00	171	3.63	0.030 ± 0.010
3–6	1.00	171	7.00	0.280 ± 0.044
3–7	1.00	171	11.18	0.407 ± 0.100
3–8	1.00	171	17.96	0.538 ± 0.121
3–5	0.75	171	3.63	0.036 ± 0.003[a]
3–6	0.75	171	7.00	0.161 ± 0.017[a]
3–7	0.75	171	11.18	0.183 ± 0.025[a]
3–8	0.75	171	17.96	0.314 ± 0.023[a]

[a] Reported previously (4).

container and particle. Vertical agitation was selected for the bulk of this work since the system of spheres is accelerated only by the bottom surface of the cylinder, and the results will correspond more closely to those expected of a large body of particles. Vertical agitation also can be expected to reduce wall effects since primary particulate motion is parallel to the sides of the container, and inhibition of motion of those particles contacting the sides is minimized. The nature and magnitude of the wall effects occurring in these studies has been evaluated by varying the dimensions of the systems and the mode of shaking and noting the changes in over-all rate of segregation and in the composition profiles within the agitation cylinder. Precise control of agitation requires that the total weight of particles be limited to a range which can be accommodated by the apparatus. For this reason, cylinders of internal diameter larger than 1 in. were not used.

Cylinders of 0.75- and 1.00-in. internal diameter were filled to various levels, and the effects of fill weight and cylinder diameter on the rate constants of several systems were determined. Results of these studies are reported in Table III. Comparison of data obtained in 1-in. cylinders for fill weights of 304 and 171 Gm. shows differences in rate constants with the higher particulate volume ratios. While this may indicate increased inhibition of separation by particle–wall interactions for the larger spheres, a second factor should be taken into account. Individual particles in 171-Gm. systems have a proportionately shorter distance to travel before becoming separated regarding the total system. This effect, however, should be independent of particle size. A further comparison of data is possible since column height is the same (about 5.5 in.) for 304-Gm. fill in the 1-in. cylinder and 171-Gm. fill in the 0.75-in. cylinder. Lower segregation rates are observed in the smaller tube, but again only with the larger particles. Good conformity to the linear relationship between particulate volume ratio and segregation rate constant was found in all systems, regardless of column diameter or fill weight.

Composition profiles at various time intervals indicate the effects of particle–wall interactions within the segregating systems. Figure 3 shows the per cent of large balls within a 1.00-in. diameter column for binary systems of $^3/_{32}$ and $^5/_{32}$ in. steel spheres. A rather symmetrical concentration curve is obtained for these systems up to infinite time (times in excess of seven half-lives). This type

Fig. 2.—First-order rate constant, k, *versus* the ratio of the difference in particulate volumes, $(V_l - V_s)$, to the particulate volume of the smaller component, V_s. Glass and steel balls were used in all runs at a 1:1 total volume ratio of the two components. The solid lines represent the least-square regression.

curve is typical of the systems composed of smaller balls and indicates little or no wall effect.

A composition profile is shown in Fig. 4 for a 304-Gm. system of $^3/_{32}$ and $^5/_{32}$ in. steel balls in a 1.00-in. cylinder. These curves, representing particle size distribution within the column at various times, are typical of systems composed of the larger sized balls, although deviation from symmetry becomes much less marked with the intermediate sized balls studied. However, asymmetry of the composition profiles extends to smaller sized balls in the 0.75-in. cylinder than in the larger tube. Decreased mobility of the balls at the lower levels is manifested by the slower rate of segregation here compared with the upper regions of the column. However, after shaking to equilibrium for periods in excess of seven half-lives, symmetrical curves are obtained in all cases. It should be mentioned that no deviation from linearity of log $(S_\infty - S)$ *versus* time plots was evident in any case, regardless of wall effect. This evaluation of the particle–wall interactions as they occur in this work allows an appraisal of the phenomenon and its influence on the observed rate constants.

