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Segregation Kinetics of Particulate Solids Systems III

Dependence on Agitation Intensity

By MORRIS D. FAIMAN* and EDWARD G. RIPPIE

Studies of the segregation behavior of particulate systems indicate the simultaneous occurrence of both segregation and mixing. The specific rate constants for these processes are calculated from statistical data and are shown to be a function of the particulate velocities. The results suggest the analogy of mechanical agitation in these idealized systems to thermal motion in molecular systems. Arrhenius-type plots of first-order rate constants *versus* the square of the reciprocal particulate velocities make possible the prediction of segregation behavior at various agitation intensities.

IN PREVIOUS reports (1, 2), the segregation occurring in particulate systems of steel and glass spheres has been characterized partially. The over-all process results in a separation of particles of different physical properties and is a function of density, particle size, and the size of the container in which the segregation occurs.

The present work indicates the manner in which energy input affects both the segregation and mixing processes which are shown to occur simultaneously.

Donald and Roseman (3, 4), in experiments with a drum mixer, have reported that increased mixer speed reduced the final degree of mixing. The results reported here suggest that this may not always be the case, but that the segregation characteristics of granulations can be expected to vary with the physical properties of their constituents. The mechanical agitation of the systems under study shows a marked similarity to the thermal motion of molecular systems. The specific forward and reverse rate constants, representing segregation and mixing, respectively, have been evaluated from statistical data

for the over-all process of segregation. These rate constants, when plotted as a function of the particulate energies, substantiate the analogy of agitation to thermal motion.

THEORY

Segregation has been shown to proceed by apparent over-all first-order kinetics to an equilibrium state in which the rates of mixing and unmixing balance (1). This suggests that both mixing and segregation, which are shown to occur simultaneously here, are first-order processes and that the observed rate constant, k_0, is the sum of the constant for segregation, k_1, and that for mixing, k_2. The process may be considered analogous to a reversible chemical reaction in which both forward and reverse steps occur simultaneously. The over-all process, if followed, will reflect the predominance of one reaction step (forward or reverse) over the other. A system of particles following this behavior (5) can be represented by

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B$$

Here, A represents the concentration of mixed particles and B the concentration of those unmixed. The rate equation for this system is given by

$$dA/dt = -k_1A + k_2B \qquad (\text{Eq. 1})$$

The concept of concentration used here relates to the relative number of spheres which may be classified as mixed or unmixed on the basis of their immediate neighbors. Thus, particles within a sample are considered unmixed in so far as they exceed their mean proportion of the total system. The remainder of particles within the sample are

