The Injection Method of Determination of Partial Volume at Infinite Dilution

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A new experimental method of determining partial volume is described. The method requires the measurement only of a series of absolute and differential pressures. It is applicable to the determination of the partial volume of an infinitely dilute solute in a gas mixture up to high pressures. Measurement by this method can be readily performed at conditions of temperature and pressure so far unexplored to yield essential data for equation of state analyses.

Experimental methods of study of pressure-volume-temperature (p-v-t) relationship of gas mixtures are numerous and highly developed. In general, for each mixture system, the procedure calls for the preparation of several mixtures of various compositions and the determination of the p-v-t relationship of each. This determination follows the same procedure employed for pure substances. Commonly, either a variable-volume, constant-mass apparatus (mostly by confinement above a mercury surface) or a constant-volume, variable-mass apparatus (Burnett expansion) is used.

In reviewing the experimental procedures for p-v-t measurements, Ellington and Eakin (*1*) observed that volumetric data of very high precision are required to yield useful derived properties for components in a mixture. Evaluation of partial enthalpy entails a loss of accuracy of about two orders of magnitude, while evaluation of fugacity entails about one order of magnitude of loss. The main contributing factor to this loss is the necessary differentiation with respect to composition.

Notable improvement in the accuracy of measurement of p-v-t properties of mixtures has been achieved in recent innovations in which a differential technique was used. Magasanik (*2*) employed a differential technique to determine mixed second virial coefficients. Benaaker and co-workers (*3*) measured heat and volume of mixing of dense gases. A common feature of these successful methods is that only differences between the mixture property and the pure component properties are measured. The pure component properties must be independently determined to complement the mixture measurements.

The experimental method described here belongs in this same category of differential measurements. The p-v-t relationship of the pure solvent must be known at the system conditions. The present method is capable of an accuracy that is perhaps one order of magnitude higher than the results obtained from previously existing methods.

THEORETICAL BASIS FOR METHOD

The partial molal volume of component 2 in a binary mixture of species 1 and 2 is defined by

$$\overline{V}_2 = \left(\frac{\partial V}{\partial n_2}\right)_{T,p,n_1} \tag{1}$$

Using the rules of transformation of partial derivatives, we can rewrite Equation (1) as

$$\overline{V}_2 = -\frac{\left(\dfrac{\partial p}{\partial n_2}\right)_{T,V,n_1}}{\left(\dfrac{\partial p}{\partial V}\right)_{T,n_1,n_2}} \tag{2}$$

Further transformation yields

$$\overline{V}_2 = \overline{V}_1 \frac{\left(\dfrac{\partial p}{\partial n_2}\right)_{T,V,n_1}}{\left(\dfrac{\partial p}{\partial n_1}\right)_{T,V,n_2}} \tag{3}$$

In the limit of component 2 becoming infinitely dilute, Equation (3) reduces to

$$\overline{V}_2 = \widetilde{V}_1 \frac{\left(\dfrac{\partial p}{\partial n_2}\right)_{T,V,n_1}}{\left(\dfrac{\partial p}{\partial n_1}\right)_{T,V,n_2}} \tag{4}$$

in which $\widetilde{V}_1$ is molal volume of pure component 1. For the purposes of the present study $\widetilde{V}_1$ is considered to be known. The determination of partial volume $\overline{V}_2$ is resolved into one of evaluating the two derivatives in Equation (4) by injecting material into an isothermal and isochoric system; hence the name the *injection method.*

APPARATUS AND PROCEDURE

The experimental measurements involve the determination of the pressure change Δp accompanying the injection of a small quantity Δn (moles) of material into an isothermal and isochoric system. A series of such injections is performed, and the limiting value of the ratio $\Delta p/\Delta n$ as Δn approaches zero represents the derivative of interest.