Composition profiles of the segregation of binary systems of $^3/_{32}$ in. *versus* $^5/_{32}$ in. and $^3/_{32}$ in. *versus* $^8/_{32}$ in. steel balls in 0.75-in. cylinders were compared for two modes of agitation. When these systems were run in the vertically split, squeeze-type cylinder previously described, curves which were similar to Fig. 4 were obtained with both systems. Comparison of these results with those obtained with the usual vertical agitation indicates that the latter mode of shaking produces less particle–wall interaction as would be expected.

SUMMARY

While the work presented here has been carried out on idealized systems under closely controlled conditions, several conclusions can be drawn which may be applied in principle to granulations or other mixtures of solids as they are encountered in pharmacy.
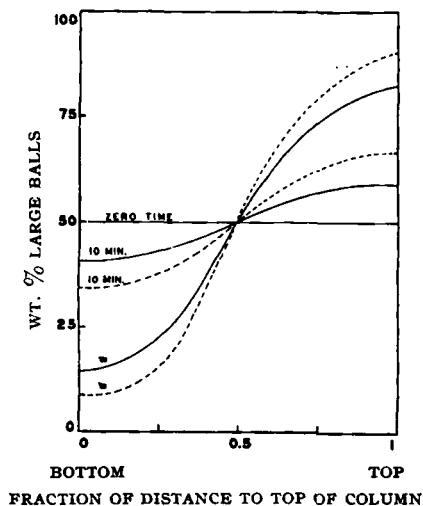
Fig. 3.—Composition profile curves in 1-in. diameter cylinders after various periods of vertical sine wave agitation for a binary system of $^3/_{32}$ and $^5/_{32}$ in. steel spheres at a 1:1 ratio (w/w). Solid lines represent a total system weight of 171 Gm., and dotted lines are for a 304-Gm. system.
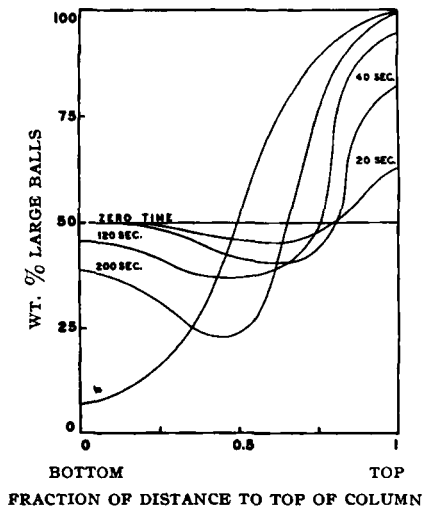
Fig. 4.—Composition profile curves in a 1-in. diameter cylinder after various periods of vertical sine wave agitation for a binary system of $^3/_{32}$ and $^5/_{32}$ in. steel spheres at a 1:1 ratio (w/w). Total weight of the balls was 304 Gm., and the curves shown are typical of those where detectable particle–wall interactions occur.

In general, segregation is not greatly influenced by density when all the particles within a given system have the same density. No detectable unmixing occurs in binary systems of equal sized spheres in which the components have a threefold difference in density. However, segregation is rapid in systems in which the small particles are more dense, but a marked retardation is evident when the larger particles are more dense. Moreover, the over-all effect of combined differences in density and size indicates a marked nonlinear interaction between these two variables.

Elasticity of the particles, reflected by the coefficient of restitution, plays a large part in segregation as observed in these studies. This is not unexpected since interparticulate transfer of kinetic energy is dependent on the degree of elasticity of the collisions.

Wall effects resulting from particle–cylinder contact cause no apparent change in the relationship between segregation rate and particle size. Linearity of the segregation rate constant as a function of particulate volume ratio is maintained within a series in which cylinder diameter and fill weight are held constant.

In application to real systems, it should be emphasized that variables other than those studied here may play a critical role in determining the segregation rate. For this reason, the conditions under which these results were obtained should be considered when using them to predict or explain granulation stability.

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