

range of instrument; ($10^{-2}M$ ethanolic KOH): bathochromic shift to 225 $m\mu$ (flat shoulder) and 215 $m\mu$ (peak).

Anal.—Calcd. for $C_{15}H_{20}Cl_2N_2O_2$: C, 53.39; H, 6.08; Cl, 21.20; N, 8.45. Found: C, 53.03; H, 5.96; Cl, 20.21; N, 8.81.

2-(N,N-Diethylamino)-2-p-tolylglutarimide (Vb)—Spectroquality DMF was used. All glassware was flame-dried, and the reaction was carried out under an atmosphere of dry nitrogen.

A solution of 16.0 Gm. (0.05 mole) of crude, but dried, 4 - carboxy - 4 - (N, N - diethylamino) - 4 - p - tolylbutyramide (IVb) in 50 ml. of dry DMF was added dropwise to a stirred suspension of 1.4 Gm. (0.057 mole) of NaH in 100 ml. of dry DMF. The mixture was stirred at 55° for 2.5 hr., by which time the formation of anion was complete as evidenced by the cessation of H_2 evolution. The bath temperature was raised to 105° and maintained at this point for 15 hr. The residue, left after distilling off the solvent under reduced pressure, was well stirred with ice water, the solution adjusted to pH

8.5 (cooling), and the product extracted with chloroform, washed with water, and dried (Na_2SO_4). Filtration and removal of the chloroform left a thick oil which solidified on rubbing with dry *n*-hexane. Recrystallizations from dry chloroform-hexane¹ yielded 1.62 Gm. (11.8%) of Vb as white crystals, m. p. 112°; infrared ($CHCl_3$): 3375, 3200 (NH); 1720 cm^{-1} (C=O).

Anal.—Calcd. for $C_{16}H_{22}N_2O_2$: C, 70.04; H, 8.08; N, 10.21. Found: C 69.95; H, 8.04; N, 10.21.

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¹ Using decolorizing carbon (Norit).

Segregation Kinetics of Particulate Solids Systems IV. Effect of Particle Shape on Energy Requirements

By E. G. RIPPIE, M. D. FAIMAN*, and M. K. PRAMODA

The relative energy requirements of the processes of segregation and mixing, which occur in systems of particulate solids, are shown to be a function of the shape and size of the particles. These energy requirements, as reflected by agitation coefficients, have been determined for several idealized systems. Granular solids, as represented by crushed quartz and pyrite, were found to behave in conformity with predictions based on the idealized systems.

PARTICLE SHAPE is known to exert a marked influence on the behavior of particulate solids. This is true, moreover, when powdered or granular material is either in a dynamic state of flow or is at rest. Little is presently known regarding the specific cause and effect relationships between bulk behavior and particle shape, a situation which arises because of difficulties in expressing the latter as a single scalar quantity.

The problem is frequently approached by the use of shape factors as a quantitative expression of the average shape of particles in a system. The function of shape factors, however, is not to express shape, but rather to relate the results of particle size measurements which have been obtained by several different methods (1). Consequently, it is possible to have different particulate solids with quite different characteristic shapes, but which all possess a similar value of a given shape factor. Further complications result when average values are used to describe particulate variables without

regard for the deviation of individual values from the mean.

The present work is intended to give quantitative information on the effects of particle shape on segregation and mixing in idealized systems where an intuitive appraisal of shape is possible. Such idealized systems, which are made up of regularly shaped particles (spheres, paired spheres, cubes, rods, and hexagonal rods), have the advantage that they may be described exactly as to shape which is uniform from particle to particle. For purposes of comparison, crushed quartz and pyrite were also studied.

Results indicate that substantial differences in bulk behavior can result from relatively minor changes in particle shape. Particle size is also shown to influence the change in rate of segregation and mixing with a change in agitation intensity.

EXPERIMENTAL

Materials—Chrome steel balls of the type and grade commonly employed in the manufacture of commercial ball bearings were used. Paired balls were prepared by spot welding two similar sized balls together. The effective distance of separation of the centers of mass was reduced by approximately 1% by the welding operation. Steel cubes and cylinders of circular and hexagonal cross section were made of cold rolled steel and case hardened in

Received May 26, 1967, from the Department of Pharmaceutics, College of Pharmacy, University of Minnesota, Minneapolis, MN 55455

Accepted for publication July 21, 1967.

This investigation was supported by grants GP-1820 and GK-471 from the National Science Foundation.

Previous paper: Faiman, M. D., and Rippie, E. G., *J. Pharm. Sci.*, **54**, 719(1965).

* Present address: University of Kansas, Lawrence, KS 66044

molten potassium cyanide. All dimensions of these three forms were 0.125 in.

