Diffusion and Solution of Gases in Thermally Softened or Molten Polymers:

Part I. Development of Technique and Determination of Data

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A technique has been developed that determines simultaneously solubilities and diffusivities of gases in molten or thermally softened polymers. Henry's law was found to hold up to 20 atm. In addition it was found that pressure had no appreciable effect on diffusion coefficients up to 20 atm. Solubilities and diffusivities were determined for systems involving nitrogen, helium, carbon dioxide, and argon in polyethylene, polyisobutylene, and polypropylene. In addition, solubilities were also determined for the preceding gases in polystyrene and polymethylmethacrylate. Other data were also obtained for neon, krypton, and monochlorodiflouromethane in various polymers.

Solubility and diffusivity data for gases in softened or molten polymers are of considerable importance to the chemical engineer. Such data are of particular interest in polymer finishing processes, where the molten polymer is blanketed with inert gas; in certain specialized operations such as foam extrusion and fluidized-bed coating; and finally in the production of condensation polymers, where the small molecule split out in the condensation reaction must be continuously removed from the polymer melt in order to achieve a high degree of polymerization.

The only studies found in the literature that considered solubilities and diffusivities of gas in softened or molten polymers were those of Lundberg, Wilk, and Huyett (*1* to *3*) and Newitt and Weale (*4*). The former investigators considered the systems nitrogen-polyethylene, methane-polyethylene, and methane-polystyrene. Their polymer samples were constrained in a sintered steel cylinder placed within a pressure vessel. The principal deficiency in their work was that they assumed their data to hold for the average of their initial and final pressures even though pressure ranges were sizable.

Newitt and Weale (*4*) studied the solution and diffusion of hydrogen, nitrogen, carbon dioxide, and ethylene in polystyrene. These workers used sorption experiments and diffusivity measurements by movement of a color boundary to determine their data. A defect in their procedure was their failure to preheat the gases used in the experimental work.

The present work was undertaken to determine simultaneously solubility and diffusivity data for a number of gas-polymer systems.

The apparatus (Figure 1) used permitted the simultaneous determination of solubility and diffusion coefficient in a single sorption experiment. In principle, the equipment and procedure were similar to those of Lundberg, Wilk, and Huyett and of Newitt and Weale.

The diffusion cells (Figure 2) were constructed from 2½-in. cold-rolled bar stock. The premolded polymer samples were contained in a cylindrical 1 in. by 1 in. diffusion cell cavity so that diffusion of gas occurred downward through the surface of the sample. The solid samples were generally about ¾ in. in height and slightly less than 1 in. in diameter.

The diffusion cells were heated in a fluidized bed which was both fluidized and heated by hot air from an electrical heater. The temperature of the diffusion cells was controlled by a temperature regulator on the air heater. Bed temperature was controlled to within ± 1°F.

The diffusion cell pressures were measured with test gauges of the Bourdon tube type. The pressure gauges were located outside of the fluidized bed and were maintained at a temperature of about 40°C.

The diffusion cells and pressure gauges were connected with 10-ft. lengths of ⅛-in. copper tubing, which was coiled and located inside the fluidized bed to permit fast preheating of the gas from the temperature of the pressure gauge to the temperature of the diffusion cell.

The diffusion cells were sealed with lead gaskets of 0.105-in. thickness and then leak tested by connecting the cells to 200 lb./sq. in. nitrogen pressure and then by immersing them in water. Absence of bubbles and maintenance of gauge pressure were taken to indicate that no leaks were present. The remainder of the system was tested by capping the lead-in lines and then using gauge pressure and soap bubbles for leak indication. One final check also remained. If test pressure continued to drop at the end of the usual time required for saturation, it was assumed that a leak existed.

Two tests were then performed simultaneously, with two different gas-polymer systems used if desired.

The overall procedure first involved saturating the molten or softened polymer with the gas at a pressure of 2 atm. or less. After the polymer was saturated at this low pressure, the pressure of the gas in contact with the polymer was suddenly raised by opening a valve between the diffusion cell and the pressure gauge. The gas pressure in the Bourdon tube of the gauge had previously been raised so as to give the desired initial pressure for the diffusion test. After initial contact of the sample and the high-pressure gas, the system pressure, barometric pressure, diffusion cell temperature, and Bourdon gauge temperature were first recorded at sixteen times between 100 and 35,000 sec. and then at longer intervals until the pressure had stopped falling and it was evident that only negligible diffusion was taking place.