Figure 1 shows the apparatus that has been developed. The main bomb and the capacitor are initially filled with pure solvent gas to the desired system pressure. The two vessels are

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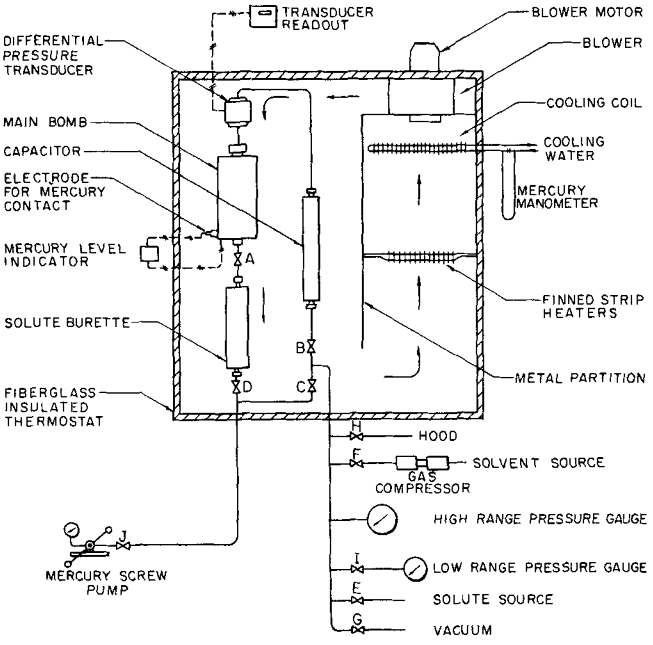

Fig. 1. Equipment for measurement of partial volume at infinite dilution.

subsequently isolated. Solute gas is successively injected into the main bomb. The incremental pressures developed by the injections are measured as differential pressures between the main bomb and the capacitor by means of a strain gauge pressure transducer.

Conceivably the incremental pressure could be measured with a high-precision pressure gauge as differences between absolute pressure readings. However, the differences of concern here are small—in the order of several pounds per square inch—while the absolute pressure might be several thousand pounds/square inch. Thus, even a moderate demand of 1% accuracy in the incremental pressure would require the absolute pressure readings to be accurate to several parts in 100,000. While this precision in pressure reading is impractical to attain, there would simultaneously be required also a temperature control of high precision—in the order of 0.01°F. As the desired accuracy is increased over 1%, the demand on absolute pressure reading and temperature control becomes even more excessive.

The measurement of differential pressure as carried out in this work is accurate to ± 0.01 lb./sq. in. At the usual differential pressure developed of about 10 lb./sq. in., the relative accuracy is about ± 0.1%. Furthermore, only moderate demands are placed on the control of the bath temperature, as the pressure fluctuations in the main bomb and the capacitor tend largely to cancel out.

The differential pressure gauge is a Consolidated Electrodynamics Corporation strain gauge pressure transducer type 4-351-0005, with a response coefficient of 4.843 lb./sq in. differential per mv. The output voltage is measured with a portable precision Leeds and Northrup potentiometer to the nearest 0.001 mv.

The air bath temperature is controlled to ± 0.05°F. by a Fisher model 22 controller. Because of capacity lag, the temperature of the main bomb body fluctuates within ± 0.02°F. as determined with a thermocouple placed in a thermowell.

The pressure vessels are rated for services up to 10,000 lb./sq. in. gauge. Their approximate volumes are: main bomb, 107 ml.; capacitor, 25 ml.; solute burette, 22 ml.

Maximum operating pressure of the apparatus is limited by the pressure transducer to 5,000 lb./sq. in. gauge.

