respectively. From a comparison of these average deviations it can be concluded that Equations (9) and (12) and Equations (10) and (13) can be used to estimate force constants with the same degree of confidence.

NOTATION

a = pressure van der Waals' constant, (cc./g.-mole)^2 atm.
b = volume van der Waals' constant, cc./g.mole
D = self-diffusivity, sq. cm./sec.
f = approximation coefficient
k = thermal conductivity, cal./sec. cm. °K.
M = molecular weight
T = absolute temperature, °K.
T_c = critical temperature, °K.
T_N = normalized temperature, $T/\frac{\epsilon}{\kappa}$
v_c = critical volume, cc./g.-mole

Greek Letters

α = constant, Equation (7)
β = constant, Equation (8)
ϵ = maximum energy of attraction for Lennard-Jones potential, ergs
η = ratio, $\Omega^{(2,2)*}[T_N]/f_\mu^{(3)}[T_N]$
κ = Boltzmann constant, 1.3805 × 10^{-16} ergs/°K.
μ = viscosity, g./sec. cm.
π = pressure, atm.
σ = collision diameter for Lennard-Jones potential, Å.
$\Omega^{(1,1)*}[T_N]$ = collision integral function
$\Omega^{(2,2)*}[T_N]$ = collision integral function

LITERATURE CITED

1. Adzumi, Hiroshi, *Bull Chem. Soc. Japan*, **12**, 199-226 (1937).
2. Bicher, L. B., Jr., and D. L. Katz, *Ind. Eng. Chem.*, **35**, 754-61 (1943).
3. Bleakney, W. M., *J. Appl. Phys.*, **3**, 123-36 (1932).
4. Comings, E. W., B. J. Mayland, and R. S. Egly, *Univ. Illinois Eng. Expt. Sta. Bull., Series No. 354*, 7-68 (1944).
5. Craven, P. M., and J. D. Lambert, *Proc. Roy. Soc. (London)*, A**205**, 439-49 (1951).
6. Everhart, W. A., and E. Mack, *J. Am. Chem., Soc.*, **55**, 4894 (1933).
7. Hirschfelder, J. O., R. B. Bird, and E. L. Spotz, *Chem. Revs.*, **44**, 205 (1949).
8. Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York (1954).
9. Ishida, Yoshio, *Phys. Rev.*, **21**, 550-63 (1923).
10. Johnston, H. L., and K. E. McCloskey, *J. Phys. Chem.*, **44**, 1038 (1939).
11. Kiyama, Ryo, and Tadashi Makita, *Rev. Phys. Chem. Japan*, **22**, 49-58 (1952).
12. Kuenen, J. P., and S. W. Visser, *Verslag Akad. Wetenschap.*, **22**, 336-43 (1913).
13. Melaven, R. M., and E. Mack, *J. Am. Chem. Soc.*, **54**, 892 (1932).
14. Nasini, A. G., *Proc. Roy. Soc. (London)*, A**123**, 692-704 (1929).
15. Rankine, A. O., and C. J. Smith, *Phil. Mag.*, **42**, 615-20 (1921).
16. Sage, B. H., W. D. Yale, and W. N. Lacey, *Ind. Eng. Chem.*, **31**, 223-226 (1939).
17. Smith, A. S., and G. G. Brown, *ibid.*, **35**, 705 (1943).
18. Titani, T., *Bull. Chem. Soc. Japan*, **5**, 98 (1930).
19. *Ibid.*, **7-8**, 255-276 (1933).
20. Trautz, M., and P. B. Baumann, *Ann. Physik*, **2**, No. 5, pp. 733-6 (1929).
21. Trautz, M., and I. Husseini, *ibid.*, **20**, 121-6 (1934).
22. Trautz, M., and F. Kurz, *ibid.*, **9**, 981-1003 (1931).
23. Trautz, M., and A. Melster, *ibid.*, **7**, No. 5, pp. 409-26 (1930).
24. Trautz, M., and K. G. Sorg, *ibid.*, **10**, 81-96 (1931).
25. Trautz, M., and R. Zink, *ibid.*, **7**, No. 5, pp. 427-52 (1930).
26. Van Cleave, A. B., and O. Maass, *Can. J. Research*, **13B**, 140-8 (1935).
27. Vogel, H., *Ann. Physik*, **43**, 1258 (1914).
28. Wobser, R., and F. Müller, *Kolloid Beih.*, **52**, 165-276 (1941).