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After the polymer was saturated at a given gas pressure, the valve between the diffusion cell and the pressure gauge was closed, and the gas pressure in the Bourdon tube was again raised. The valve was then reopened and the polymer saturated again at a higher pressure, with pressure being recorded as a function of time as in the previous phase. This same procedure was followed for as many additional higher pressures as desired. A more detailed description of apparatus and procedures is given elsewhere (*5*).

Polymer samples were weighed before and after each test on an analytical balance. Viscosity-average molecular weights were also determined before and after the test. Details of these determinations are given elsewhere (*5*). No change in weight or in viscosity-average molecular weight was taken as evidence that there was no appreciable polymer degradation during the exposure of the polymer to high temperature.

Typical experimental data for the system argon-polyethylene are shown in Figure 3. Additional points not shown in these figures were taken for times ranging up to 100,000 sec. From such data it was possible to compute both values of solubility and diffusivity.

The former quantity was calculated from the initial and final pressure values, temperature, system volume, and sample weight. A plot of solubility vs. pressure for typical gas-polymer systems at constant temperatures is given in Figure 4. As can be seen the data indicate that Henry's law behavior is followed over the pressure range studied. Henry's law constants for the systems studied are listed in Table 1. These data were calculated from experimental solubilities that were determined from 7 to 20 atm. pressure. Precision of the solubility data was generally better than 8%.

The Henry's law constant value for the system nitrogen-polyethylene determined in the present work compared favorably with that reported by Lundberg and co-workers (0.111 vs. 0.103 cc. [(STP)/(g.)(atm.)]. In addition the Henry's law constants of the present work were of the same order of magnitude as Henry's law constants reported by Astarita (*6*) for solution of gases into polymer solutions. Some disagreement, however, was found between the present work and that of Newitt and Weale. Specifically, Henry's law constant values for the systems nitrogen-polystyrene and carbon dioxide-polystyrene were found to be 0.049 and 0.220 cc. [(STP)/(g.)(atm.)] as compared with Newitt and Weale's values of 0.0275 and 0.0608 cc. [(STP)/(g.)(atm.)]. The discrepancy is believed to be due to the failure of Newitt and Weale to preheat their gas properly.

Pressure-time curves as in Figure 3 were used to compute diffusivities. For diffusion in a cylindrical system such as that used in the present work Fick's second law