TABLE I.—RATE AND EQUILIBRIUM CONSTANTS FOR SEGREGATION AND MIXING OF BINARY MIXTURES OF STEEL AND/OR GLASS BALLS

No.	Ball Sizes, 32nd in.	Amplitude Total, in.	Frequency, c.p.m.	Velocity, in. sec.$^{-1}$	k_0 (min.$^{-1}$) 95% CL	k_1 (min.$^{-1}$)	k_2 (min.$^{-1}$)	$\bar{S}_\infty$ (95% CL)	K
1	3:5	0.100	1030	4.038	0.02 ± 0.005	0.011	0.012	0.24 ± 0.01	0.953
2	3:5	0.141	1030	6.712	1.24 ± 0.19	0.278	0.960	0.11 ± 0.03	0.289
3	3:5	0.174	1030	8.678	2.56 ± 1.09	0.578	1.978	0.11 ± 0.01	0.292
4	3:5	0.195	1030	9.893	5.77 ± 1.54	1.373	4.401	0.12 ± 0.03	0.312
5	3:5	0.200	1030	10.179	4.61 ± 1.21	0.940	3.672	0.10 ± 0.03	0.256
6	3:5	0.141	856	4.627	0.16 ± 0.02	0.075	0.087	0.23 ± 0.04	0.866
7	3:5	0.141	935	5.664	0.44 ± 0.08	0.182	0.262	0.21 ± 0.07	0.695
8	3:5	0.141	1119	7.577	1.66 ± 0.25	0.458	1.203	0.14 ± 0.02	0.381
9	3:5	0.141	1238	8.637	2.16 ± 0.52	0.492	1.666	0.11 ± 0.02	0.295
10	3:5	0.100	1400	6.841	1.23 ± 0.21	0.223	1.011	0.09 ± 0.04	0.220
11	3:5	0.174	925	7.430	1.49 ± 0.50	0.427	1.066	0.14 ± 0.04	0.401
12	3:7	0.100	1030	4.038	0.19 ± 0.02	0.129	0.057	0.35 ± 0.04	2.268
13	3:7	0.141	1030	6.712	0.98 ± 0.09	0.776	0.204	0.40 ± 0.02	3.808
14	3:7	0.174	1030	8.678	2.76 ± 0.19	2.189	0.575	0.40 ± 0.08	3.808
15	3:7	0.195	1030	9.893	3.06 ± 0.43	2.092	0.966	0.34 ± 0.03	2.165
16	3:7	0.200	1030	10.179	3.04 ± 0.31	2.256	0.784	0.37 ± 0.10	2.876
17	3:7	0.141	856	4.627	0.48 ± 0.05	0.341	0.141	0.35 ± 0.03	2.425
18	3:7	0.141	935	5.664	0.71 ± 0.04	0.555	0.153	0.39 ± 0.03	3.630
19	3:7	0.141	1119	7.577	1.70 ± 0.18	1.301	0.397	0.38 ± 0.03	3.274
20	3:7	0.141	1238	8.637	1.74 ± 0.15	1.322	0.417	0.38 ± 0.06	3.167
21	3:7	0.100	1400	6.841	0.96 ± 0.18	0.683	0.274	0.36 ± 0.06	2.497
22	3:7	0.174	925	7.430	0.90 ± 0.08	0.701	0.198	0.39 ± 0.06	3.545
23	3:6	0.100	1400	6.841	0.42 ± 0.09	0.256	0.167	0.30 ± 0.06	1.538
24	3:6	0.141	1030	6.712	0.44 ± 0.04	0.278	0.164	0.31 ± 0.06	1.688
25	3:6	0.174	925	7.430	0.45 ± 0.06	0.330	0.120	0.37 ± 0.01	2.759
26	4:8	0.100	1400	6.841	0.44 ± 0.09	0.297	0.139	0.34 ± 0.05	2.145
27	4:8	0.141	1030	6.712	0.41 ± 0.10	0.296	0.113	0.36 ± 0.06	2.623
28	4:8	0.174	925	7.430	0.56 ± 0.06	0.396	0.162	0.36 ± 0.05	2.448
29	3:5 mm.^{a}	0.100	1400	6.841	0.38 ± 0.06	0.264	0.116	0.30 ± 0.02	2.273
30	3:5	0.141	1030	6.712	0.47 ± 0.09	0.330	0.144	0.30 ± 0.01	2.298
31	3:5	0.174	925	7.430	0.46 ± 0.06	0.335	0.129	0.31 ± 0.04	2.600
32	3:6 mm.^{a}	0.100	1400	6.841	0.82 ± 0.10	0.618	0.198	0.33 ± 0.03	3.114
33	3:6	0.141	1030	6.712	0.93 ± 0.11	0.710	0.220	0.33 ± 0.07	3.235
34	3:6	0.174	925	7.430	0.85 ± 0.10	0.686	0.166	0.35 ± 0.07	4.143

^{a} Binary mixtures of $^3/_{32}$-in. steel balls with glass balls (diameters in millimeters).

considered mixed. This concept of concentration is dependent upon the number of particles within the sample (scale of scrutiny) as is the usual chemical meaning of the term.

