## Thermodynamics of Granular Systems

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•GRANULAR SYSTEMS are assemblies of a very large number of grains. Winterkorn (2) was the first to recognize and utilize the analogies of such systems with molecular systems. He initiated an entirely new line of research, which proved to be very fruit-ful. The analogies employed by him and others with the kinetic theory of molecular systems, exemplified in the treatment of granular systems as macromeritic liquids, are ultimately a part of statistical thermodynamics.

A special branch of statistical thermodynamics of granular systems can be developed rigorously on the basis of the following axioms:

- Axiom 1: A granular system consists of a finite, though very large, number of grains that are in contact with their neighbors. The individual grains possess distinct and permanent shapes.
- Axiom 2: At a state of equilibrium, the grains are in positions of rest, characterized by a certain degree of order.
- Axiom 3: Any movement is governed by the laws of mechanics.

From this system of axioms it is possible, in principle, to deduce all laws of a special statistical thermodynamics of granular systems, although this meets in part with very great formalistic difficulties. For this reason, this type of deduction has so far been successful only with respect to a few laws. This method, however, possesses a fundamental defect: the temperature of a granular system cannot be theoretically derived. This is perfectly obvious if one realizes that the concept of temperature is inherently alien to mechanics. The deductive process leads rather to a geometric analogue of the temperature of molecular systems. While this is useful in many respects, it cannot give a real account of the actual temperature of a granular system. For this reason, we shall forego in this paper further treatment of statistical thermodynamics, except for a few pertinent observations.

Inspired by the Winterkorn concept, we have opened up a new path in this paper: temperature and heat content are determined on the basis of the energy principle from properties of granular systems that can be measured macroscopically. For this purpose we had to derive and apply a "special classical thermodynamics of granular systems." Temperature and heat content are derived for definite work processes and general conclusions are drawn.

#### GRANULAR ASSEMBLIES AS THERMODYNAMIC SYSTEMS

If the volumes of the individual grains are small as compared with the total volume of the granular system, then the bulk behavior of the system will be that of a homogeneous medium. Such systems can be treated with the methods of classical thermodynamics.

#### Type of Thermodynamic System

Basic for the methodology developed is the definition of the volume of, or space occupied by, the granular assembly, which is then called a thermodynamic system. The system's boundaries are chosen in a manner as to render treatment of the phenomena that occur on them as simple as possible. The experiment illustrated in Figure 1 produces results that are pertinent to many problems; it will be utilized in the following

\*Paper translated by Hans F. Winterkorn.



Figure 1. Grain assembly as a thermodynamic system; mechanical equilibrium at the pressure piston.

investigations. We choose as system boundaries the interior surfaces of the container (dashed lines). The container walls and the pressure piston are the environment of this system. This environment can be considered as practically rigid, since any deformation suffered by it upon load application will be very small in comparison with the deformation of the system. The space within the system boundaries represents a quasihomogeneous closed thermodynamic system; it is considered as closed because during a process no material is allowed to pass across the system boundary.

# Condition of State of the Thermodynamic System

The state of equilibrium of a system can be expressed by a few parameters. In the simplest thermodynamic system, the ideal gas, the parameters of state are the volume, v, the internal pressure, p (which for static equilibrium of the system must be equal to the external pressure), and the temperature,

T. In accordance with experience, these parameters are mutually interdependent, which can be expressed by

$$f(\mathbf{v},\mathbf{p},\mathbf{T}) = \mathbf{0} \tag{1}$$

or explicitly

$$\mathbf{v} = \mathbf{f}(\mathbf{p}, \mathbf{T}) \tag{2}$$

Equation 1 or 2 is called the equation of state of this system. The simplest thermodynamic system possesses, therefore, two independent thermodynamic parameters; in Eq. 2, p and T were defined as independent, hence the third parameter, v, would have to be calculated in accordance with the equation.

An equation of state becomes more complicated as the particular thermodynamic system becomes more complicated. More complicated systems are non-ideal gases and, especially, condensed systems such as liquids and solids. In the general case of the latter, we have, instead of the volume, a strain tensor with six independent components and, instead of the uniform internal pressure, a stress tensor, also with six independent components. The rigorous treatment of such equations becomes very difficult and often even impossible.

Granular assemblies can also be considered as condensed systems. They are in a particular state of aggregation that shows partly "liquid" and partly "solid" characteristics. Representative of the liquid properties is the lack of a characteristic form or shape of the system. Maintenance of the external form under load application is possible only through the action of counter-forces. Solid properties derive from a capacity to maintain a characteristic internal order or packing. In the presence of external counter-forces, the volume of the granular systems is a function of the external loading.

The experimental arrangement shown in Figure 1 depicts an especially simple thermodynamic model of a granular system that takes into account the foregoing conditions of its particular state of aggregation. The volume of the system can be given absolutely in cubic centimeters or specifically in cubic centimeter per cubic centimeter of solids or in cubic centimeters per gram of solids. Preferred for many good reasons is the use of the specific volume, v, defined by

$$v = 1 + \epsilon (cm^3/cm^3)$$
(3)

wherein  $\epsilon$  = void ratio;  $\epsilon$  can be calculated from the vertical compressibility of the system. The mathematical treatment of the problem requires the use of differentials. Although the granular system does not possess a differential volume element, its formal introduction is justified by the previous assumption of quasi-homogeneity of the system. The differential of the specific volume d(1 +  $\epsilon$ ) is that of d $\epsilon$ ; therefore, the void ratio,  $\epsilon$ , is sufficient for the characterization of the specific volume of a granular system.

The internal stress condition of the system shown in Figure 1 can also be very simply expressed: all section stresses are proportional to the loading stress, p. The lateral stresses can be obtained by use of the coefficient of pressure at rest,  $\lambda_0$ , and so on. Therefore, the loading stress, p, is ultimately sufficient for the description of the stress state of the system.

As a final parameter of state, there remains the temperature, T; accordingly, we obtain the following as an equation of state for the system exemplified in Figure 1:

$$\epsilon = f(\mathbf{p}, \mathbf{T}) \tag{4}$$

#### The Thermodynamic Process

The equation of state (Eq. 4) characterizes a special state of equilibrium of the granular system. Changing one of the parameters disturbs the system and initiates movement; in other words, a thermodynamic process takes place. The parameters become variables, and the equation of state expresses a functional relationship that indicates direction and magnitude of change resulting from variation of the independent parameters.

If the variables are changed only to a very small extent, then the state of the granular system also deviates only to a very small extent from the equilibrium state; such processes are called quasi-static. They proceed so slowly that no mass forces become mobilized within the system. The entire course of such processes can be followed by means of thermodynamic methods. If, however, the process proceeds so fast that mass forces arise, then one deals with non-static changes of state. If, as is usually the case, a system is in a state of equilibrium before and after a non-static change of state, then the initial and final states are susceptible to thermodynamic



Figure 2. Experimentally determined compression function for a coarse sand.

treatment while the intermediate states are not. The main thermodynamic processes in granular systems that proceed as a result of externally applied forces are mixing, separation or segregation, densification (compression and expansion), shear, and consolidation. All these processes can be investigated with thermodynamic methods. This shall be done for the densification process.

### HEAT IN THE COMPRESSION PROCESS

A complete description of the process comprises two parts: first, a statement of the changes in the parameters brought about by the process, and second, a statement of the energy changes involved in the process.