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} \tag{1}$$

will hold, provided that diffusion occurs only in the axial

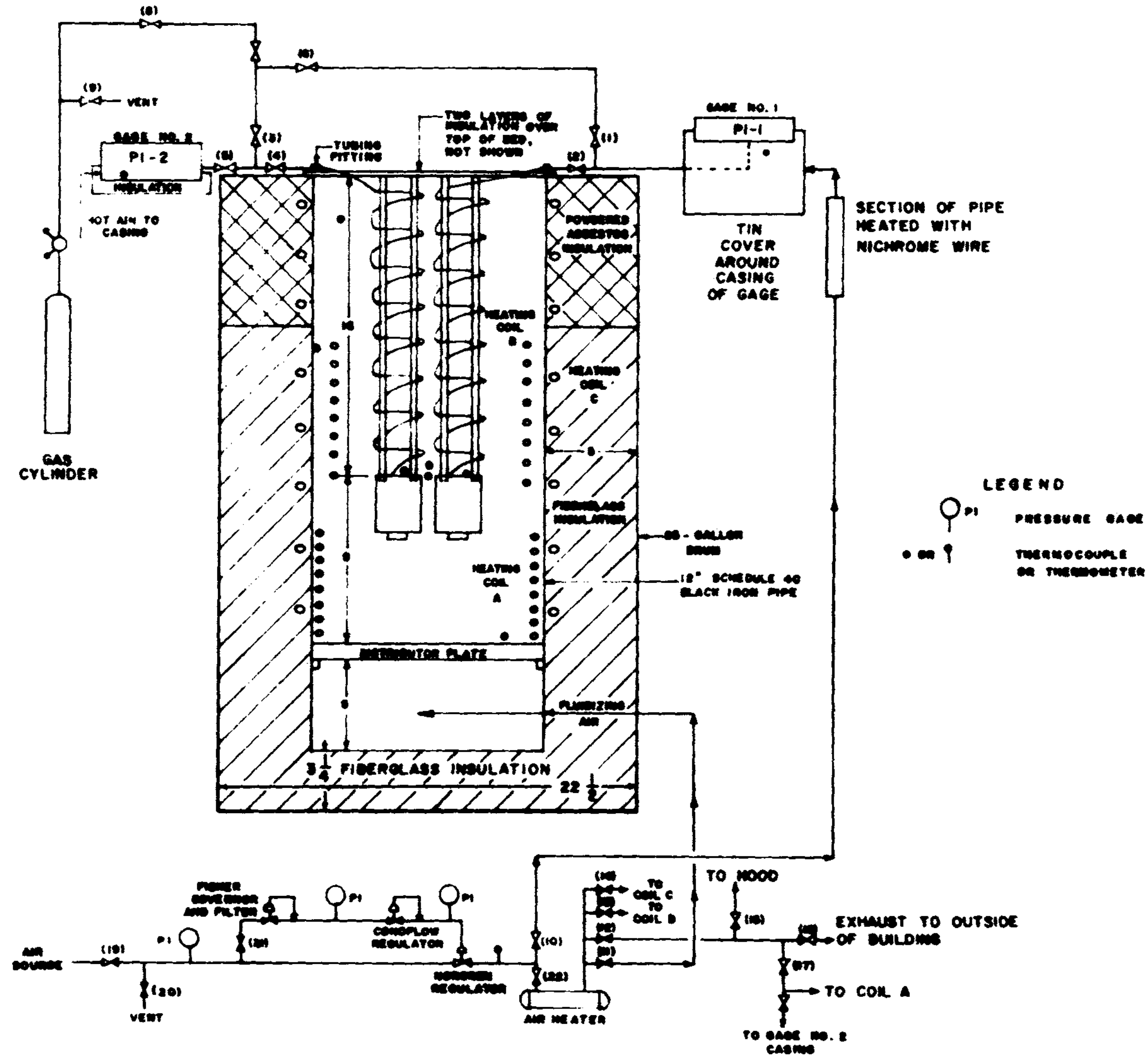

Fig. 1. Overall schematic of apparatus.

direction, that there are no radial and angular concentration gradients, and that the diffusion coefficient is isotropic and independent of concentration.

For softened amorphous polymer or a molten crystalline polymer there should be no preferred molecular orientations and a completely amorphous nature. This should make the assumption of an isotropic diffusion coefficient valid.

Absence of appreciable wall effects, temperature gradients, and convection of gas in the polymer sample validate the assumption of only axial diffusion.

Finally, the low gas concentrations in the polymer assure the independence of diffusion coefficient with concentration.

Crank (7) and Jost (8) have solved Equation (1) for the following boundary conditions:

1. $C = C_o$ for $0 < z < L$ at $t < 0$

(C_o is, in the present work, the gas dissolved in the polymer at saturation in the previous experiment. The elimination of a concentration profile was assured by allowing the gas to remain in contact with the polymer 12 to 14 hr. past the time when gas pressure stopped falling.)

2. $$D \frac{\partial C}{\partial z} = 0 \text{ at } z = 0;\ t \geqq 0$$

(In the experimental system this states that no gas diffuses across the bottom boundary of the polymer.)

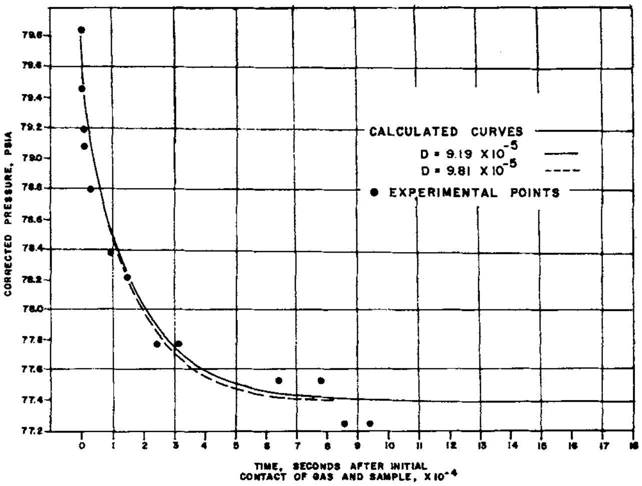

Fig. 3. Pressure vs. time for argon-polyethylene system at 77.2 lb./sq.in.abs. initial pressure and 368°F.