The authors have found (1, 2) the standard deviation from the mean composition, S, to be a useful index of segregation. The value of S in granular systems will progress from zero for a completely mixed system, to the equilibrium value, S_∞, as segregation progresses. Denoting the standard deviation of a completely unmixed system as σ, the concentration of mixed and unmixed particles will be

$$A = A_0(\sigma - S)/\sigma \text{ and } B = A_0 S/\sigma \quad \text{(Eq. 2)}$$

where the subscript 0 denotes initial values. Substituting Eq. 2 into Eq. 1 gives

$$dA/dt = -k_1 A_0(\sigma - S)/\sigma + k_2 A_0 S/\sigma \quad \text{(Eq. 3)}$$

When $t = \infty$, and the system is at equilibrium, the rate of change of A with time will equal zero.

$$dA/dt = 0 = -k_1 A_0(\sigma - S_\infty)/\sigma + k_2 A_0 S_\infty/\sigma$$

It is evident from this equation that the equilibrium constant, K, will be related to S_∞ and σ as follows

$$K = k_1/k_2 = S_\infty/(\sigma - S_\infty) \quad \text{(Eq. 4)}$$

Combining Eqs. 3 and 4, we obtain

$$dA/dt = -k_1 A_0(\sigma - S)/\sigma + k_1 A_0(S/\sigma)(\sigma - S_\infty)/S_\infty$$

This may be simplified to give

$$dA/A_0 = -k_1[(S_\infty - S)/S_\infty]dt \quad \text{(Eq. 5)}$$

Since from Eq. 2, $dA/A_0 = -dS/\sigma$, Eq. 5 can be written as a function of the statistical quantities only.

$$d \ln (S_\infty - S) = -k_1(\sigma/S_\infty)dt$$

Integration from time zero to time t gives

$$\ln[(S_\infty - S)/S_\infty] = -k_1(\sigma/S_\infty)t \quad \text{(Eq. 6)}$$

Combining Eq. 4 with the expression, $k_0 = k_1 + k_2$, the observed rate constant, k_0, may be shown to equal $k_1\sigma/S_\infty$. Equation 6 then may be written as a function of k_0.

$$\ln[(S_\infty - S)/S_\infty] = -k_0 t$$

Rate constants obtained by plotting $\ln(S_\infty - S)$ *versus* time, as done in this and previous work (1, 2), are consistent with this equation and may be resolved into their component segregation and mixing rate constants by

$$k_1 = k_0 K/(K + 1)$$

and

$$k_2 = k_0/(K + 1)$$

EXPERIMENTAL

Materials.—Systems consisting of 1:1 binary mixtures, by weight, of chrome steel balls of various sizes and 1:1 binary mixtures of steel and glass balls, by volume, were studied. Experiments were carried out in brass cylinders of 1-in. internal diameter.

Procedures.—The general procedure previously reported (1) was followed with respect to particle size analysis, calculation of standard deviation, and computation of the confidence limits of the observed rate constants. The systems were subjected to vertical sine wave motion of various frequency–amplitude combinations. Amplitudes were held to within ±0.001 in. and frequencies to within ±5 c.p.m. of the stated values. For this purpose, an improved shaker was constructed which allowed more precise control and adjustment of frequency and amplitude than had been possible previously.

Weights of the systems containing steel balls only were maintained at 304 Gm. Where steel and glass balls were mixed, a volume of glass balls was used equal to that of 152 Gm. of steel balls.

RESULTS AND DISCUSSION

Frequency and Amplitude Dependence.—In an effort to determine the functional relationship between over-all segregation rate and amplitude of agitation, determinations were carried out at a frequency of 1030 c.p.m., with amplitudes varying from 0.100 to 0.200 in. Data for mixtures of $^3/_{32}$-in. balls with both $^5/_{32}$- and $^7/_{32}$-in. balls are shown in Table I, where a general increase in k_0 is shown to occur with increasing amplitude. The relationship is nonlinear and can be expected to vary with the particular frequency selected.

Values of k_0 for these mixtures of steel balls were also determined at a fixed amplitude of 0.141 in. at five different frequency values. These data, listed in Table I, show an increased segregation rate with frequency increase, as expected. Again, a nonlinear relationship of k_0 is evident, and the relative increase in rate can be expected to depend on the amplitude.