Operation of the apparatus follows the steps:

1. The main bomb and the capacitor are connected by opening valves A, B, C, and D. Pure solvent gas is charged into the bombs until the desired system pressure is established. The pressure is indicated by a calibrated precision Heise Bourdon tube gauge.
2. Valve B is closed to isolate the capacitor.
3. Valve A is closed to isolate the main bomb. The solute burette is evacuated and then filled to some low pressure with the solute gas. A calibrated low pressure test gauge M reads the pressure.
4. Lines between the mercury screw pump and the vacuum pump are evacuated and then filled with mercury to valves C and D. Valves D and A are opened and solute gas is displaced by mercury into the main bomb. The mercury screw pump is used to force the mercury level up and down the solute burette a number of times. The induced expansion and compression of the contents of the main bomb promote mixing. Finally, the mercury level is brought to a precise position set by the mercury level indicator, thus restoring the volume of the main bomb content.
5. The emf developed by the strain gauge differential pressure transducer between the main bomb and the capacitor is read on a potentiometer. This emf measures the pressure change that has been brought about by the injections.

Steps 3 to 5 comprise an injection. Usually three or four consecutive injections are made to each fresh content of the main bomb.

This sequence of steps applies equally well to the determination of both derivatives in Equation (4). The only difference in experimental procedure that distinguishes the two derivatives is the solute gas is used as the injection material in the determination of $(\partial p/\partial n_2)$, while the solvent gas itself is used as the injection material in the determination of $(\partial p/\partial n_1)$.

The effective volume of the main bomb is fixed by the position of the electrode tip which is inserted slightly in the ¼-in. tubing above valve A. A mercury slug must fill the tubing at all times while a pressure reading is made. This condition is always satisfied after the solute injections, as these injections are forced displacements by mercury. However, after the initial filling with fresh solvent, the tubing above A is empty. A mercury slug is therefore specially forced into the tubing. The differential pressure developed by this slug is noted and added on to the gauge reading to give the true system pressure.

EXPERIMENTAL RESULTS

Results of the measurement are in the form of a series of pressure readings $p_1, p_2, \ldots p_i \ldots$ of the burette content before the injections, and a corresponding series of emf readings $e_1, e_2, \ldots e_i \ldots$ from the transducer-potentiometer combination after the injections. These data

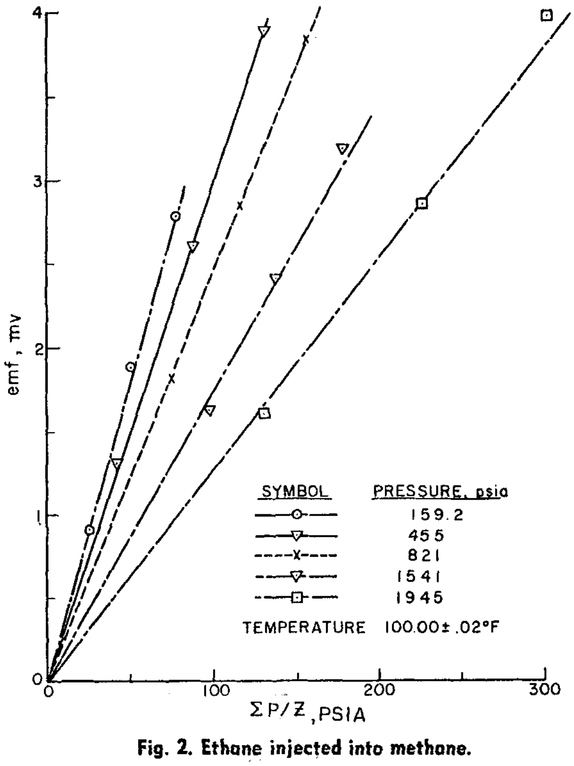

Fig. 2. Ethane injected into methane.

TABLE 1. INJECTION OF ETHANE INTO METHANE EXPERIMENTAL RESULTS AT 100.00 ± 0.02 °F.

