

This solution was obtained by Lee and others (8) and is given as follows:

$$\left[ \frac{\partial(p/p_s)}{\partial x} \right]_{x=X, \theta=\theta} = 1 - 2e^{-\pi^2 \tau} \quad (5)$$

$$\left[ \frac{\partial(p/p_s)}{\partial x} \right]_{x=X, \theta=\infty} = 1 - 2e^{-\pi^2 \tau} + 2e^{-4\pi^2 \tau} - 2e^{-9\pi^2 \tau} + 2e^{-16\pi^2 \tau} - 2e^{-25\pi^2 \tau}$$

The conclusions are shown in Figure 3. When air is introduced, the saturated state should be reached in a shorter time. To eliminate errors in vaporization of diffusing material during weighing and during saturation in the apparatus before the experiment is started, the following procedure was used.

Benzene or water was weighed after air had been introduced for 30 to 40 min. and again after 5 or 6 hr. The rate of diffusion was determined from the weight at the shorter period minus the weight at the longer period.

#### EXPERIMENTAL RESULTS

Diffusion takes place through the air, screen, packed bed, and turbulent air layer (Figure 4). If one calls the effective diffusivities of these layers  $D_f$ ,  $D_s$ ,  $D_e$ , and  $D_t$ , and the partial pressure of the air above the liquid in the container and at the top of the packed bed  $P_{a0}$  and  $P_{a1}$ , the following equation is derived:

$$N = \frac{\pi}{RT} \ln \frac{P_{a1}}{P_{a0}} \left/ \left[ \frac{\Delta X_a}{D_f} + \frac{\Delta X_s}{D_s} + \frac{\Delta X_e}{D_e} + \frac{\Delta X_t}{D_t} \right] \right. \quad (6)$$

With the total length  $\Delta X_{ap}$  and apparent diffusivity  $D_{ap}$  based on partial pressures  $P_{a0}$  and  $P_{a1}$  considered,

$$N = \frac{D_{ap}\pi}{RT \Delta X_{ap}} \ln \frac{P_{a1}}{P_{a0}} \quad (7)$$

From Equation (6) and (7)

$$\Delta X_{ap}/D_{ap} = \Delta X_a/D_f + \Delta X_s/D_s + \Delta X_e/D_e + \Delta X_t/D_t \quad (8)$$

$$1/D_{ap} = [\Delta X_a/D_f + \Delta X_s/D_s + \Delta X_t/D_t - (\Delta X_a + \Delta X_s + \Delta X_e)/D_e] 1/\Delta X_{ap} + 1/D_e \quad (9)$$

$D_{ap}$  was obtained experimentally. Since the depth of bed was changed and other conditions were kept constant,  $1/D_e$  was obtained at  $\Delta X_{ap}$  equals 0 in the plot of  $1/D_{ap}$  and  $1/\Delta X_{ap}$ .

Liquid-level change during experimentation was so small that the effect was neglected. The same fractional void was maintained throughout the experiments.

No effect due to the shape of packing materials was found. Crushed calcite and sand were previously screened into three groups: 6 to 8, 8 to 10, and 10 to 14 mesh.

Figures 5, 6, and 7 give the results.

#### EXPERIMENTS ON ELECTRIC CONDUCTIVITY

In the study of thermal diffusion the temperature gradient can be estimated from the electric-voltage gradient. It was assumed that diffusion through packing materials was similar to the case of electric conduction. Thus effective diffusivity obtained in this experiment was compared with electric conductivity, a bridge being employed to determine electric resistance. Electric conductivity of the solution in the packing material voids was determined. When shot lead was used as a packing material, electric resistance was so small that it could not be measured. No effect due to height was found. (See Figure 8.) The concentration of this solution was so high that surface electric conductivity on  $\zeta$  potential was neglected.

#### EXPERIMENTAL RESULTS

Wyllie studied the relationship between voids and electric conductivity in the packing bed, for example glass beads, sand (16) and ion exchange resin (11).

Electricity was conducted three ways: from packing material to solution, through packing material, and through solution. In the case of a nonconductor, the fractional area of fluid  $c$  equals the ratio of specific electric conductivity of the packed bed to that of the fluid itself; that is,  $k_e/k_f$ . The relationship between  $k_e/k_f$  and fractional void  $\epsilon$  is shown in Figure 10. Wyllie (16) mentioned that the following equations can be used: Archie's equation (1)

$$F = \epsilon^{-1.3} \quad (10)$$

Slawinski's equation (13)

$$F = (1.3219 - 0.3219\epsilon)^{2/\epsilon} \quad (11)$$

where  $F$  equals  $1/c$ . When the fractional void is small, Equation (10) can be applied, and when it is large, Equation (11) can be used. From Equations (10) and (11)

$$c = \epsilon^{1.3} \quad (12)$$

$$c = \epsilon/(1.3219 - 0.3219\epsilon)^2 \quad (13)$$

Equations (12) and (13) are shown in Figure 10.

In the case of diffusion  $c$  is considered to equal the ratio of effective diffusivity  $D_e$  to diffusivity  $D_f$  without packing. The ratio  $D_e/D_f$  vs. fractional void  $\epsilon$  is shown in Figure 11, in which data obtained by Piret and others (9) are also plotted. These experimental results show that the relationship between effective diffusivity and the fractional void in the packed bed will coincide with that of electric conductivity and fractional voids.