Manuscript received June 13, 1960; revision received January 17, 1961; paper accepted January 18, 1961.

Six-Stage Vapor-Liquid Equilibrium Unit

ROBERT H. McCORMICK, PAUL BARTON, and M. R. FENSKE

Pennsylvania State University, University Park, Pennsylvania

Accurate vapor-liquid equilibrium data are of great importance in the design of pilot plant and industrial fractional-distillation equipment. Today particularly, when compounds of high purity are required for the petrochemical and many other industries, it is necessary to know the factors that affect the efficient separation of the compounds in multicomponent systems.

Single-plate vapor-liquid equilibrium units have been utilized for many years in the study of binary systems and relatively simple multicomponent mixtures. Myers (*1*) developed a two-plate equilibrium unit patterned after the Othmer design (*2*) to more accurately determine equilibrium data on binary systems. The unit consisted of two glass stills equipped with condensers and lines to connect the two stills.

But for mixtures in which the relative volatilities approach unity or for mixtures which cannot be analyzed accurately, the single- or two-plate equilibrium units are inadequate for the determination of accurate equilibrium data. A versatile multiplate vapor-liquid equilibrium unit is needed.

Herring (*3*) developed a six-plate vapor-liquid equilibrium unit which contained six helix-packed sections of Pyrex glass through which vapor and liquid flowed concurrently on each stage but countercurrently between the stages.

The unit described in the present work is a versatile six-stage unit which can be operated at pressures ranging from atmospheric to 400 lb./sq. in. abs., and at temperatures of 25° to 400°F. Each stage consists of a still equipped with a condenser, a heater, and a mechanical mixer. Auxiliary lines connect the stages, so the terminal samples represent a six-plate separation. Samples of vapor and liquid can be removed from each of the stages so that any number of the stages may be utilized to determine equilibrium relationships. For equilibrium data on binary or multicomponent mixtures that are difficult to determine accurately in a single stage, this unit provides as many as six stages. If the change in composition over the stages is small or if the relative volatility is not affected greatly by composition, the relative volatility calculated directly from the data may be assigned to the arithmetical average composition of the liquid in the stills. If the relative volatility changes appreciably with composition, on the other hand, the conventional X-Y diagram for vapor-liquid equilibrium of binary mixtures may be constructed from three- and five-plate data by the method of Reed and Myers (4).

The advantage of using a unit with more than one stage in the determination of vapor-liquid equilibria is seen from the following equation (5):

$$\left(\frac{y_a}{y_b}\right) = \alpha^n \left(\frac{x_a}{x_b}\right) \text{ or}$$

$$\alpha = \sqrt[n]{\frac{y_a\, x_b}{y_b\, x_a}} = \sqrt[n]{\text{E.F.}} \quad (1)$$

This equation permits the calculation of relative volatility from the vapor composition and liquid composition incurred in a separation over n stages. Thus, relative volatility is a function of the nth root of the enrichment factor. More accurate relative volatilities may be calculated in this way for a given analytical procedure than is possible from a one-stage separation; for example, if the relative volatilities for a system from a single-stage equilibrium unit deviate from 1.04 to 1.06 due to inaccuracies in analysis, this deviation can be decreased to 1.048 to 1.052 by using a six-stage unit. This advantage is important, because the most frequent source of error in relative-volatility determinations in conventional single-stage units is caused by inaccuracies or uncertainties in analyses of the samples, rather than by the design of the unit.

Even though the greatest use of this multistage equilibrium unit will be to determine data on systems with a low relative volatility, or those difficult to analyze, it can also be utilized advantageously for mixtures that can ordinarily be studied in a single-stage unit. By sampling intermediate stages when studying such mixtures, one can determine equilibrium points over a relatively wide concentration range in a single test.

FLOW DIAGRAM

Each of the six individual stages in the unit is patterned after the Othmer equilibrium still and has a separate condenser. Auxiliary flow lines connect the stages. The complete unit is mounted inside a thermostatically controlled, well-insulated, constant-temperature box. A schematic drawing of the unit is shown in Figure 1. The vapor rising from the boiling liquid in the first still is condensed (D_1) and flows into the second still, where it is mixed with the liquid in this still. The vapor rising from the second still is condensed (D_2) and flows into the liquid in the third still, and so on. The vapor leaving the sixth still is condensed (D_6) and returned to the boiling liquid in the sixth still. A weir or overflow tube in each of the stills, except still 1, maintains a constant level in each still. In this way the liquid from a still overflows (O_2, O_3, O_4, O_5, and O_6) into the lower numbered still. Any excess liquid charged to the unit eventually overflows into the first still.