Initial methane press., lb./sq. in. abs.	e_i, mv.	$\Sigma p_i/z_i$, lb./sq. in. abs.
159.2	0.927	25.46
	1.890	51.58
	2.795	77.42
307	1.127	33.47
	2.292	68.27
	3.405	101.95
455	1.324	43.28
	2.624	86.98
	3.899	130.46
821	1.823	75.77
	2.862	116.53
	3.856	156.48
1,036	0.914	37.62
	1.795	73.98
	2.649	109.52
1,541	1.637	98.26
	2.431	137.25
	3.211	178.43
1,945	1.622	131.37
	2.873	225.39
	3.986	306.50

TABLE 2. INJECTION OF METHANE INTO METHANE EXPERIMENTAL RESULTS AT 100.00 ± 0.02 °F.

Initial methane press., lb./sq. in. abs.	e_i, mv.	$\Sigma p_i/z_i$, lb./sq. in. abs.
164.3	1.516	40.34
	2.778	73.48
	3.959	105.00
	5.103	135.66
406	1.222	35.50
	2.558	71.87
	3.735	108.23
	4.912	138.89
433	1.551	43.37
	3.229	91.70
	4.697	132.04
601	1.487	44.44
	2.787	82.76
	4.385	130.55
1,018	1.118	36.67
	2.338	77.65
	3.598	121.52
1,117	1.359	43.59
	2.900	92.24
	4.175	133.45
1,631	1.623	53.61
	3.178	105.40
	4.782	158.37
2,062	2.181	69.68
	4.121	134.49
	6.132	204.27
	8.100	271.90
830	1.192	37.77
	2.364	74.38
531	1.347	38.85
	2.588	76.19
	4.040	116.33
714	1.342	41.21
	2.549	79.40

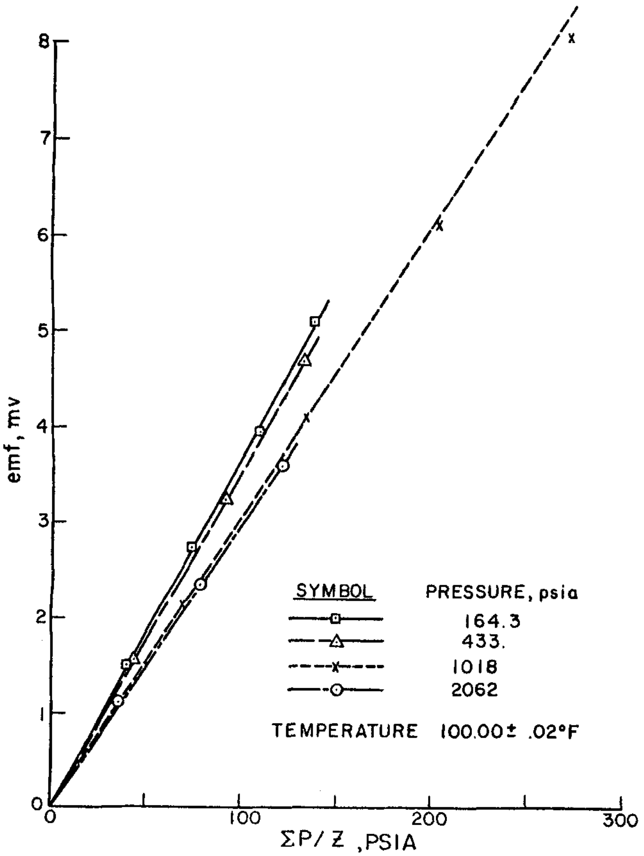

Fig. 3. Methane injected into methane.

apply to one fixed temperature and pressure condition of the solvent in the main bomb.

Let V denote the volume of the burette, and z_i the compressibility factor of the burette content at p_i. The number of moles n_i of the burette content is given by

$$n_i = \left(\frac{V}{RT}\right)\frac{p_i}{z_i} \tag{5}$$

Let k denote the response coefficient of the pressure transducer in pounds per square inch per millivolt such that

$$\Delta p_i = k\ e_i \tag{6}$$

where Δp_i denotes the differential pressure developed after the i^{th} injection.