# Experimental Determination of the Compression Function

The first part of the process description deals with obtaining the state



Figure 3. Logarithmic compression function for coarse sand data.

function. Equation 4 represents geometrically an area or surface in space. This makes its visual presentation quite difficult. Elimination of one of the three variables reduces the geometric presentation of the function to a curve in a plane, which can be easily visualized. Such elimination is achieved practically by keeping the parameter that is to be eliminated constant during the process. Then the relationship between the remaining variables is no longer influenced by the constant parameter.

For the quasi-static compression process, it can be assumed that the temperature, T, does not change during the process. This assumption will be justified later on. The state function for the compression process is then

which is also called the compression function. It is determined experimentally by determination of the volume changes resulting from changes in applied pressure. From these, the void ratios,  $\epsilon$ , are plotted against the pertinent pressures (Fig. 2). This method of determination is always possible, at least in principle.

 $\epsilon = f(p)$ 

#### Analytical Determination of the Compression Function

For many purposes, a closed mathematical form of the compression function is desirable. Since all densification processes proceed essentially in the same manner, one can use phenomenologic approaches for this purpose.

The Logarithmic Compression Function—A simple densification law can be derived from the logical assumption that the change in void ratio per change in compressive stress decreases with increasing compressive stress (at large compressive stresses the densification process is already far gone):

$$\frac{\mathrm{d}\epsilon}{\mathrm{d}p} = -\frac{\xi_1}{(\mathbf{P}_a^* + \mathbf{P})} \tag{6}$$

in which  $\xi_1$  and  $P_a^*$  are coefficients. This equation, which we owe to Terzaghi (1), represents the differential equation of the consolidation process. Integration gives

$$\epsilon = \epsilon_{a} - \xi_{1} \ln \frac{P_{a}^{*} + P}{P_{a}^{*}}$$
(7)

in which  $\epsilon$  = void ratio at static pressure p, and  $\epsilon_a$  = original void ratio. Figure 3 shows the logarithmic compression law for the test series shown in Figure 2. The shaded triangle helps to visualize the geometric significance of the compression law (Eq. 6) employed and of the coefficients  $\xi_1$  and  $P_a^*$ .



Figure 4. Densification function in semi-logarithmic presentation.

The coordinate system of Figure 4 has a linear ordinate and a logarithmic abscissa. The logarithmic function (Eq. 7) forms a straight line in this system. This method can be utilized for an approximate graphic determination of the function expressed by Eq. 7.

The Exponential Compression Function—Another densification law can be deduced from the fact that the void ratio decreases with increasing densification and tends to-ward a limiting value:

$$\frac{\mathrm{d}\epsilon}{\mathrm{d}p} = -\xi_2 \left(\epsilon - \epsilon_0\right) \tag{8}$$

VOIDS BATH

The integral of this equation is

COMPARISON OF

$$\xi = \xi_1 + 2 \xi_2 H$$

in which  $\epsilon_0$  is the minimum void ratio and  $\xi_2$  and a are coefficients. Equation 9 matches a function developed by Kezdi (3) in a different manner.

Figure 5 shows the exponential densification function for the test series shown in Figure 2. The shaded triangle allows easy visualization of the geometric meaning of the densification law employed (Eq. 8), and of the coefficients  $\xi_2$  and  $\epsilon_0$ . Figure 6 employs a coordinate system with logarithmic ordinate and linear abscissa. Accordingly, Eq. 9 is represented as a straight line.

	Static Consolidation Pressure, $p(\epsilon)$ , in $kp/cm^2$						
Vold Ratios From:	0	1	2	3	4	5	
Experiments	0.83	.0.73	0.70	0.67	0.64	0.63	
Logarithmic function $\epsilon = 0.83 - 0.166 \log \frac{p + 0.333}{0.333}$	0.83	0.73	0.69	0.66	0.64	0.63	
Exponential function $\epsilon = 0.62 + 0.21e^{-0.648p}$	0.83	0.73	0.68	0.65	0.64	0.63	

WENTAL AND MATHEMATICAL

TABLE 1

. (9)



Other Compression Laws—Equations 7 and 9 can be made to fit a series of test data by proper choice of the respective coefficients. According to the laws of algebra, such fitting is more successful the larger the number of coefficients, i.e., the higher the powers of the independent variables that can be taken into account. This can be done very simply by the use of binomial formulations, e.g.,

$$\frac{d\epsilon}{dp} = \frac{-\xi_1}{(P + Pa)^n} \text{ or}$$
$$\frac{d\epsilon}{dp} = -\xi_2(\epsilon - \epsilon_0)^n$$

The most general manner would be a polynomial expression such as

Figure 5. Exponential compression function for coarse sand data.

 $\frac{\mathrm{d}\epsilon}{\mathrm{d}p} = \frac{\xi_1}{(a+bp+cp^2+\ldots)}$ 

;

Integration of such expressions is somewhat more difficult and leads to a function whose structure may be quite complicated. The question arises whether or not it is worth-while to use such complicated expressions. Table 1 gives a comparison of void ratios determined by means of the simple compression functions (Eqs. 7 and 9) with those determined experimentally. The numerical values were determined either rigorously in accordance with statistical methods or approximately by the use of judiciously selected test data.

Table 1 shows good agreement of the analytical values with those obtained by experiment even though all calculations were based on a deliberately selected uneven test



Figure 6. Plot of the logarithm of  $(\epsilon - \epsilon_0)$  vs the pressure.

series. Consequently, at least for all practical purposes, there is no need for greater accuracy and refinement.

Fundamental Significance of the Exponential Compression Function—The Complete Compression of a Granular System—In accordance with Axioms 1 and 2, every assembly of grains possesses a particular densest state of packing which shall be designated as "zero state." This can be proved as follows: For spheres of the same size, irrespective of the actual diameter,  $\epsilon_0 \simeq 0.35$ . In the case of mixtures of spheres of two or more sizes,  $\epsilon_0$  is a function of the gradation or size distribution. Real grains also possess shapes that deviate from the spherical. This lends importance to their orientation in packing. As a matter of principle, though, every granular assembly possesses a minimum void ratio,  $\epsilon_0$ , that defines a state of highest order and densest packing in accordance with geometrical compatibility. The exponential compression function (Eq. 9) is in harmony with this concept and, therefore, is of fundamental significance. In contrast to this, the logarithmic compression function (Eq. 7) is only able to describe the consolidation behavior within the range of actual test data and does not permit of extrapolation.

Secondary Compression Effects—Often the actual behavior of granular systems does not agree completely with the ideal assumptions made in the preceding paragraph. The deviations are caused by subsequent secondary densification effects that are superimposed on the fundamental behavior described previously. The causes for this are mainly as follows:

1. Influences of orientation: The degree of orientation depends mainly on the densification method employed. Some methods favor orientation as, for example, vibratory densification; others, like impact methods, are antagonistic to orientation. If liquid phases are present in a granular system (e.g., water in soil or hot bitumen in asphaltic mixtures), even methods that are normally antagonistic to ordering bring about a high degree of orientation. The higher this degree, the greater is the density.

2. Influences of grain fragmentation: Contrary to Axiom 1, real grains possess a finite material strength. They can be fragmented if overstressed. Limited degrees of grain fragmentation may result in increased density of the system.