These data, while showing the general dependence of the over-all process on agitation, do not suggest the relationship between frequency and amplitude. To resolve this, six test systems were studied.
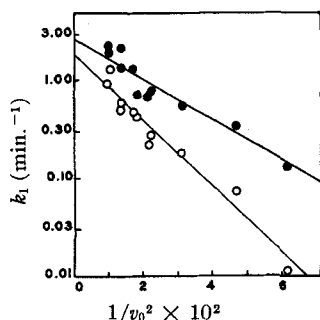
Fig. 1.—Plot of log k_1 (first-order rate constant of segregation) *vs.* reciprocal square of the particulate velocity. Key: ●, $^3/_{32}$–$^7/_{32}$ in. steel balls; ○, $^3/_{32}$–$^5/_{32}$-in. steel balls.
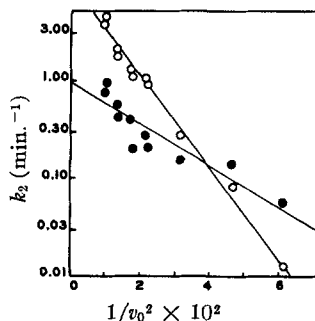
Fig. 2.—Plot of log k_2 (first-order rate constant of mixing) *vs.* reciprocal square of the particulate velocity. Key: ●, $^3/_{32}$–$^7/_{32}$ in. steel balls; ○, $^3/_{32}$–$^5/_{32}$ in. steel balls.

Steel balls of the following sizes were mixed: $^3/_{32}$–$^5/_{32}$, $^3/_{32}$–$^6/_{32}$, $^3/_{32}$–$^7/_{32}$, and $^4/_{32}$–$^8/_{32}$ in. Steel balls, $^3/_{32}$ in., also were mixed with 5- and 6-mm. glass balls. The over-all segregation rate constants of these systems then were determined at a frequency of 1030 c.p.m. and an amplitude of 0.141 in. The amplitude then was set at 0.100 in. and the frequency adjusted to produce the same over-all rate of segregation, in each of the six systems, as previously. This process was repeated at an amplitude of 0.174 in. Data from these determinations presented in Table I, No. *2, 10, 11, 13, 21, 22, 23–34,* do not give a clue to the functional relationship between the two variables. However, the possibility that agitation of elastic steel balls, under the conditions of these experiments, may be analogous to the thermal motion of molecules is strongly suggested by the latter data and will be discussed further.

Analogy of Agitation to Thermal Motion.—If this analogy is assumed to exist, basic differences can be seen between molecular and particulate systems, which make its demonstration difficult. Most obvious is the lack of perfect elasticity in particulate systems which results in kinetic energy losses. Other losses can be attributed to friction between particles. When the process of segregation is compared with a chemical reaction, an important fundamental difference in the interpretation of energy of activation should be recognized. Whereas the energy of activation of a chemical reaction has a well-defined meaning, the energy of activation for segregation or mixing is a space–time average for all the particles in the system. The local environment of particles throughout the system can be expected to vary considerably from particle to particle at any time. Furthermore, the environment of a given particle will change with time as segregation progresses. These factors should be taken into account in the interpretation of Arrhenius-type plots of segregation rate constants which will be discussed later.

The experiment described in the previous section, in which equivalent modes of agitation were investigated, lends support to the hypothetical equivalence of agitation to temperature. Here, the six systems studied, corresponding to six different chemical reactions, each with a different temperature coefficient, were found to exhibit insignificant variation in their characteristic k_0 values with the three frequency–amplitude combinations. One then con-
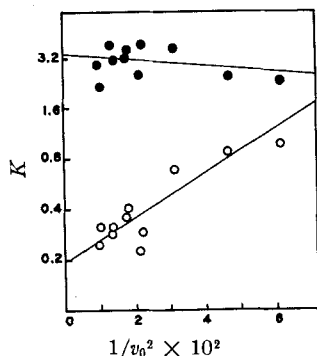
Fig. 3.—Semilog plot of equilibrium constant *vs.* the reciprocal square of the particulate velocity. Key: ●, $^3/_{32}$–$^7/_{32}$ in. steel balls; ○, $^3/_{32}$–$^5/_{32}$ in. steel balls.

cludes that the agitations were equivalent in effect and that the temperature of agitation was the same under all three conditions.