Natural quartz and pyrite were crushed and sieved through U. S. Standard sieves. Following sieving, the quartz was purified by washing with 5% HCl after soaking overnight in the acid. The material was oven dried following a distilled water wash. The crushed pyrite was washed with distilled water and oven dried. After drying, both materials were again sieved before use.

Procedure—Equipment and procedure were essentially as reported previously (2-4) with regard to particle size analysis, calculation of system standard deviation, and computation of the rate constants for segregation and mixing. Agitation coefficients are defined as the slope of a plot of the natural logarithm of the rate constant for a given process *versus* the square of the reciprocal of the velocity imparted to the particles by the shaker.

The particulate systems were subjected to a vertical sine wave agitation in brass cylinders of 1-in. internal diameter which were hard chrome plated, when used with quartz and pyrite, to resist abrasion. Amplitudes and frequencies of agitation motion were held to within ± 0.001 in. and ± 5 c.p.m. of the stated values, respectively.

Systems comprised of steel particles were 304 Gm. in total weight and those of quartz and pyrite were 92 Gm. and 150 Gm., respectively.

RESULTS AND DISCUSSION

Agitation coefficients, as defined earlier, represent proportionality constants between the natural logarithm of the rate constant under consideration and the reciprocal of the energy imparted to the particles by the shaker. Large values of agitation coefficients indicate a high degree of dependency of the rate process on agitation and, therefore, a relatively high energy requirement for the process.

No well defined trend is apparent between the particle size ratio, V_r , (the ratio of particulate volumes of the two components) and the agitation coefficients of segregation and mixing, as shown on lines 4-7 in Table I. It is apparent, however, that the equilibrium agitation coefficients of these same systems tend to decrease with a decrease in the average particle size.

Paired Spheres—Unexpected results were obtained for the mixtures of single and paired balls, and are shown on lines 8 and 9 of Table I. The energy requirements for both segregation and mixing are less than in the same systems containing no paired particles, as shown on lines 6 and 7.

In addition to the results reported in Table I, binary mixtures of $\frac{3}{32}$ -in. paired spheres and $\frac{7}{32}$ -in. paired spheres, and $\frac{3}{32}$ -in. paired spheres and $\frac{7}{32}$ -in. single spheres were agitated at an amplitude of 0.141 in. and a frequency of 1030 c.p.m. The data indicated that segregation either had not occurred, or that the rate was immeasurably small. In contrast, binary systems of the same size single balls (Table I, line 7) segregate fairly rapidly. Binary mixtures of single and paired balls of similar size ($\frac{3}{32}$ -, $\frac{5}{32}$ -, and $\frac{7}{32}$ - in.) exhibited no tendency to segregate.

It appears, from these observations, that in a binary mixture where the smaller component was paired, segregation of the system either decreased or did not occur. When the larger component only

TABLE I—AGITATION COEFFICIENTS FOR IDEALIZED BINARY SYSTEMS

System	V_r	Segregation Coeff.	Mixing Coeff.	Equilibrium Coeff.
$\frac{1}{16}$ -in. cube	15.3	21
$\frac{1}{16}$ -in. hex.	14.3	24
$\frac{1}{16}$ -in. cyl.	12.0	36
$\frac{1}{16}$ -in.- $\frac{1}{8}$ -in.	8.0	41	84	-42
$\frac{1}{16}$ -in.- $\frac{5}{32}$ -in.	15.6	46	74	-28
$\frac{3}{32}$ -in.- $\frac{5}{32}$ -in.	4.6	79	106	-27
$\frac{3}{32}$ -in.- $\frac{7}{32}$ -in.	12.7	51	46	5
$\frac{3}{32}$ -in.- $\frac{5}{32}$ -in. ^a	9.3	42	45	-3
$\frac{3}{32}$ -in.- $\frac{7}{32}$ -in. ^a	25.4	34	31	4

^a Paired balls.

was paired, segregation was found to occur. This is consistent with the theory that the large and small components compete for void space created by particulate motion.

Nonspherical Particles—Over-all segregation of systems containing particles other than spheres or paired spheres showed an atypical pattern. A typical graph of such a system undergoing segregation is shown in Fig. 1, which represents a mixture of $\frac{1}{16}$ -in. steel balls and $\frac{1}{8}$ -in. steel cubes agitated at an amplitude of 0.141 in. and a frequency of 1030 c.p.m. The standard deviation is seen to increase, decrease, and then increase again. Similar results occurred with binary mixtures of $\frac{1}{16}$ -in. spheres with both of the other nonspherical shapes studied.