3. Flow phenomena: In the presence of liquid phases in the granular system, permanent flow deformation can be observed when certain methods are employed in the compression of the system.

Practical Determination of Zero State—Despite the secondary densification effects mentioned, it is always possible to recognize the fundamental behavior of granular systems from the results of practical densification methods. The commonly used methods result in a state of very dense packing with grain fragmentation normally held within very narrow limits. Only use of excessive densification efforts results in fundamentally different internal structures having no further thermodynamic relationships with the original systems. The flow phenomena previously mentioned only change the external form of the system. Therefore, they do not interfere with the possibility of estimating the zero state void ratio that is characteristic for the system. For practical purposes, one may choose as zero state that which results from sufficient densification by such common methods as vibration-to-volume constancy, Proctor densification, or Marshall test.

### Work of Compression of a Granular System

The first part of the treatment of the compression process terminates with the development of the compression function. The second and properly thermodynamic part is concerned with the energies involved. An important portion of these is the external work required for the compression. It can easily be seen that the concept of work as product of force times distance in the direction of the force used in classical stereomechanics is no longer sufficient in the case of densification, if one takes into account only the external conditions for arriving at the total work involved. Determinant is rather the work accepted by the system, which is governed by the internal state of the system. Employing the original definition of mechanical work, the work performed is 98

the product of the force acting at the system boundaries and the translation of the boundaries in the direction of the force. The differential of the work is then

$$dw = p \cdot F \cdot ds = p \cdot dv \tag{10}$$

where

 $p \cdot F =$ force at the system boundary (p =pressure, F =area);

ds = differential of the translation of the boundary; and

dv = differential of the translation volume.

If a boundary translation process moves the system from state 1 to state 2, then the total work is represented by the integral of Eq. 10:

$$w_{12} = \int_{1}^{2} p \cdot dv$$
 (11)

This integral can be solved if the function p = p(v) is known. This function is identical with the state function developed in the first part of the description of the densification process. For granular systems we have then, instead of Eq. 11,

 $w_{12} = \int_{1}^{2} p(\epsilon) d\epsilon$  (12)

Here  $w_{12}$  is the specific compression work for  $1 \text{ cm}^3$  of material and, using the factor  $1/\rho$  ( $\rho$  = density of material in g/cm<sup>3</sup>), for 1 g of solid material. The special position of the derived thermodynamic work concept—which must be considered as an expansion of the mechanic work concept—shall be illustrated by means of an extreme example: The system is represented by a rigid body on a rigid foundation that is impacted externally by a falling mass [weight G (kp), height of fall h (m)]. The kinetic energy at the moment of impact of the falling mass on the system boundary is derived most simply from its identity with the potential energy, i.e., the product of G × h (mkp). However, the work performed on the system equals zero since the system boundary does not move in a rigid system. If, however, one considers under the same external conditions a compressible system such as a granular assembly, then this will accept work in accordance with Eq. 12. Its amount is smaller than G × h. The integral of Eq. 12 can be interpreted geometrically. It is proportional to the area between the compression line and the  $\epsilon$ -axis in the case of horizontal strips. The graphic presentation of the compression line in a p/ $\epsilon$  diagram shall, therefore, be called the work diagram. Its area can be determined with a planimeter or by compass addition.

By the use of mathematical compression functions, we obtain closed expressions for the compression work that can be integrated. With Eq. 7, the ln function:

$$w_{12} = \xi_1 p_e - p_a^* (\epsilon_a - \epsilon_e) \operatorname{cmp/cm}^3$$
(13)

With Eq. 9, the e function:

11.

$$w_{12} = \frac{\epsilon_a - \epsilon_e}{\xi_2} \text{ cmp/cm}^3$$
 (14)

The coefficient  $\xi_1$  possesses the dimensions of a void ratio  $(\text{cm}^3/\text{cm}^3)$  while  $\xi_2$  has the dimensions of an inverse pressure  $(\text{cm}^2/\text{p})$ . Using pertinent numerical factors,  $w_{12}$  can be expressed in other units, e.g., mkp/dm<sup>3</sup>, mkp/kg, ft-lb/ft<sup>3</sup>. For the numerical example given earlier, we find, for a  $\rho$  value of 2.7 g/cm<sup>3</sup>, a  $w_{12}$  value of 1.09 mkp/kg from the ln function and 1.19 mkp/kg from the e function. The difference of 8.4 percent



Figure 7. Sign convention.

in the calculated work finds its explanation mainly in the complete coverage of the densification range down to the zero state by the e-line. The results are influenced only to a very small degree by the slightly different course of the two functions within the measuring range.

#### External Friction Work

The compression work as calculated in the previous section has one shortcoming. The calculated values contain not only the compression work proper, but also the work required to overcome the external friction, i.e., the friction between the system and its surroundings (wall friction). In actual cases, this external friction work cannot be separated from the total work. It is possible, however, to give estimates of plausible values. The ex-

ternal friction work arises from the tangential stresses at the system boundaries. According to Coulomb, these stresses are directly proportional to the radial stresses and hence to the pressures which effect the densification. The friction work is proportional to the densification work. In specimens that possess relatively small ratios of surface to volume, the external friction may account for as much as 20 percent of the total work; less favorable specimen forms can result in much larger proportions of the external friction work. Accordingly, the wall friction influence can be taken into account in a simple manner by multiplication of the total work with an appropriate coefficient. For the calculation of limiting values and ranges, the external friction work may be neglected in first approximation in the case of specimens possessing small surface/volume ratios.

#### Heat in the Compression Process

It may appear astounding that heat appears this late in a treatise on thermodynamics. As a matter of fact, the heat, q, is only a particular form of energy (which crosses the system boundary together with other forms). Hence, there is nothing special about it. Both heat and work are products of a process and not parameters of state.

Energy Balance for the Compression Process—In accordance with the energy principle, all energies involved in a process are conserved. In addition to the work, w, and heat, q, mentioned previously, there exists the internal energy, u, of the system. The latter depends only on the state of the system and is, therefore, a state parameter. Employing the sign convention shown in Figure 7, the energy principle yields the following equation for a thermodynamic process:

$$\Delta u = q - w$$

where

 $\Delta u = u_2 - u_1$  = change in internal energy, u, during a change in state from 1 to 2;

q = heat that crosses the system boundary during the process =  $q_{12}$ ;

w = work that crosses the system boundary during the process =  $w_{12}$ .

Equation 15 states that the difference between the energies gained and the energies lost remains in the system as an increase in internal energy.

At this point the following comments are indicated. All three energy forms—work, w, heat, q, and internal energy, u—must be inserted in Eq. 15 in the same units. In common use are mkp/kg, kcal/kg, mkp/dm<sup>3</sup>, kcal/dm<sup>3</sup>, and other units. Definite conversion factors exist between the various units, such as 1 kcal  $\approx$  427 mkp or 1 mkp  $\approx 2.34 \times 10^{-3}$  kcal.

(15)

Figure 7 shows the direction of the resultant energy fluxes during the densification

processes: mechanical work is performed on the system, heat is produced. The type of energy conversion process that takes place is analogous to that in a heat pump. The efficiency of the action mechanism in the granular system is reduced as a result of secondary effects. The expended work is not entirely changed into heat (passing through internal energy), but a definite portion of it may be used in grain comminution work.