An analysis of the motion imparted to the balls by the cylinder is possible since the motion of the cylinder is sine wave and can be differentiated to give the velocity and acceleration at any time. The balls will be left in free flight when the downward acceleration of the cylinder becomes equal to that of gravity. If the balls at the bottom of the cylinder are assumed to be at rest in the cylinder, at the time the downward acceleration becomes equal to gravity in each cycle the velocity with which they are projected into the remaining bulk of the balls comprising the system can be calculated.

According to the kinetic theory of gases, the kinetic energy of any gas is directly proportional to its absolute temperature. Thus, if the layer of balls adjacent to the bottom of the cylinder can be considered to be in a gaseous state, at the instant after they have been thrown free their temperature should be proportional to the square of their velocity, v_0. Comparison of v_0 values with k_0 values in Table I shows a nonlinear relationship, where the rate constants rank in the same order as v_0. Moreover, when $v_0 = 0$, no effective agitation occurs, and segregation also does not occur. This was true for many agitation conditions studied where both frequency and amplitude exhibited nonzero values.

Figures 1 and 2 represent Arrhenius-type plots of specific rate constants for both segregation and mixing, derived from the over-all rate constants and the calculated equilibrium constants. Deviation of the points from the regression lines are within limits predicted from the 95% confidence limits of k_0.

It is interesting to note that the $^3/_{32}$–$^5/_{32}$ in. system exhibits a larger agitation coefficient of both segregation and mixing than that shown by the $^3/_{32}$–$^7/_{32}$ in. systems. This suggests that the energy of activation necessary for both processes in the former

system is greater. Beyond their theoretical implications, the plots are useful in the prediction of segregation under various agitation conditions. A cylinder, attached to the hopper of a tablet machine and filled with a test system such as those used in these studies, can be expected to reflect the probable effect of vibrations on tablet granulations within the hopper. It will not give an indication of segregation caused by granulation flow during its transfer from hopper to tablet die.

Figure 3 shows a semilog plot of the equilibrium constant as a function of reciprocal v_0^2 for these same systems of $^3/_{32}$–$^5/_{32}$ and $^3/_{32}$–$^7/_{32}$ in. steel balls. Values of the reported equilibrium constants were calculated from triplicate determinations of the equilibrium standard deviations and do not deviate significantly from the regression line. Again, the $^3/_{32}$–$^5/_{32}$ in. system shows a greater dependence on v_0.

Mixing Studies.—According to theory, one would expect the observed over-all rate constants of mixing to equal those of segregation in systems of the type studied here. However, when initially unmixed systems were agitated with the large balls on top, over-all rate constants of mixing were lower than those found for segregation under the same conditions of agitation. This may be explained by recognizing that initially only a fraction of the total volume of the system is available for mixing in previously unmixed systems, while the process of segregation can occur initially over the entire volume in previously mixed systems. The same equilibrium value is ultimately reached from both directions.

SUMMARY

Segregation and mixing processes observed in idealized systems of spherical particles subjected to sine wave motion show an analogy to molecular systems, and agitation of these systems appears analogous to the thermal motion of molecules. Segregation has been found to depend directly on the energy imparted to the balls by the shaker. Semilogarithmic plots of the specific rate constants for segregation and mixing *versus* reciprocal v_0^2 show linearity over a wide range of velocities. These curves allow the prediction of forward and reverse rate constants in systems of this type under various agitation conditions. They may be extended to other systems to allow evaluation of the effects of surface character, particle shape, and particulate elasticity on the agitation coefficient of segregation.

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