When the unit is operating at steady state and total reflux, the composition of the liquid in the second still is the same as that of the distillate from the first still, the liquid in the third still is the same as the distillate from the second still, and so on.

For the unit to operate as six theoretical plates or stages, which would meet true equilibrium conditions, the vapor leaving each still must be in equilibrium with the liquid in that still. In case any or all of the stills consistently yield more or less than one theoretical plate, a steady state can be reached that does not represent true equilibrium conditions. The experimental conditions necessary for true equilibrium were established by studying the unit with binary hydrocarbon mixtures for which equilibrium data are known.

CONSTRUCTION

A scale drawing of a single stage is shown in Figure 2. The complete unit comprises six of these stages, connected as shown schematically in Figure 1. The main part of the stage consists of a series 13-R-20 Jerguson gauge especially designed so that all the parts shown in Figure 2 might be fitted into or attached to it. All parts in contact with either vapor or liquid are stainless steel in order that a wide variety of chemicals may be studied.

The still for each stage is a 3.7-in. length of 1-in. O.D. stainless steel pipe welded to the bottom of the Jerguson gauge. Heat is supplied to the still electrically.

Contacting of the boiling liquid with the rising vapors and mixing of the liquid streams entering each still are enhanced by the use of a magnetically operated bucket pump which lifts the liquid from the still and sprays it down through the rising vapors. The positions of the various parts of this mixing device are illustrated in Figure 2. A detailed drawing of the bucket pump is shown in Figure 3. The amplitude, or length of stroke for the pump, is 0.3 in. The frequency of the pump stroke can be changed from 120 to 250 cycles/min. The capacity of the pump, using a cold liquid, varies from 170 ml./min. at 120 cycles/min. to 360 ml./min. at 250 cycles/min.

Each stage has a separate cold-finger condenser as shown in Figure 2. A 3-ml. reservoir for sampling, through which the condensed distillate continuously flows, is directly beneath the condenser.

The complete six-stage unit and auxiliary parts are mounted in a well-insulated box in which the temperature can be controlled from about 25° to 400°F. Electric heaters mounted in the box supply the heat, and a refrigerating system supplies cooling to the box and to the condensers. The box is 63 in. long, 43 in. high and 14 in. deep. It is fabricated from ⅜-in. Transite sheets bolted to a 1.5-in. angle-iron frame. Soft asbestos boards with aluminum foil between the two layers are mounted on the inside of this frame to supply insulation.

A window was placed directly in front of each stage so that the operation might be observed. To prevent a possible explosion due to a leak of hydrocarbon, a carbon dioxide atmosphere is maintained inside the box. A blower constantly circulates the gas in the box, and over the heaters, which are mounted in an annular space along the inside of the box, or over the cooling coils in an external refrigerating system.

The six stages are connected through a common manifold attached to the top of the cold-finger condensers. Thus each still operates at the same pressure. A surge tank is connected to the manifold for elevated-pressure operation. Nitrogen or some other inert gas is used in the surge system to maintain the desired pressure above the condensers during operation.

Thermocouples are mounted in each still to determine the temperature of the boiling liquid. Thermocouples are also mounted at several places in the air space in the box, and the heat input is regulated to yield a constant temperature in the box and adiabatic operation for the individual stages.

OPERATION

The total volume of liquid required to operate this unit satisfactorily is 50 to 55 ml./stage, or a total of 300 to 350 ml., depending somewhat on operating conditions. The total space occupied by vapors, exclusive of the surge system, is about 100 ml./stage. The surge system has a total volume of 4,700 ml.

In operation the boil-up rate in each stage can be varied from 5 to 35 ml./min. This corresponds to replacing the total volume of liquid in each stage by liquid overflowing from the next higher stage every 2 to 10 min. The condensate reservoir at the bottom of each condenser has a volume of 3 ml. and is so built that it is continuously purged. At the boil-up rates mentioned, this reservoir is purged 2 to 12 times/min. The vapor in the unit is replaced or purged from 1 to 70 times/min., depending upon the boil-up rate, the pressure, and the temperature of operation. For a three-carbon atom hydrocarbon at 300 lb./sq. in. abs., the 100-ml. vapor space/stage would yield about 6 ml. of liquid hydrocarbon.