The internal energy, u, is rigorously defined by Eq. 15 for the compression process of a granular system. This emphasizes the basic assumptions made, namely, that energy amounts deriving from motion (mass effects), gravity (due to the weight of the grains), and other energy forms must be negligibly small.

The heat, q, can be determined as follows:

$$q_{12} = m \cdot c (T_2 - T_1)$$
 (16)

in which

m = mass of the system;

- c = specific heat per unit mass; and
- $T_1, T_2$  = absolute temperatures of the system in degrees K;  $\Delta T$  (°K) is numerically equal to  $\Delta T$  (°C).

In accordance with Eq. 16,

$$q_{12} = c\Delta T \tag{17}$$

Knowledge of  $q_{12}$  and  $w_{12}$  permits calculation of  $\Delta u$ .

Limit Values of Temperature and Heat in the Compression Process-Maximum values for temperature change and heat production can be obtained from a type of limit calculation under the assumption that during the densification process no external friction work and no grain comminution work will be performed. The energy fluxes which obtain during the process can be divided into two components by means of a mental experiment and can be clearly presented with the aid of the following artifice. In the first part of the process, no heat is lost through the system surface. Therefore,  $q_{12} = 0$  and, according to Eq. 15, the energy balance is

$$\Delta u = -w_{12} \tag{18a}$$

The increase in internal energy,  $\Delta u$ , of the system shows itself in a measurable increase in temperature.

In a second part of the process, the heated system is cooled to environmental temperature, whereby an amount of heat energy,  $-q_{12}$  is transferred from the system to its environment. According to Eq. 15, this portion is

$$\Delta u = -q_{12} \tag{18b}$$

For the total process, the limiting value is then

$$q_{12} = +w_{12}$$
 (18c)

Consequently, using Eq. 17, we obtain (also as limiting value) for the temperature increase

$$\Delta t = \frac{+W_{12}}{c}$$

Employing the numerical data from the example previously mentioned (hard rock particles of c = 0.18 kcal/kg-deg, air of c = 0.25 kcal/kg-deg; and for the granular system, c = 0.2 kcal/kg-deg):

$$\Delta t = \frac{1.19 \text{mkp/kg}}{0.2 \text{ kcal/kg-deg}} = \frac{1.19 \times 2.34 \times 10^{-3} \text{kcal/kg}}{0.2 \text{ kcal/kg-deg}} = 1.39 \times 10^{-2} \text{ deg}$$

The signs with which the energies are listed in the equations must correspond with the convention shown in Figure 7. Other granular systems will give different values for the temperature increase resulting from the compression work. According to practical experience, the order of magnitude of such temperature increases is  $10^{-1} \text{ deg C}$  or K.

Significance of Temperature and Heat for the Compression Process—The numerical example in the previous section demonstrates the fundamental difficulty of taking into account the temperature and heat changes involved in processes that take place in granular systems. All thermal effects occurring are small and cannot be measured with common thermometric devices. It can be easily calculated that the small temperature changes cause only very small thermal expansion of the individual grains and of the entire granular systems. Likewise, the resulting thermal stresses in the grains are very small compared with the compression stresses and can, therefore, be neglected. The significance of this is that, for all practical purposes, one can assume isothermal changes (T = constant) in the development of equations of state for granular systems. Granular systems are poor heat conductors, although their thermal conductivity increases with increasing density. Thermal exchange with the environment takes place only slowly. The system, after experiencing temperature increase as treated in the previous section, returns to its original temperature, which is the same as that of its environment.

A practically quasi-static compression proceeds much faster than this temperature equalization. For this reason it is sufficiently accurate for many cases to assume adiabatic processes in the development of energy equations that serve practical purposes. Temperature and heat, which are of paramount importance in the thermodynamics of molecular systems, have little influence on such simple processes experienced by granular systems as mixing, segregation, compression, expansion, and shear.

<u>Geometric Analogue of the Temperature</u>—As was mentioned in the introduction, thermodynamic methods are preferentially applied to molecular systems. According to the kinetic theory, the internal energy of a molecular system is the sum of the energies of molecular motion (translation, rotation, vibration, etc.), the intensity of which is greater the higher the temperature. The vibratory movement of the molecules or particles around their positions of rest requires a certain free space; this results in lesser density with increasing energy content. There exists, therefore, an analogy between the temperature of a molecular system and the relative density of a granular assembly. The "zero state" of a granular system corresponds to the zero temperature of a molecular system. These relationships and their consequences are germane to the Winterkorn concept.

#### Some Practical Hints for Determination of Thermodynamic Parameters

The Internal Causes of Temperature Increase—The foregoing thermodynamic considerations are silent with regard to the causes—peculiar to the granular systems—of heat production during the densification process. Only the fact of temperature increase is recorded; nevertheless, this increase is obviously due to the internal friction of the granular system.

If one makes the simplifying assumption that the work of internal friction is performed uniformly during the compression process, then it is proportional to a coefficient of internal friction,  $\tan \overline{\phi}$ , and to the range of densification,  $h(\epsilon_a - \epsilon_0)$ . In the ideal case, this internal work is equal to the external work, and hence

$$\tan \overline{\varphi} = \frac{\xi_3 \times \text{area of the work diagram}}{(\epsilon_a - \epsilon_0)}$$
(19)

Equation 19 is of the type of the Winterkorn formula, although the individual factors do not have the same meaning;  $\tan \overline{\varphi}$  is not the same as the coefficient obtained in the



Figure 8. Dry density vs moisture content in Proctor compaction test.

shear test but instead is an average (calculated) friction coefficient that is characteristic for the compression process. It is, however, very probable that a functional relationship exists between these two coefficients of internal friction. The size of the area of the work diagram indicates the capacity of the granular system to change mechanical work into heat energy.

Determination of Work of Practical Compression Processes-Quantitative knowledge of the work involved in a compression process is of fundamental significance, not only for the determination of temperature and heat effects, but also as a measure of the economy of compression and densification processes. The term compression work,  $w_{12}$ , shall denote the specific (per unit of mass or of volume) work accepted by the system that brings about a permanent change of the granular system from state 1 ( $\epsilon_1$ ) to state 2 ( $\epsilon_2$ ). The corresponding work diagram comprises a compression and an expansion curve. In the following, we shall describe a procedure for the determination of the compression work, using as an example a granular system that is partially saturated with liquid. Such systems are of outstanding importance for the construction industry.

Thermodynamics of a Partially Saturated Granular System-Densification of a partially saturated system proceeds under squeezing of film liquid into available pore space. If the latter is large enough to accommodate the liquid phase, even at complete densification of the granular system, then no liquid will be squeezed out of the system during the compression process. We are then dealing with a closed thermodynamic system. Figure 8 shows the well-known relationships between Proctor densities and liquid contents. Plotting of the void ratios against the densification work (lower part of Fig. 8) produces monotonous curves that resemble the compression lines. Obviously, partially saturated systems show similar densification behavior as dry granular systems. They may be considered thermodynamically as quasi-homogeneous, and the equations that were derived for the dry systems may logically be applied to them. The void ratio of the dry or wet system, or the porosity, n, may serve as the volumetric parameter of state. (The densification range comprises only a certain portion of the porosity range.)