## COMMUNICATIONS TO THE EDITOR

### Physical Interpretation of the Relaxation Method in Heat Conduction

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The use of the relaxation method for numerical solutions of engineering problems was pioneered by Southwell (1). It was introduced to the field of steady state heat conduction by Emmons (2)

and further developed by Dusenberre (3). (See also references 4 to 7.) The essential requirement that the relaxation procedure must converge to give an exact solution of the difference equations was

demonstrated by Southwell (1) and more rigorously by Temple (10), both using the terminology of elastic-stress problems.

When the convergence proof is stated in thermal terms, it becomes apparent that this method is related to Prigogine's theorem on the minimum production of entropy (8). The one-dimensional problem of a slab with constant surface temperatures, which is divided into  $N$  layers for computational purposes, will be considered. For this system the theorem reduces to the assertion that for fixed values of temperatures  $t_0$  and  $t_N$  all other

$t_i$  assume such values as to minimize the production of entropy in the system.

The rate of entropy production per unit volume is  $-(q''/T^2) \text{ grad } T$  (8), where  $q''$  is the heat flux and  $T$  the absolute temperature. Hence one may approximate  $\Phi$ , the entropy production per unit area, by

$$\Phi = - \sum_{i=1}^N \frac{q_{i-1,i}''}{T_i^2} \left( \frac{T_i - T_{i-1}}{\Delta x} \right) \Delta x \quad (1)$$

$$= \frac{k}{\Delta x} \sum_{i=1}^N \left( \frac{t_i - t_{i-1}}{T_i} \right)^2$$

where  $k$  is the thermal conductivity,  $\Delta x$  the thickness of each layer, and  $t$  the temperature in degrees centigrade or Fahrenheit. Assuming that  $|t_N - t_0| \ll T_0$ , one may write

$$\Phi \equiv \frac{(\Delta x) T^2 \phi}{k} \cong \sum_{i=1}^N (t_i - t_{i-1})^2 \quad (2)$$

The problem now reduces to minimizing  $\Phi$ .

If one differentiates with respect to  $t_i$  and chooses a new value  $t_i^*$  to minimize  $\Phi$  with respect to this variable, one finds

$$t_i^* = \frac{t_{i+1} + t_{i-1}}{2} \quad (3)$$

Corresponding to  $t_i^*$  is a new  $\Phi^*$  such that [with the help of Equation (3)]

$$\Phi - \Phi^* = (t_{i+1} - t_j)^2$$

$$+ (t_i - t_{i-1})^2 - (t_{i+1} - t_i^*)^2$$

$$- (t_i^* - t_{i-1})^2$$

$$= -2(t_i - t_i^*)$$

$$\cdot [t_{i+1} + t_{i-1} - (t_i + t_i^*)]$$

$$= (-2t_i + t_{i+1} + t_{i-1})$$

$$\cdot \left( \frac{t_{i+1} + t_{i-1}}{2} - t_i \right)$$

$$\therefore \Phi^* - \Phi = -\frac{r_i^2}{2} \quad (4)$$

where

$$r_i \equiv t_{i+1} + t_{i-1} - 2t_i \quad (5)$$

To minimize  $\Phi$  one may now choose the point with the greatest  $r_i$  (or one of such points if the  $r_i$ 's are equal for several  $j$ ) and apply Equation (3); new  $r_i$ 's may then be computed and the process repeated. One now notes that the  $r_i$ 's are identical with the residuals in the relaxation method and that this procedure is identical with the basic one-dimensional relaxation procedure.

To show that this process converges to the desired solution one first notes that  $\Phi$ , as defined by Equation (2), is positive definite and hence has a lower bound of zero. Furthermore Equation (4) shows that  $\Phi$  must decrease in each step of the process. It follows that  $\Phi$  must approach a unique limit  $\Phi_{min}$ . Hence for any prescribed  $\epsilon^2/2$ ,  $\epsilon > 0$  there must be a stage in the relaxation process after which  $\Phi - \Phi^* < \epsilon^2/2$ . It follows from Equation (4) that  $|r_i| < \epsilon$ , which completes the convergence proof. The analysis is

readily extended to two or three dimensions.

When the temperature difference is not small compared with the absolute temperature, the interpretation is somewhat more complicated, although the steady state solution is still a state of minimum entropy production. In any case the relaxation procedure may also be considered as a minimization of the thermal dissipation function defined by Biot (9).

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## Heat Transfer

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The comments of Leva and Wen\* concerning the exclusion of the data of Van Heerden, et al., in working up the external surface correlation are appreciated. However, we wish to make the following comments.

While these data were not treated because of a lack of bed density (or

fraction solids) values, we were of course aware that methods were available for estimating these quantities and that these methods need to be used for applying the correlation. However it was not felt that the large amount of time required for estimating bed voidages for the many Van Heerden runs could be justified, at the expense of working on the other data used, because of the limited usefulness of the Van Heerden data. While it is true

that they represent a careful study of many variables and cover a wide range, all the work was done at a single and very low value (1.18) of  $L_H/D_T$ . Since the later studies of Van Heerden (cited in our paper) appear to show a strong and complex  $L_H$  effect in the region of low  $L_H/D_T$ , it was felt that conclusions resulting from the use of these data would be less profitable than those resulting from the study of data at higher  $L_H/D_T$

\*A.I.Ch.E. Journal, **5**, No. 1, 7M (1959).