The bucket pump stirs the boiling liquid, mixes the liquid streams which enter the still, and provides additional contact between the vapor and liquid. Lifting the liquid from the still and spraying it down through the rising vapors effectively increases the vapor-liquid contacting. It is estimated that the pumping rate for the liquid at its boiling point can be varied from about 100 to 250 ml./min., which is

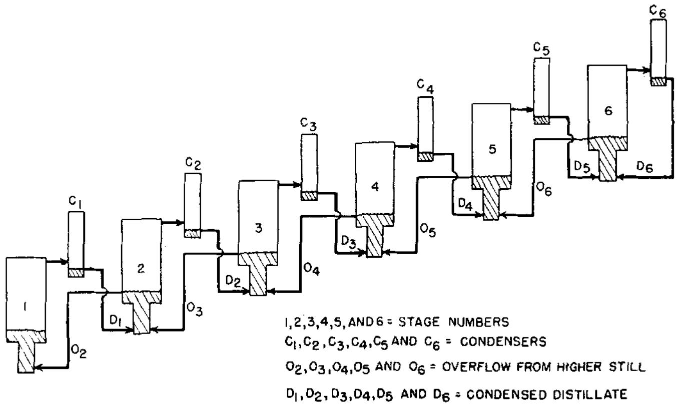

Fig. 1. Flow diagram of six-stage vapor-liquid equilibrium unit.

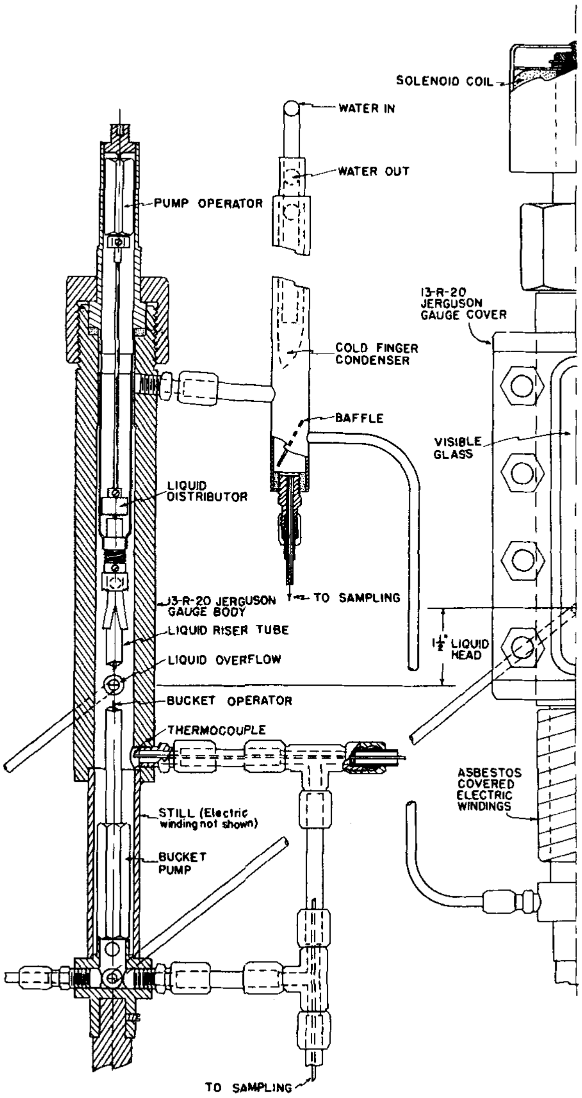

Fig. 2. Construction of stages in the six-stage vapor-liquid equilibrium unit.

equivalent to pumping the total liquid in the stills from 2 to 5 times/min. The ratio of the pumping rate to the boil-up rate can be varied from about 3 to 50. By maintaining this ratio high, the rising vapor contacts more liquid and as a result, equilibrium should be more nearly approached.

The vapor travels about 3 in. beyond the liquid spray from the pump outlet before it enters the condenser section. Tests which employ binary hydrocarbon mixtures with known relative volatilities have shown that this space is sufficient to eliminate entrainment of liquid droplets in the vapor.

It is important that the temperature of the box be maintained close to that of the liquid boiling in the stages. If the temperature is too high, vapor lock may occur in the connecting lines and stop or retard the flow of liquid. Also any liquid splashed on the walls of the vapor-liquid contacting section would be flash vaporized, resulting in a somewhat lower stage efficiency. If the box temperature is too low, condensation on the walls of the stages occurs and, due to the concentration gradient set up by the partial condensation of the vapors, an efficiency exceeding 100% may result.