Note: Homogeneous domains in a system are called "phases" in thermodynamics. Partially saturated macromeritic systems behave in the compression process as "thermodynamically" single-phase systems. In contrast thereto are the phases as defined in molecular physics, which may be designated as "mechanical" or, better still, "physical" phases, with reference to their characterization as gaseous, liquid, or solid. In this usage (also employed by Terzaghi), the system described earlier would be composed of three phases (solid, liquid, and gas). In the field of macromeritics, systems composed of three phases may behave like solids and can be densified by pressure and impact; two-phase systems possess liquid characteristics and can be poured and pumped.





Internal Consolidation During the Compression Process—The consolidation mechanism of a saturated system is well known. A similar process also takes place in partially saturated systems since the flow of liquid into the free pore space requires time. Because no liquid leaves the system, this process can be designated as internal consolidation. An ideal quasi-static compression process must proceed extremely slowly and requires an infinite length of time to reach complete internal consolidation. If stepwise loading is employed, then the corresponding volume change should be read only after practical completion of the consolidation. Premature application of the next loading step leads to

smaller consolidation readings than are characteristic for equilibrium conditions: The curves for incomplete compression processes lie above those for equilibrium conditions. Figure 9 shows compression curves for a slow test (practically completely consolidated) and a fast test (incomplete consolidation). The work diagram shows that attainment of a certain state of densification,  $\epsilon_p$ , requires more work the faster the consolidation energy is supplied. For the determination of this work, a knowledge of the total stress condition is sufficient. Separation of the stresses into intergranular (effective) and pore water stresses is of no particular interest at this stage.

Simple Pressure Test as a Comparison Process—The densification under continuously or stepwise increased pressure-as in the test illustrated in Figure 1-lends itself especially well to simple analysis. In practice, however, densification is achieved almost exclusively by processes of repeated loadings. A loading cycle consists of loading resulting in compression of the system and unloading resulting in expansion. If this cycle is repeated many times, then the incremental consolidations become ever smaller. The system tends toward its ultimate state, i.e., the "zero" state. It should be emphasized here that, in actual repeated compression processes, secondary densification effects are superimposed on the primary reaction mechanism. This must be considered in the evaluation of the test data. Figure 10 shows a repeated and a single compression process. Both shall effect the same permanent densification,  $(\epsilon_a - \epsilon_o)$ . It can easily be seen that the densification work of the repeated processes is larger than that which corresponds to the area limited by the ultimate pressure, pw, since the individual work areas of the loading cycles are partially superimposed on each other. It is also obvious that this work is not as large as corresponds to the area of the single compression process. This is because the load removal in the cyclic process returns



Figure 10. Comparison of effectiveness of single and repeated compression.



Figure 11. Mechanism of densification by rolling.

the system into the range of high initial compression response. The work required for the simple compression test represents an upper limit for the work required for repeated cyclic load applications.

Practical Application of the Comparison Process-In accordance with the contents of the two preceding sections, the compression work, sufficiently accurate for practical calculations, can be obtained from the work diagram of a simple compression process proceeding at the same rate. For the calculation of the proper rate of piston movement in the press, some very simple assumptions have been found to be adequate. If we assume, e.g., that, in the case of a rubber-tired roller, the pressure increases continuously from initial to final contact (contact pressure) (see Fig. 11), then

$$v_{p} = \frac{h' \cdot v_{W}}{D}$$
(20)

Numerical example: for h' = 2mm,  $v_w = 9 \text{ km/h}$ , and D = 30 cm, we find,

$$v_p = \frac{0.2 \text{ cm} \times 150 \text{ m/min}}{30 \text{ cm}} = 1 \text{ m/min} = 1000 \text{ mm/min}$$

The comparison presupposes equal thickness of layer and test specimen. In the case of dynamic loadings, much higher action rates are found. These can be calculated from the characteristics of the vibration process, or they must be determined experimentally for impact densification. Dynamic analysis of gaseous systems shows that changes in state can be considered as quasi-static as long as the rate of progression of volume change is small compared with the velocity of sound. This is the reason why, in mechanical engineering, processes occurring in gaseous systems in motor cylinders can be treated as quasi-static up to piston velocities of 500 m/min. In the case of high-frequency vibrations, however, an increasing portion of the work is eaten up by the acceleration of component parts of the system.

Efficiency of Densification—A short reference to efficiency of densification appears to be indicated. The question may be asked why the ideal quasi-static compression process, with its comparatively low energy requirements, is not used in practice. The explanation resides in the limitations of thermodynamics as a scientific and technical tool: classical thermodynamics does not know time. (This is why an independent theory of reaction rates had to be developed.) Practical industrial processes must be completed within a certain limited time period. This leads to the concept of production efficiency as a quotient of work required to do a job and the time within which

Type of Compression Process	Compression Work (mkp/kg)	Time Required (min)	Efficiency (mkp/min-kg)
Ideal quasi-static	small	infinite	zero
Practically quasi-static (test press; road roller)	medium	medium	small to medium
Dynamic (impact, vibration)	large	small	medium to large

TABLE 2 PRODUCTION EFFICIENCY OF VARIOUS DENSIFICATION PROCESSES

it is done. Table 2 gives a qualitative listing of several processes with regard to their production efficiency.

Accordingly, it is possible to increase production efficiency by increasing the intensity of the compression process even though this also increases the total work required. This is the reason for the technical importance of practically quasi-static and dynamic compression processes. An example is the improvement of densification by roller through increase of the roller velocity. Despite decrease of the densification effect for a single roller pass, increase in number of roller passes per unit of time results in a greater densification effect for the same total time.

Additional Applications—It has been shown that, solely from the macroscopic behavior of dry or partially saturated granular systems, we could determine temperature changes and other thermal effects by the use of thermodynamic concepts. In the same manner, the specific enthalpy and entropy of a granular system can be determined. Basic for all such calculations is the exact determination of the work received by the system. It may be expected that further development of the theory of irreversible processes and its application to macromeritic systems will expand the practical usefulness of thermodynamics.

The compression of saturated granular systems involves the squeezing out of liquid; this normally takes place only with liquids of low viscosity such as water and hot or cutback bitumens. Thermodynamically, such systems must be considered as open since material flows across the system boundaries.

## DEPENDENCE OF THERMODYNAMIC PARAMETERS ON THE SYSTEM COMPONENTS

#### **Concept of Mixed-Phase Character**

In a previous section the concept of a thermodynamic phase was explained. The assumed quasi-homogeneity of the granular system does not give an insight into internal conditions. Such insight may be gained, however, if one employs the concept of a thermodynamic mixed system. A mixed phase is defined as a quasi-homogeneous phase composed of several constituent physical phases that can be individually recognized. A component is defined as a physical phase necessary for the construction of the quasihomogeneous system. For example, the components of a gas mixture are the several different types of molecules that compose the mixture.

## Granular Systems as Thermodynamic Mixed Phase Systems

Granular systems represent complicated configurations in space. Hence a wide variety of geometric characteristics may be considered as "components." In Table 3, components and resulting characteristics of granular systems are coordinated and arranged in accordance with two ordering or classification principles. The horizontal subdivision takes account of the fundamental character (geometric, mechanical, thermodynamic) of the granular system. The vertical subdivision takes into account the role played by characteristic attributes (material variables, granulometric variables, system variables). This type of tabulation has proved of considerable value in many investigations.