For small values of Δn and Δp, one of the partial derivatives in Equation (4) is approximated by

$$\left(\frac{\partial p}{\partial n_2}\right)_{T,V,n_1} = \frac{k\ e_{i2}}{\left(\frac{V}{RT}\right)\sum_i \frac{p_{i2}}{z_{i2}}} \tag{7}$$

Here Euations (5) and (6) have been used. The second subscript indicates quantities associated with solute injection.

Similarly, the other derivative in Equation (4) is approximated by

$$\left(\frac{\partial p}{\partial n_1}\right)_{T,V,n_2} = \frac{k\ e_{i1}}{\left(\frac{V}{RT}\right)\sum_i \frac{p_{i1}}{z_{i1}}} \tag{8}$$

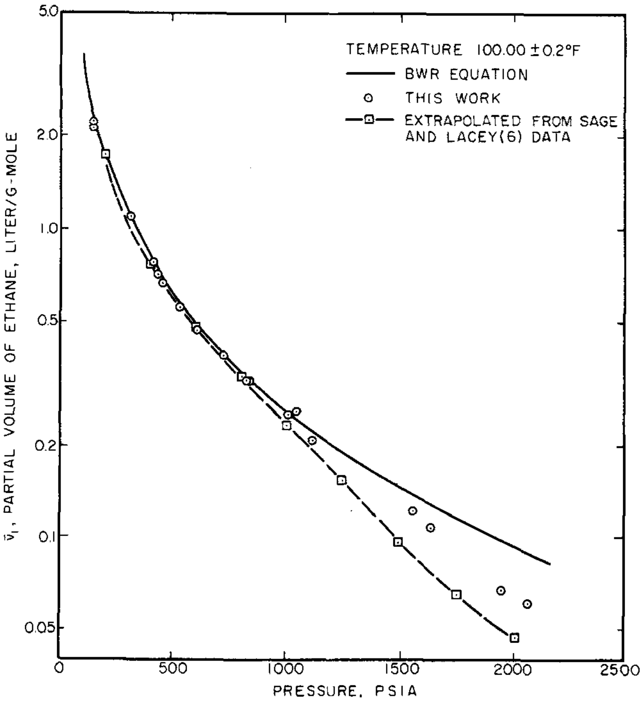

Fig. 4. Partial volume of ethane at infinite dilution in methane at 100°F.

Here the second subscript indicates quantities associated with solvent injection.

Substitution of Equations (7) and (8) into Equation (4) leads to

$$\overline{V}_2 = \widetilde{V}_1 \left[\frac{e_{i2}}{\sum\limits_i \left(\frac{p_{i2}}{z_{i2}}\right)} \right] \Bigg/ \left[\frac{e_{i1}}{\sum\limits_i \left(\frac{p_{i1}}{z_{i1}}\right)} \right] \qquad (9)$$

Equation (9) shows that k, V, and T cancel out; the values of k and V need not be known for the determination of the desired partial volume as long as these values stay constant.

The constancy of k, the transducer response coefficient, is generally accepted, and has been checked out experimentally in this work. Care must be exercised to differentiate between the linearity of the strain gauge response (meaning constancy of k in the above usage) and the drift of the response coefficient with temperature and total pressure. Nothing is stated here regarding the latter point because of its irrelevance to the present discussion.

It was found that at the small Δp and Δn used in the experiments, the quotients $e_i/(\sum\limits_i p_i/z_i)$ were independent of i for small values of i. This established the linearity between Δp and Δn within the experimental range. The use of Equation (9) in place of Equation (4) became fully justified for the present set of experimental data.

Experimental measurement was carried out to determine the partial volume of ethane in methane in order to check out the apparatus. Temperature was fixed at 100°F. Ethane was the infinitely dilute solute gas and methane the solvent gas. The methane and ethane were Phillips Petroleum Company pure grade hydrocarbons with minimum purities of 99 mole %.