The unit operates most satisfactorily when the temperature of the box is maintained within ± 5°F. of the boiling point of the liquid in the stills. This temperature gradient does not appreciably affect the number of theoretical stages in the unit.

After all the operating conditions have been regulated and are constant, at least 3 hr. is required for equilibrium to be reached. All streams should be flowing evenly because an interruption in any of these flows changes the liquid levels and disrupts the equilibrium in the stages.

At temperatures above 300°F. the present electric solenoid coils used to operate the bucket pumps should be removed, since the insulation on these coils decomposes at such temperatures. Without the solenoid coils the pumps are inoperative, and so, as only natural convection is available for liquid mixing, the amount of vapor-liquid contact is reduced. Under these conditions at least 5 hr. of continuous running is needed to reach equilibrium conditions.

One method of removing samples from the unit is to withdraw the desired samples simultaneously while the unit is in operation. A more convenient method, however, is suddenly to increase the pressure of the unit about 50 lb./sq. in. by adding additional inert gas while simultaneously shutting off the still heats and the pumps. This stops the boiling in the stills and the vapor sample reservoirs remain full, in effect "freezing" the equilibrium compositions. The vapors are condensed and this material then mixes with the liquid in the still. Since the vapor composition is different from that of the liquid, the resulting mixture in the still is not an equilibrium sample. Therefore the only still sample used in the relative volatility calculations is that from the first still, which is removed before shutting down the unit with increased pressure. For all the other stages the distillate samples are utilized.

For operation at atmospheric pressure or relatively low pressures, the amount of vapor condensed is small, 0.5 to 1.0 cc., and does not appreciably affect the results. In these cases the still samples can be used for relative volatility calculations.

EFFICIENCY TESTS

To determine the efficiency and to study the conditions necessary for optimum operation, the unit was tested

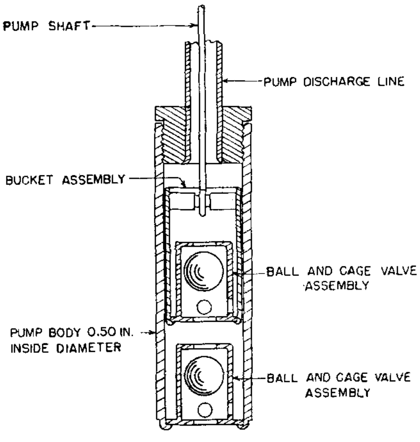

Fig. 3. Bucket pump used in six-stage vapor-liquid equilibrium unit. The entire pump has been fabricated from 18-8 type 304 stainless steel without soldering or welding.

TABLE 1. EFFICIENCY TESTS ON SIX-PLATE VAPOR-LIQUID EQUILIBRIUM UNIT

Test no.	Average temperature in stills, °F.	Pressure, lb./sq. in. abs.	Sample composition, mole % (first component listed)		Relative* volatility	No. of theoretical plates [calc. from eq. (1)]
			Distillate, sixth stage	Bottoms, first stage		
Test mixture: methylcyclohexane:toluene						
1	215	atm.	67.3	29.6	1.305	5.95
2	215	atm.	67.3	26.7	1.315	6.35
3	215	atm.	68.0	27.1	1.31	6.45
4	215	atm.	67.9	27.3	1.31	6.35
5	215	atm.	68.1	28.6	1.31	6.25
6	214	atm.	67.9	27.9	1.31	6.3
7	213	atm.	67.8	26.9	1.315	6.4
8	215	atm.	66.8	26.3	1.315	6.35
Test mixture: *n*-heptane:methylcyclohexane						
9	206	atm.	53.7	43.4	1.074	5.85
10	206	atm.	53.6	43.2	1.074	5.9
Test mixture: *n*-decane:trans-decahydronaphthalene						
11	354	atm.	66.1	29.3	1.29	6.05
12	357	atm.	65.9	27.9	1.29	6.3
13	355	atm.	66.9	29.9	1.29	6.1
14	354	atm.	66.1	27.8	1.29	6.35
Test mixture: propylene:propane						
15	90	185	65.4	47.2	1.135	5.9
16	139	341	58.8	44.9	1.10	5.9
					Average	6.2