It is significant for the physical state of granular systems that the "material" variables (e.g., the mechanical properties of different minerals) exert only a secondary influence on the system properties, or that their contributions (as in the case of heat contents but not in thermal conduction) are simply additive (see also the numerical example following Eq. 18). This shows the special nature of granular or macromeritic systems; the fact that their system properties are largely independent of the "material" properties of their granular components has its logical analogue in the properties of chemical compounds compared with their atomic constituents.

Granulometric variables describe the corpuscular characteristics of the individual grains. Of these, a necessary number is selected as "components" which must be sufficient for the characterization of the mixed phase. It would seem logical to consider all grains of the same diameter and shape as one component. However, the great

variety of diameters and forms represented in a mixture would result in a very large number of components. A simple assortment of independent variables was obtained in a previous investigation by this author in the following manner:

1. Grain diameter (symbol k) as characteristic of the individual grain.

2. Type of gradation of a mixture (symbol q) = amount of particles possessing a certain diameter k, expressed as a proportion of a standard diameter (e.g.,  $k_{max}$ ). The components k and q are, therefore, independent of each other. The choice of q as an independent component is especially advantageous because it is often possible to express the gradation in a closed mathematical function. A well-known method of defining a continuous gradation is by the equation

$$y = \left(\frac{k}{k_{max}}\right)^{q}$$
(21)

in which  $k_{max}$  is the maximum particle size, y is the weight portion of all particles smaller than k, and q is an exponent that is usually smaller than  $\frac{1}{2}$ .

3. Grain form parameter (symbol  $f_i$ ). It can be demonstrated that there cannot exist a universal parameter that comprises all influences of the grain form on the resulting properties of the system. It is necessary, rather, to express with special parameters,  $f_i$ , the influence of specific forms on specific properties. The statistical laws governing distribution of forms or shapes within a granular mixture render it possible to employ parameters of very simple structure.

System variables describe the type of granular system. For simple processes, as for the compression process described earlier, the simple state parameters  $\epsilon$ , p, and T suffice for the description of the state of the system. Their places may be taken by others of the systems variables listed in Table 3 (derived state parameters). If one treats the granular system as a mixed system, then the equation of state must contain also the independent components:

$$f(\epsilon, p, T, k, q, f_i) = 0$$
 (22)

#### Corresponding States of Granular Systems

Equation 22 is quite complicated. Simple relationships between a parameter and a component are obtained through elimination of all the excess variables by keeping them constant. This happens if one treats the different systems always in corresponding states. The latter are defined by identical packing and orientation of the system components; therefore, only one parameter,  $M_i$ , is required for the description of a particular state of the system. Its dependence on the variable component  $K_k$  has the form

$$M_i = f(K_k)$$

(23)

It is obvious that zero states of granular systems are corresponding states. Correspondence between states exists when

 $\frac{1+\epsilon_0}{1+\epsilon_k} = \text{constant}$ (24)

where  $\epsilon_0$  = void ratio of the zero state and  $\epsilon_k$  = void ratio of the corresponding state. It follows from this that the so-called critical void ratio characterizes corresponding states. It should be pointed out here that, according to Eq. 24, corresponding states of liquid-containing granular systems must have the same degree of pore saturation.

## Zero Diagrams and Their Analytic Treatment

A zero diagram is the graphic expression of Eq. 23 applied to zero-state systems. There exist two different types of zero diagrams, each of which may be utilized in like

Type of System	<u>Geometric</u> : Variable (a) (a)	<u>Mechanics</u> : Variables (a) + (b) (b)	Thermodynamic: Variables (a) + (b) + (c) (c)	
	Material Densit	-		
Group I: Material- Variables		Material friction $\tan \varphi$ (1) Strength $\sigma_{c}$ (kp/cm <sup>2</sup> ) Elasticity E (kp/cm <sup>2</sup> )	Specific heat c (kcal/kg deg) Therm. exp. coeff. α (deg-¹) Ther. cond. coeff. λ in J/cm s deg	
<u>Group II:</u> Granulometric Variables				
, · ·	$\begin{array}{ccc} & \underline{Mass \ District}\\ Specific grain number: & Z_{S} (St)\\ Grain number \ distrib.: & \Delta Z_{S} = f(k)\\ \underline{Shape:} & function \ for \ O_{S}: & f_{O}\\ & Z_{S}: & f_{Z} \end{array}$	oution		
	Function for $\epsilon$ : f k: f <sub>k</sub>	Function for $\tau$ : $f_{\tau}$ $E_{v}$ : $f_{E}$	Function for $w_m$ : $f_m$ $w_k$ : $f_k$	
Group III:	Specific volume $v = 1 + \epsilon(1)$	Loading $p(t)$ in $kp/cm^2$ s	Temperature T (deg K)	
System Variables	Void ratio $\epsilon(1)$ Porosity n = $\epsilon/1 + \epsilon(1)$ Degree of density D = 1 - n(1)	(g/cm <sup>-</sup> ) Manner of loading t Deformations and constraints Experimental variables		
· ·	Relative packing D <sub>rfl</sub> = D/D <sub>O</sub> (1) Permeability k (cm <sup>2</sup> )	System strength $\tau$ in kp/cm <sup>2</sup> With the parameters: initial strength C(kp/cm <sup>2</sup> ) friction coeff. tan $\varphi$ (1) System elasticity E <sub>v</sub> (kp/cm <sup>2</sup> )	System properties Specific heat (kcal/kg deg) Thermal expansion (deg <sup>-1</sup> ) Thermal conduct. (J/cm s deg K) Specific intern. energy u (kcal/kg) Specific entropy s (kcal/kg) Specific enthalpy h (kcal/kg) Specific mix. work w <sub>m</sub> (mkp/kg) Specific comp. work w <sub>k</sub> (mkp/kg)	

ARRANGEMENT OF PARAMETERS THAT ARE OF GREATEST THERMODYNAMIC SIGNIFICANCE IN GRANULAR SYSTEMS





(b) M. b)

v(a)

M.(a)

Figure 12. Pure additivity of component properties.



Figure 13. Partial additivity of component properties.

manner to obtain valid relationships between characteristic  $M_i$  and component  $K_k$ . Zero diagrams exist only in a few simple forms; these are susceptible to mathematical analysis.

The first type of zero diagram is defined by Eq. 23 itself. The second type represents the influence of the component  ${\rm K}_k$  as a resultant of two "pure components" so that Eq. 23 becomes

$$M_i = f(M_i(a), M_i(b), y)$$
 (25)

in which

 $M_i(a)$  = characteristic of a granular system which comprises only the component (a),  $M_i(b)$  = characteristic of the "pure component" (b), and

y = general measure of the proportions of both pure components in the mixture.

Zero diagrams of the second type, corresponding with Eq. 25, show a very close relationship with the so-called phase diagrams employed in many areas of physics, such as the melting point diagrams in metallurgy and mineralogy, the boiling point diagrams, and others. Such diagrams shall be used for demonstrating the fundamental methodology of the analytic treatment of their course and information content.

<u>Rectilinear Course of a Zero Diagram</u>—If by experiment or by theory a rectilinear course of the zero diagram is found, this shows that the property  $M_i$  of the mixture is a purely additive function of the proportions of the components and the degree to which they possess the property of interest (Fig. 12):

$$M_{iv}(a + b) = y(a)M_i(a) + y(b)M_i(b)$$
 (26)

Regarding the proportions, we have

$$y(a) + y(b) = 1$$
 (27)

<u>Monotonous Rise of a Zero Diagram</u>—The course of the majority of zero diagrams is not rectilinear after Eq. 26, but curvilinear. In the case of a monotonous rise, we can define a partial additivity of the desired property in the following manner:

$$M_{iy}(a + b) = y(a)M_i^*(a) + y(b)M_i^*(b)$$
 (28)

where  $M_i^*(a)$ ,  $M_i^*(b)$  = partial properties.