3. $C = C^*$ at $z = L$; $t \geqq 0$

(This states that the concentration at the gas-polymer interface is a constant. This is not exactly correct in the present work, since gas pressure was varied. The assumption that this value is constant, however, greatly simplified

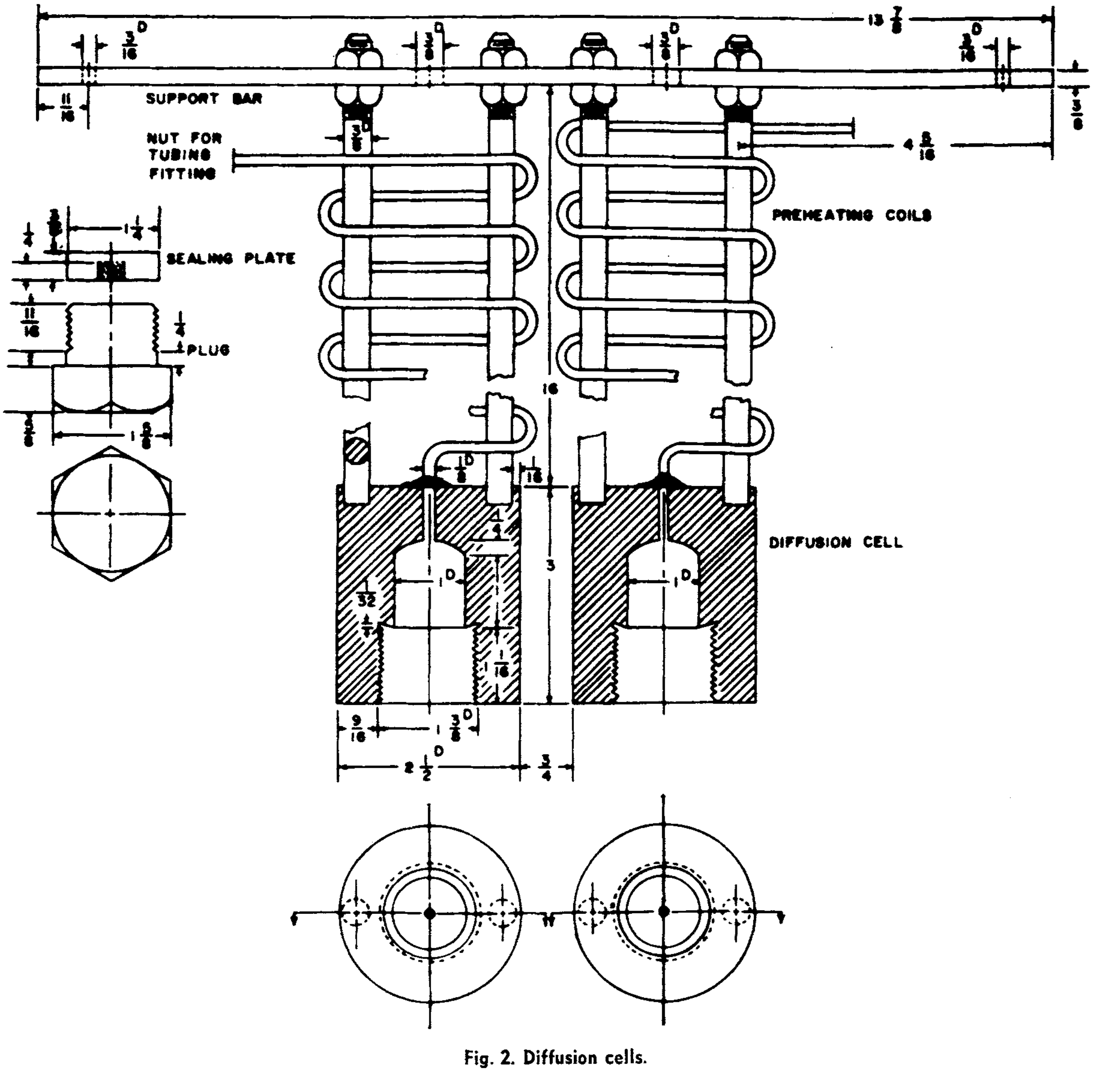

Fig. 2. Diffusion cells.