Figure 2 shows the results of injection of ethane into methane. Figure 3 shows similar results for injection of methane into methane. In these figures pressure increments are expressed in terms of observed emf, and number of moles of total injection in terms of $\sum\limits_i p_i/z_i$. For clarity not all the data are included in the figures. However, the two complete sets of data are recorded in Tables 1 and 2. Coefficients $e_i/(\sum\limits_i p_i/z_i)$ are formed from each data point to approximate $(\partial p/\partial n)$. It is observed that at the same system pressure these coefficients assume an essentially constant value—variations among them are within measurement error. The arithmetic average of the coefficients at the same system pressure is then taken to represent $(\partial p/\partial n_i)_{T,V,n_j}$ except for a constant factor of multiplication.

The compressibility factor z_i of ethane in the burette is determined by referring to literature values reported by Sage et al. (*4*). The compressibility factor of methane in the burette is calculated by means of Benedict, Webb, and Rubin equation of state with parameters determined by Douslin et al. (*5*).

Douslin's methane results (*5*) are used also to calculate the pure solvent molar volume V_1 of Equation (9). This value, when combined with the average values of the coefficients $e_i/\Sigma_i(p_i/z_i)$ of Tables 1 and 2, gives $\overline{V}_2$, the partial molal volume of ethane in methane. The final result is shown in Figure 4.

DISCUSSION

The results of this work are compared with partial volume extrapolated from Sage and Lacey's tabulated values at finite concentrations (*6*). The extrapolation extended over a 10 mole% to reach zero concentration. Some uncertainty was necessarily introduced in this process. The extrapolation procedure has been described (*9*).

A comparison of the results of this work is also made with calculated values from Benedict, Webb, and Rubin equation of state. The equation parameters for methane are taken from Douslin (*5*); the parameters for ethane are from Opfell et al. (*7*). The combining rules for the parameters as originally proposed by Benedict et al. are used in forming mixture parameters. As shown in Figure 4, the different sources agree at pressures up to about 1,000 lb./sq.in.abs. From there on, considerable divergence is observed. It appears that the validity of the injection methane of measurement of partial volume in dense gas mixtures is established.

The linearity of the response emf as a function of the injection quantity cannot in general be taken for granted, but must be carefully established from examination of the data. Nonlinearity can certainly result from excessively large injections. When such is the case, the injection quantity should be reduced until linear response is observed.

The injection method is potentially capable of high accuracy. The accuracy of the present results is limited mainly by the pressure gauges. The low pressure gauge for measuring burette content is accurate to about ± 0.2 lb./sq.in. As the burette pressure is usually in the order of 50 to 100 lb./sq.in.abs., the relative accuracy of measurement of Δn is in the order of ± 0.4 to ± 0.2%. The high pressure Heise gauge is accurate to ± 1 lb./sq.in. This leads to an adequate relative accuracy at system pressures above 1,000 lb./sq.in.abs., but poorer relative accuracy at progressively lower system pressures.

A detailed analysis of the various contributing factors to experimental errors has been carried out. The results show that the present partial volume data are accurate to about 2% at 200 lb./sq.in.abs. and about 1% at 2,000 lb./sq.in.abs. The analysis also shows that an accuracy of 0.2% can be attained when the pressure gauges are replaced with high precision instruments.

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NOTATION

e = emf developed by the strain gauge differential pressure transducer
k = response coefficient of the transducer, defined in Equation (6)
n = number of moles
p = pressure
R = gas constant
T = absolute temperature
V = system volume
$\bar{V}$ = partial molal volume
$\tilde{V}$ = molal volume of a pure substance
z = compressibility factor, $p\tilde{V}/RT$