For the determination of the unknown  $M_1^*(a)$  and  $M_1^*(b)$  of Eq. 28, we need a second independent equation, which can be obtained from a second experimentally determined point,  $(y + \Delta y)$ , taken in the vicinity of y:

$$M_{i}(y+\Delta y) (a + b) = [y(a) + \Delta y] M_{i}^{*}(a) + [y(b) - \Delta y] M_{i}^{*}(b)$$
(29)

Equations 28 and 29 yield then the desired partial values, e.g.,

$$M_{i}^{*}(a) = M_{iy}(a + b) + y(b) \frac{\Delta M_{iy}(a + b)}{\Delta y}$$
 (30)

whereby

$$\Delta M_{iv}(a+b) = M_{i}(v+\Delta v)(a+b) - M_{iv}(a+b)$$

Figure 13 shows that the partial additivity is restricted to the range  $y/y+\Delta y$  in which the curve can be replaced by its tangent or its secant. Other values of the particular partials hold outside of this range. Partial values are, therefore, typical thermodynamic parameters that correctly reproduce the properties of a system without necessarily reflecting an inherent reality. If the plots are only slightly curved over the entire range, then one can assume constancy of the partials in first approximation and hence, practically, pure additivity.

Extremal Course of a Zero Diagram—An extremal course of a particular physical parameter can almost always be explained by a counterplay of two oppositely acting causes. Often this can be expressed as a mathematical function. In the case of granular systems, the general situation is much simpler since extremal forms of zero diagrams always are found in similar types.

One can then establish a reference base and construct on it similar zero diagrams by addition of increments of component properties. The method is shown in Figure 14 for rectilinear zero diagrams. It can be used in a similar manner for curvilinear diagrams. We assume

$$M_i(a+b) = M_{il} + y(a)\Delta M_i(a) + y(b)\Delta M_i(b)$$
(31)

where  $M_{il}$  = reference base and  $\Delta M_i(a)$ ,  $\Delta M_i(b)$  = increments.

 $\Delta M_{i}(b)$   $M_{i}^{\dagger}$  Y(b)Y(b)

#### <u>Calculation of Resultant Properties of</u> Granular Systems

Explanation of the Method—The additivity laws derived above represent an armory that permits the execution of simple, thermodynamically justified calculations of a number of properties,  $M_i$ , of a granular system. If a property of interest can be related to a reference basis, then the law expressed by Eq. 31 is used most frequently. With the chosen assortment of independent components of a granular system, we obtain very generally

$$M_{i} = M_{il} + \Delta M_{i}(k) + \Delta M_{i}(q) + \Delta M_{i}(f_{i})$$
(32)

where

M<sub>il</sub> = amount of property of reference base,



 $\Delta M_i(k)$  = increment because of grain size k,

 $\Delta M_i(q)$  = increment because of type of gradation q, and

 $\Delta M_i(f_i)$  = increment because of grain shape.

The individual increments can themselves be additively structured.

<u>Numerical Example:</u> Porosity of a Granular System—In certain applications the porosity, n, is preferred over the void ratio. Both properties are functionally connected as follows:

$$n = \frac{\epsilon}{1+\epsilon} \quad ; \quad \epsilon = \frac{n}{1-n} \tag{33}$$

The relationship  $n = f(\epsilon)$  represents geometrically an equilateral hyperbola whose coordinates are rotated 45 degrees and whose origins are shifted a certain amount. However, within the range of practically observed porosities, i.e., 0.1 < n < 0.4, one may choose a linear relationship between the two properties; this is sufficiently accurate for macroscopic purposes. The relationships that have been found to hold for the void ratios can then be used, at least in first approximations, for the porosities, too. According to Eq. 32, we can then write

$$\mathbf{n} = \mathbf{n}_1 + \Delta \mathbf{n}(\mathbf{k}) + \Delta \mathbf{n}(\mathbf{q}) + \Delta \mathbf{n}(\mathbf{f}_1) \tag{34}$$

where  $n_1 = minimum$  porosity of reference system. One may choose n = 0.26, i.e., the minimum porosity of a system of spheres of equal size. The different increments are found by statistical or graphical evaluation of experimental data from well-planned investigations:

 $\Delta n(k)$  = increment because of grain size  $k_{max}$  of system

=+0.02 for 2 mm < k<sub>max</sub> < 5 mm

 $= \pm 0.00$  for 8 mm <  $k_{max} < 12.5$  mm

= -0.02 for 18 mm < k<sub>max</sub> < 25 mm

 $= -0.05 \text{ for } 35 \text{ mm} < k_{\text{max}} < 45 \text{ mm}$ 

 $\Delta n(q)$  = increment because of type of gradation for distribution law Eq. 21 = ±0.00 for single grain size mixtures q > 1

= -0.10 for open-graded mixtures 1 > q > 0.6

= -0.20 for dense mixtures 0.5 > q > 0.3

 $\Delta n(f_n)$  = increment because of grain shape

 $= \pm 0.00$  for spheres

= +0.10 for rounded grains (small surface/volume)

= +0.17 for broken grains (small surface/volume)

Intermediate values are obtained by linear extrapolation. Consider the following numerical example: A granular system, 0-12.5 mm, densely graded (q = 0.5), consists of 75 percent broken grains and 25 percent spherical grains. The porosity, n, is then:

 $n_{l} = 0.26$   $\Delta n(k) = -0.20$   $\Delta n(q) = -0.20$   $\Delta n(f_{n}) = 0.75 \times 0.17 = 0.13$   $0.25 \times 0.10 = 0.03$  0.16 = 0.16 0.22

The porosity of this system in the zero state is found to be 0.22 or 22 percent.

It should be noted here that the degree of accuracy of this type of calculation may not be sufficient for certain applications. In such cases one should check by experiment. However, this method of calculation reflects correctly the trend of influence of the various components as determined by thermodynamic laws and represents, therefore, an irreplaceable aid for the construction of granular systems. It can be expected that a higher degree of accuracy may be attained in the future in such calculations from statistical evaluation of more extensive experimental data and as a result of greater differentiation in the assignment of increments.

Calculations for Other Properties of Granular Systems-In like manner one can obtain additive equations for permeability, shear resistance (especially the shear parameter,  $\tan \varphi$ , modulus of deformation, E<sub>v</sub>, and others. In doing this, one has to keep in mind that void ratio and porosity are scalar properties, while the mechanical characteristics are vectors and functions of direction in space. The application of addition equations to vector properties, M<sub>i</sub>, requires more severe rules of elimination. Only such states of granular systems can now be called corresponding as are obtained with the same method of densification, since only thus can they be assumed to possess the same degree of orientation. Also, in the case of changes in state, the same experimental conditions and type of deformation must be used if the behavior and properties of systems are to be compared. Thus, there exist no generally valid additive equations for the shear parameter,  $\tan \varphi$ . Rather, there are special addition formulae for the different types of shear tests, i.e., for direct shear, triaxial shear, etc. It is obvious that similar relationships can be established for the parameters that are more properly considered as being of thermodynamic character. For the thermal parameter of heat content-which in Table 3 is listed as a material parameter-assumption of simple additivity is sufficient. It can be considered as a scalar property.