Table 1. Experimental Values of Henry's Law Constant at 371°F.

Polymer	Gas	Henry's law constant, cc. (STP)/(g.)(atm.)
Polyethylene	Nitrogen	0.111
Polyethylene	Carbon dioxide	0.275
Polyethylene	Monochlorodiflouromethane	0.435
Polyethylene	Argon	0.133
Polyethylene	Helium	0.038
Polypropylene	Nitrogen	0.133
Polypropylene	Carbon dioxide	0.228
Polypropylene	Monochlorodiflouromethane	0.499
Polypropylene	Argon	0.176
Polypropylene	Helium	0.086
Polyisobutylene	Nitrogen	0.057
Polyisobutylene	Carbon dioxide	0.210
Polyisobutylene	Krypton	0.114
Polyisobutylene	Argon	0.102
Polyisobutylene	Helium	0.043
Polystyrene	Nitrogen	0.049
Polystyrene	Carbon dioxide	0.220
Polystyrene	Monochlorodiflouromethane	0.388
Polystyrene	Argon	0.093
Polystyrene	Helium	0.029
Polymethylmethacrylate	Nitrogen	0.045
Polymethylmethacrylate	Carbon dioxide	0.260
Polymethylmethacrylate	Krypton	0.122
Polymethylmethacrylate	Argon	0.105
Polymethylmethacrylate	Neon	0.126
Polymethylmethacrylate	Helium	0.066

the solution of equation without appreciably affecting the computed diffusivities. Checks showed that the approximation increased diffusion coefficients by generally 1 or 2% and occasionally by higher values up to 10%.)

The final solution is

$$\frac{C-C_o}{C^*-C_o} = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\exp\left[-D(2n+1)^2\frac{\pi^2 t}{4L^2}\right]\cos\left(\frac{(2n+1)\pi z}{2L}\right) \tag{2}$$

For average concentration

$$\frac{\bar{C}-C_o}{C^*-C_o} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[\frac{-D(2n+1)^2\pi^2 t}{4L^2}\right] \tag{3}$$

This can be rewritten in terms of pressures as

$$\frac{P_i-P'}{P_i-P_f} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[\frac{-D(2n+1)^2\pi^2 t}{4L^2}\right] \tag{4}$$

The method of obtaining diffusivities was as follows. A diffusivity value was computed for each pressure-time experimental point. Each of these calculated diffusivity values was then used to generate separate pressure-time curves. The diffusivity yielding the generated curve which gave the lowest percent deviations with the experimental data was selected as the appropriate value. Calculations were carried out on an IBM-7040 computer. Figure 3 is a typical example of calculated pressure-time curves and experimental data.

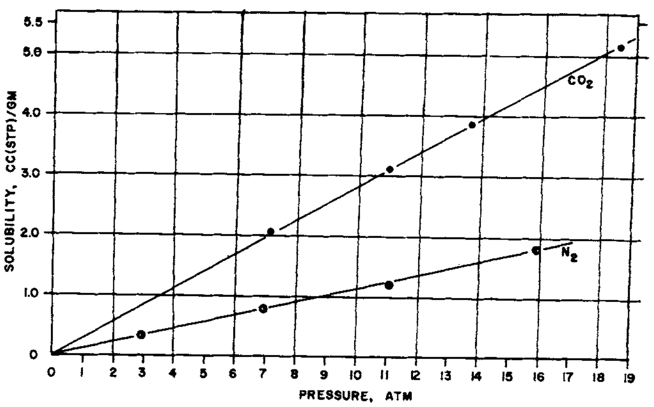

Fig. 4. Solubility vs. pressure for nitrogen-polyethylene and carbon dioxide-polyethylene at 372°F.

Diffusivity data are given in Table 2. Values were not obtained for polystyrene and polymethylmethacrylate since these samples separated from the cell walls, making it impossible to use the model described previously. Precision of the diffusivity data was generally better than 15%.