LITERATURE CITED

1. Ellington, R. T., and B. E. Eakin, *Chem. Eng. Progr.*, 59, No. 11, 80 (1963).
2. Magasanik, D., Ph.D. dissertation, Illinois Inst. Technol. (1963).
3. Benaaker, J. J. M., B. van Eijnsbergen, M. Knoester, K. W. Taconis, and P. Zannbergen, "Advances in Thermophysical Properties," p. 114, Am. Soc. Mech. Engrs., New York (1965).
4. Sage, B. H., D. C. Webster, and W. N. Lacey, *Ind. Eng. Chem.* **29**, 658 (1937).
5. Douslin, D. R., R. H. Harrison, R. T. Moore, and J. P. McCullough, *J. Chem. Eng. Data,* **9**, 358 (1964).
6. Sage, B. H., and W. N. Lacey, *Monogr. API Res. Proj.*, 37, Am. Petrol. Inst., New York (1950).
7. Opfell, J. B., C. J. Pings, and B. H. Sage, "Equations of State for Hydrocarbons," Am. Petrol. Inst., New York (1959).
8. Benedict, M., G. B. Webb, and L. C. Rubin, *J. Chem. Phys.* **8**, 334 (1940).
9. Chao, K. C., paper presented at AIChE Dallas meeting (Feb., 1966).

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Flow Characteristics of Horizontally Moving Stable Aqueous Foams

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An empirical study was made of the flow characteristics of a stable aqueous foam (based on dilute solutions of saponin) moving horizontally inside a duct. Characteristic foam data have been determined experimentally, namely, drainage, interfacial areas, and related dimensions such as lamella thickness and foam cell size, fractional liquid holdups, foam velocities, and extent of gas channeling through the foam. Simple correlatability of drainage, interfacial area, and fractional liquid holdup in terms of basic parameters such as the liquid flow rate entering the apparatus, and the longitudinal position in the duct has been demonstrated. The sometimes simple dependence on the geometry of the perforated gas-liquid contactor and on the physical properties of the foaming solutions (surface tension and bulk viscosity) has also been described.

In the application of moving foam systems to specific purposes such as the recently reported results on mass transfer (*16*), it is necessary to know what the factors governing the behavior of such foams are and in which way they operate.

Extensive and somewhat controversial findings were reported in the areas of foaming in general and behavior of stagnant foams in particular (*1, 4* to *7, 9* to *11, 14*). In one case mention has been made of a linear relationship between the velocity of a moving foam plug and the shear stress (*10*), but the data, as reported, were scarce and limited only to that particular relationship. By and large, however, the interest in moving foams is centered around the techniques of gas absorption, particle collection, and separation by foam fractionation. All these techniques are based on empirical treatments of vertical operation in columns of varied designs, and their literature has been rather extensively reviewed elsewhere (*15*). Recently, an attempt was made to derive a theoretical model describing interstitial drainage in a stagnant or moving vertical foam fractionation column and agreement with experimental data was reported (*8*).

The applicability of studies of vertical foam columns to the case of horizontal foam movement is, however, not apparent; direct investigations of horizontal foam flow will therefore be necessary to fully understand and define its mechanism.

The present empirical study describes the flow behavior of a foam that is made to move horizontally inside a duct completely filled by it. The foam is produced from a solution of 0.2% by weight (in most cases) of saponin* in deionized water and, as such, belongs to the category of slow draining, true polyhedral-bubble systems.

The characteristic factors studied are drainage flow rates, interfacial areas and average lamella (film) thicknesses, fractional gas and liquid holdups, and extent of gas channeling effects. These factors are reported as functions of the basic parameters: liquid flow rate entering the apparatus,† gas flow rate, position in the duct, geome-

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* Saponin is an extract of naturally occurring glucosides, nonionic in character, and known to produce very stable slow draining foams. The 0.2% concentration was found to be the minimum amount permitting good operation of the foam apparatus over a wide range of gas and liquid flow rates (*15*).

† It should be noted here that because of foam drainage, the horizontal liquid flow rate in the duct decreases in the downstream direction. The liquid flow rate entering the apparatus is, of course, the easiest to measure and control.