The parameters of internal energy, u, and entropy, s, as well as specific process parameters (specific mixing work,  $w_m$ , and specific compression work,  $w_k$ ) whose behavior is similar to that of state parameters, can be calculated from addition-type equations. The justification for such procedure in the case of specific process parameters derives from the system of axioms, which stipulates that the underlying processes are completely irreversible. Accordingly, only one reaction path is possible. The work required to overcome the influence of the true elasticity of the grains is so small that it can be neglected.

#### General Applications of the Mixed-Phase Character of Granular Systems

General Correspondence Principle for Mixed Systems—Formulation of a general correspondence principle is useful for many practical problems. This will be demonstrated on the example of the porosity, n, of a granular system. The principle holds,





Figure 15. Porosity as a function of particle shape (binary mixture).

however, very generally for the properties of any system. In Figure 15 are plotted the porosities, n, of mixtures of two types of grains (round and fragmented). Both possess the same grain diameter and an approximately similar shape factor. The pore space of a system consists of a network of channels and cavities. The sharper the edges of the grains, the larger will be the angle spaces formed on contact of neighboring grains and the larger the porosity This holds true for the of the total system. "pure component" in which grains of the same type are in contact. In a mixed system, however, grains of the same character are no longer in direct contact; rather, in accordance with the principle of uniform distribution (axiom 2), they are well distributed and surrounded by grains of different character. However, as can be easily visualized, the shape of the

fragmented grains exert an influence on the size of the angle spaces even in contact with grains of other shapes. Every individual grain, therefore, makes a characteristic contribution, depending on its shape, to the total porosity of the system.

This principle can be generalized as follows: Each independent component makes a characteristic contribution to the properties of a system in accordance with its proportion in the system. The mathematical form of this correspondence principle follows Eq. 32. The present derivation, however, shows the internal relationship that, even in the case of complete separation of particles of the same kind in a mixture, their characteristic influence is maintained. Under these conditions, one cannot help being reminded of Dalton's law, which says: Each gas in a mixture of several gases behaves in a manner as if it were alone in the space of the container.

Experimental Determination of Phase Diagrams in Physics—It has already been pointed out that many phase diagrams of physics are in close agreement with zero diagrams of granular systems. The thermodynamic systems whose behavior finds expression in the phase diagrams consist of a network of ions, atoms, or molecules. It can be demonstrated that the corpuscular, rather than the "chemical," character of their elementary components determines the macroscopic behavior of such systems. One can prove a relationship between the ionic size of an element and its position in the periodic system.

The thermodynamic systems whose behavior finds expression in the zero diagrams consist of a network of grains of many different sizes and forms. Experiments on, and analysis of, granular systems disclose the conditions and reasons responsible for the various forms of zero diagrams: monotonous rise is always found in cases of good agreement in size and shape of two mixing partners. In such cases, an individual grain of one mix partner can be substituted for one of the other components without resulting change in the lattice structure. Extremal forms of zero diagrams result from great differences in shape and form of the grains of the two mix components. Substitution of a grain from one component by one from the other results in far-reaching disturbance of the lattice structure (axiom 1). Granular systems represent a singular experimental means for demonstration of analogous phenomena that occur in molecular systems.

### SUMMARY AND OUTLOOK

This treatise deals with some special and some general aspects of thermodynamics. Among the special topics are the clarification of the influence of temperature and heat in work processes on granular systems. Work processes are defined as those in which the granular system receives work, as in mixing, segregation, compression, expansion, and shear. In order to determine the amount of heat produced, it is necessary to have a valid theoretical concept supported by experimental data of the macroscopic properties of granular systems and especially of the work,  $w_{12}$ , involved in the compression process. For this purpose, a method was proposed in which a simple compression test was used as comparison process. It was shown that the influence of temperature and heat in such work processes is comparatively small, and that the temperature changes are also very small.

We designate as heat processes those in which heat is adduced to the granular system, as in heating and cooling. This group of processes was not considered in the present treatise. It is obvious that, because of the large temperature differences normally employed in industrial processes of this type, the influence of heat and temperature is very significant.

Beyond the scope of these special "heat" aspects, insights of greater generality were obtained and formulated. These are of great importance for the understanding and further investigation of granular systems:

1. Granular systems can be considered as thermodynamic systems. This immediately yields more trenchant or new definitions of known phenomena. Examples of this are the system of axioms, the state of complete compression of a granular system, secondary densification effects, criterion for corresponding states, and internal consolidation. 2. The methodology that has been developed permits use of simple analytical functions for the expression of a large number of relationships existing between macroscopic parameters. Examples are the compression function, compression work, application of an analogue process, and laws of additivity. The only assumptions needed are that the chosen analytical functions yield a correct reproduction of the macroscopic behavior of the granular system. For many problems, thermodynamic methodology furnishes especially elegant solutions.

3. In accordance with classical methodology, thermodynamic parameters may be determined in two fundamentally different manners: First, they may be calculated from direct macroscopic measurements as discussed in the preceding paragraph; second, they can be calculated or estimated from the composition of the system by utilizing the concept of mixed-phase character. An example is the determination of the porosity. Hints were given for the determination of other mechanical and thermodynamic parameters. The concept of mixed-phase character permits a deep insight into the internal structure of a system; this can be expressed in a general principle of corresponding states.

4. The limitations of classical thermodynamic methodology have been pointed out. This methodology loses its power whenever the factor of time governs the physical phenomenon. Examples are production efficiency of compression processes and the time-dependence of internal consolidation. It is quite possible that the existing boundaries may be pushed back by the use of special methodologies such as the theory of irreversible processes (or by the generalized activation theory).

There can be no justifiable doubt that classical thermodynamics will become an important instrument for the treatment of problems concerned with the behavior of granular systems, since the results are of immediate practical applicability. All problems in which energy is involved, in the form of work or heat, can be treated accurately and in an interesting manner.

The theory of granular systems is made complete by the introduction of thermodynamic concepts. The structure of this theory is reflected in the arrangement of Table 3. It comprises physical disciplines of widely differing character. The geometry of granular systems (also doubling as a physical discipline) was already in the center of interest during the past century. The mechanics of granular systems was introduced by Terzaghi in 1925 (1). This resulted in a tremendously fertile expansion of the theory. Finally, we owe to Winterkorn (2) the introduction of thermodynamic methodology, whose development is proceeding very rapidly at the present time. This may be considered as the completion and crowning of the theory of granular systems.

#### REFERENCES

- 1. Terzaghi, Karl von. Erdbaumechanik auf bodenphysikalischer Grundlage. Leipzig and Wien, 1925.
- Winterkorn, Hans F. Macromeritic Liquids. Spec. Tech. Publ. No. 156, p. 77-89, 1953.
- Kezdi, Arpad. Grundlagen einer allgemeinen Bodenphysik. VDI Zeitschrift, Vol. 108, No. 5, p. 161, Feb. 1966.
- 4. Becker, R. Theorie der Wärme, Berlin, 1964.
- 5. Holl, Alfred. Das Kornhaufwerk, in Strassenbautechn., 1967.