The diffusion coefficients of the present work were of the same order of magnitude as those determined by Astarita (*6*) for gas-polymer solution systems as well as for those found by Newitt and Weals (*4*) for gas thermally softened polystyrene systems. The agreement with Newitt and Weale appears to be anomalous because of the previously noted disagreements for Henry's law constants. The explanation for this apparent anomaly lies in the fact that Newitt and Weale determined Henry's law and diffusion coefficients separately, using two different techniques. The diffusion coefficient for the nitrogen-polyethylene system determined in the present work was somewhat higher (6.0 × 10^{-5} vs. 4.3 × 10^{-5} sq. cm./sec.) than that found by Lundberg and co-workers. However, as pointed out earlier, the pressure changes in the latter investigations' system, although fairly sizeable, were assumed to hold constant at some average intermediate value.

Characteristics of the polymers used in this study are reported elsewhere (*5*). Checks made for a number of

Table 2. Experimental Values of Diffusion Coefficient at 371°F.

Polymer	Gas	Diffusion coefficient, sq. cm./sec. × 10^5
Polyethylene	Nitrogen	6.04
Polyethylene	Carbon dioxide	5.69
Polyethylene	Monochlorodiflouromethane	4.16
Polyethylene	Argon	9.19
Polyethylene	Helium	17.09
Polypropylene	Nitrogen	3.51
Polypropylene	Carbon dioxide	4.25
Polypropylene	Monochlorodiflouromethane	4.02
Polypropylene	Argon	7.40
Polypropylene	Helium	10.51
Polyisobutylene	Nitrogen	2.04
Polyisobutylene	Carbon dioxide	3.37
Polyisobutylene	Krypton	7.30
Polyisobutylene	Argon	5.18
Polyisobutylene	Helium	12.96

polyethylene and polypropylene samples of different types yielded essentially the same diffusivity and solubility data.

CONCLUSIONS

1. A technique has been developed for the simultaneous measurement of diffusivities and solubilities or gases in softened and molten polymers.
2. Henry's law was found to hold in such systems up to 20 atm.
3. Henry's law constants were determined for nitrogen, carbon dioxide, argon, and helium in polyethylene, polypropylene, polyisobutylene, and polymethylmethacrylate, as well as for neon, krypton, and monochlorodifluoromethane in some of these polymers.
4. Diffusion coefficients of gases in softened or molten polymers were found to be fairly independent of pressure up to 20 atm.
5. Diffusion coefficients of gases were determined for nitrogen, carbon dioxide, argon, and helium in polyethylene, polypropylene, and polyisobutylene as well as for monochlorodiflouromethane (except for polyisobutylene.)

NOTATION

c = cc. (STP)/g. of polymer
c^* = cc. (STP)/g. of polymer at saturation in experiment under consideration
$\bar{c}$ = average concentration of gas in polymer at time t
c_0 = cc. (STP)/g. of polymer at saturation in previous experiment
D = diffusion coefficient, sq. cm./sec.
L = height of polymer sample, cm.
P' = absolute pressure at time t, atm.
P_f = final equilibrium pressure, atm.
Pi = initial pressure, atm.
t = time, sec.
z = axial position, cm.

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Upper and Lower Bounds for Solutions to the Transport Equation

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The collocation method and a maximum principle are used to generate pointwise, improvable upper and lower bounds for solutions of the transport equation. This new method of analysis is applicable to the unsteady state transport equation with a specified velocity field as well as to other problems which have a maximum principle. An application to unsteady state transfer to a fluid in ideal stagnation flow illustrates the method.

Because analytical solutions of the equations of change for realistic mathematical models are so rare, the engineer must of course rely often on approximate solutions in analyzing transport phenomena. The method of weighted residuals (*1* to *3*) is a very general class of error-distribution approximating schemes with features the engineer finds attractive; but, unfortunately, the method suffers from the deficiency that usually no error bounds can be placed on the approximate solution. In a succession of approximate solutions there may be no stage at which it is possible to state how good the approximation is, even though a proof of ultimate convergence may be available. This paper outlines a method of approximate solution which combines the collocation method, which is one version of the method of weighted residuals, with a maximum principle to provide *pointwise, improvable upper and lower bounds* for a scalar field such as temperature or concentration. The method is limited to those problems for which a maximum principle has been proved, but these include a large class of problems of concern to the chemical engineer—in particular, the unsteady state transport equation with a known velocity field.

The idea of combining an approximation method with a maximum principle has been applied previously by

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