* Relative volatility data
Methylcyclohexane-toluene (*8*)
n-heptane:methylcyclohexane (*8*)
n-decane:trans-decahydronaphthalene (*6*)
Propane:propylene (*7*)

with binary hydrocarbon test mixtures of methylcyclohexane:toluene *n*-heptane:methylcyclohexane, and *n*-decane: trans-decahydronaphthalene at atmospheric pressure, and with propylene: propane at higher pressures. The equilibrium data for these four systems are fairly well established. The relative volatility for methylcyclohexane:toluene varies from 1.08 to 1.63, depending upon the concentration of the two hydrocarbons, while that for *n*-heptane:methylcyclohexane is constant at 1.074 over the entire concentration range. The *n*-decane:trans-decahydronaphthalene system has a constant relative volatility of 1.29 over the concentration range studied (*6*). For the propylene:propane system, the relative volatility ranges from 1.10 to 1.135 (*7*).

The equilibrium samples for the first three systems were analyzed by refractive index measurements, and gave compositions which are accurate to ± 0.3 percentage units. The propylene: propane system was analyzed by gas chromatography with an accuracy of ± 0.5 percentage units.

The efficiencies, or theoretical plate measurements, for sixteen tests made on this unit with these four test mixtures are shown in Table 1. Other tests were made to establish the optimum operating conditions. The theoretical plate values for the toluene:methylcyclohexane mixture vary from 5.95 to 6.45, and in most cases the values are somewhat higher than six plates. It is interesting to note that even though the relative volatility of this test mixture varies from 1.22 to 1.42 over the concentration range, the relative-volatility values used, which correspond to the arithmetical average composition of the liquid in the six stills, gave values of efficiency identical to those determined by a graphical method derived from plate-to-plate calculations. This latter method takes into account the change in relative volatility with composition.

The two tests using the *n*-heptane: methylcyclohexane mixture show good efficiencies of 5.85 and 5.9 theoretical plates. The *n*-decane:trans-decahydronaphthalene mixture gave values ranging from 6.05 to 6.35 theoretical plates without the use of the pumps. In run 13 the samples were simultaneously withdrawn during operation of the unit; whereas in the remainder of the runs the unit was shut down with increased pressure before sampling. The data indicate that both methods of sampling are satisfactory.

The two tests with propylene:propane gave efficiencies of 5.9 theoretical plates, operating at pressures of 185 and 341 lb./sq. in. abs.

The overall average of the sixteen tests is 6.2 theoretical plates. All these tests are considered satisfactory and much of the deviation from 100% efficiency can probably be attributed to analytical inaccuracies and to uncertainties in the relative volatility data used for the test mixtures. Other sources of deviation from 100% efficiency relate to the operation of the unit and have been discussed earlier.

Equilibrium samples from the individual stages showed deviations of as much as 10% in the theoretical plate value, but in the majority of the tests each stage yielded from 0.94 to 1.06 theoretical plates. Much of this deviation can be attributed to analytical uncertainties.

It is very probable that uncertainties in the analyses and in the relative volatility data used account for deviations of up to ± 0.2 theoretical plates for a six-stage separation. Thus the six-stage unit can be considered to operate as six theoretical plates.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of W. G. Braun, W. L. Brouse, and R. A. Rusk in the design and construction of this unit. They are also grateful to the Esso Research and Engineering Company for financial aid.

NOTATION

a = more volatile component
b = less volatile component
E.F. = enrichment factor = $\frac{y_a}{y_b}\frac{x_b}{x_a}$
n = number of theoretical plates
α = relative volatility
y = concentration in vapor, mole %
x = concentration in liquid, mole %

LITERATURE CITED

1. Myers, H. S., M.S. thesis, Pennsylvania State Univ., University Park, Pennsylvania (June, 1948).
2. Othmer, D. F., *Ind. Eng. Chem.*, **20**, 743 (1928).
3. Herring, J. P., M.S. thesis, Pennsylvania State Univ., University Park, Pennsylvania (September, 1948).
4. Reed, T. M., III, and H. S. Myers, *Ind. Eng. Chem.*, **44**, 914 (1952).
5. Fenske, M. R., *ibid.*, **24**, 482 (1932).
6. ————, H. S. Myers, and Dorothy Quiggle, *ibid.*, **42**, 649 (1950).
7. Hanson, G. H., R. J. Hogan, W. J. Nelson, and M. R. Cines, *ibid.*, **44**, 604 (1952).
8. Private communication.

Manuscript received January 3, 1961; revision received June 12, 1961; paper accepted June 14, 1961. Paper presented at A.I.Ch.E. meeting.