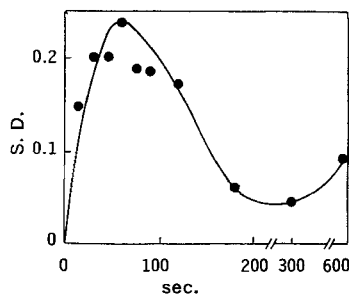


Fig. 1—Standard deviation as a function of agitation time for a 1:1 w/w mixture of $\frac{1}{16}$ -in. steel balls and $\frac{1}{8}$ -in. steel cubes agitated at a frequency of 1030 c.p.m. and an amplitude of 0.141 in.

The reason for this anomalous behavior became apparent when a Lucite cylinder was used, permitting the process to be viewed. It was found that the angular particles, when originally mixed with the balls, had a random orientation. After a short period of segregation in which the angular particles migrated to the top, they were found to orient themselves with their flat surfaces to the sides of the cylinder and to move in a reverse direction down the sides. In effect, convection currents were set up which accounted for the cycling behavior of the standard deviation. This behavior was not observed for systems other than those containing angular particles.

Segregation rate constants were obtained for these systems by fitting a quadratic equation to the data

TABLE II—AGITATION COEFFICIENTS FOR CRUSHED QUARTZ AND PYRITE

System 12/14-70/80 Mesh	Segregation Coefficients	Mixing Coefficients	Equilibrium Coefficients
Quartz	19	2	17
Pyrite	50	49	1

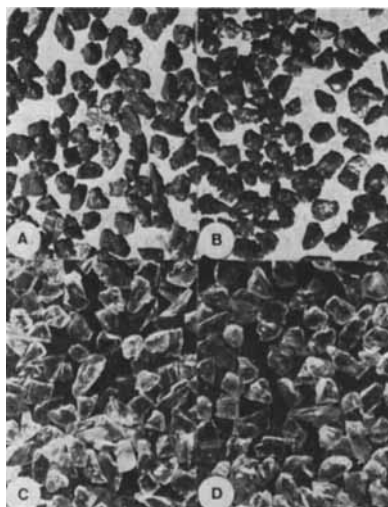


Fig. 2—Key: A, 12/14 mesh pyrite; B, 70/80 mesh pyrite; C, 12/14 mesh quartz; D, 70/80 mesh quartz. Materials are magnified to the same apparent size to show their characteristic particle shapes.

over the initial period of segregation. The coefficient of the linear term in the equation is thus proportional to the initial segregation rate and can be used to compute the segregation agitation coefficients. These are listed on lines 1-3 in Table I.

This coefficient can be seen to increase as the particles become more nearly spherical. The volumes of the angular particles lie between those of the $\frac{1}{8}$ and $\frac{9}{32}$ -in. balls so that comparisons can be made among the first 5 lines of Table I. The lower energy apparently required for segregation of the systems containing the more angular particles cannot be explained on the basis of the data at hand.

The agitation coefficients for the equilibrium values in the last column of Table I can be seen to be the numerical difference between the agitation coefficients for segregation and mixing. Apparent discrepancies are due to rounding to a reasonable number of significant figures.

Results of studies on two granular systems, crushed quartz and pyrite, are presented in Table II. These data agree qualitatively with those re-

TABLE III—AGITATION AMPLITUDES AND FREQUENCIES EMPLOYED AND THEIR CORRESPONDING PARTICULATE VELOCITIES

Amplitude, in.	Frequency, c.p.m.	Particle Velocities, in./sec.
0.200	1030	10.18
0.195	1030	9.89
0.174	1030	8.68
0.174	925	7.43
0.141	1238	8.64
0.141	1119	7.58
0.141	1030	6.71
0.141	935	5.66
0.141	856	4.63
0.100	1400	6.84
0.100	1030	4.04

lating to the angular shapes. While no attempt was made to measure shape, it was readily apparent (Fig. 2) that crushed quartz of a given mesh size is more angular than pyrite of the same size. The higher values of the agitation coefficients of pyrite for both segregation and mixing can be expected on the basis of data in Table II.

Conditions under which the foregoing data were obtained are summarized in Table III. With the exception of the data on lines 6 and 7 of Table I which were determined from studies at all 11 agitation conditions, agitation coefficients were calculated from data obtained under the three conditions represented by lines 1, 7, and 11 in Table III.

SUMMARY

A useful indication of the relative energy requirements for the processes of segregation and mixing, as they occur in idealized particulate systems of the type studied here, may be obtained from the determination of agitation coefficients. Such coefficients are somewhat analogous to activation energies for molecular processes but possess certain important fundamental differences from the latter as indicated previously (4).

The energy requirements of both segregation and mixing have been shown to depend on the shape and relative size of the particles involved. Two granular systems possessing different particulate characteristics were found to behave in conformity with predictions based on the idealized systems. The general method appears to be applicable to the study of other particulate variables as they influence diffusive segregation and mixing.

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