A New Apparatus for Liquid Phase Thermal Diffusion

EDWARD VON HALLE and S. H. JURY
University of Tennessee, Knoxville, Tennessee

A horizontal thermal diffusion column is described in which the inefficiencies caused by the forgotten effect and parasitic remixing are avoided. Experimental results obtained on the separation of water-ethyl alcohol mixtures are presented along with a phenomenological theory for the performance of the column.

Thermal diffusion arises when a uniform mixture is subjected to a temperature gradient; it leads to a state of nonuniform composition. For example, if a homogeneous binary mixture in a closed vessel is heated at one end and cooled at the other, a relative motion of the two components is induced in the mixture, one component tending to concentrate in the hotter region and the other in the colder region. Although the thermal diffusion effect was first observed in a liquid solution more than a century ago, it has only been recently that thermal diffusion has been considered practical for the separation of the components of a liquid mixture.

The first multistage thermal diffusion apparatus utilizing the principle of countercurrent flow was devised by Clusius and Dickel (*1*) in 1938. In this apparatus, now commonly called a *thermogravitational column* or *Clusius-Dickel column*, a confined fluid is subjected to a horizontal temperature gradient. Natural thermal convection currents are thereby established in the column, the flow being directed upward in the neighborhood of the hot wall and downward adjacent to the cold wall. This countercurrent flow multiplies the single-stage separation effect and concentrates at the top of the column that component which is enriched at the hot wall and at the bottom of the column that component which is enriched in the cold wall.

Several practically complete separations of liquid mixtures have been obtained with the thermogravitational column. Yet, despite this apparent success, thermal diffusion has not been accepted industrially as a promising method for separating mixtures, primarily because thermal diffusion is, by its very nature, a thermodynamically irreversible process and therefore requires a relatively high energy consumption to achieve a given separation. Because of this, thermal diffusion is generally a feasible process only when the more conventional methods of distillation, extraction, etc., fail to provide the desired separation economically. It has been shown, however, that thermal diffusion will effect separations where other methods fail. Korsching et al. (*2*) have further enriched an azeotropic mixture of ethyl alcohol and water by thermal diffusion; Jones and Milberger (*3*) have effected separations in mixtures of organic liquids in which the components have had similar molecular weights; and thermal diffusion is known to be an effective method for concentrating isotopic mixtures and was used at Oak Ridge for the large-scale production of UF_6 enriched in the light isotope of uranium, U-235.

Since thermal diffusion is intrinsically an expensive process, a thermal diffusion plant must be designed for maximum efficiency to be competitive with other processes. The Clusius-Dickel column contains certain features which do not promote efficient plant operation. For example, it can be shown that for a given plant product rate and product composition, there is an optimum rate at which material should flow upward and downward in each column comprising the plant. This flow rate in the Clusius-Dickel column is not an independent variable but is a function of the physical properties of the mixture, the temperature difference imposed, and the dimensions of the column. In general it is possible, once the solution behavior is known, to size the equipment to achieve these optimum flow rates, but then the equipment cannot operate efficiently at any other product specifications. However, it is quite conceivable that for some liquid mixtures the velocities of the streams due to natural convection would be so small as to preclude the sizing of the columns to obtain the optimum flow rates. Furthermore, it is not impossible, as one might first expect, for the velocity of the thermal convection stream to vanish. Several cases have been reported in the literature where the more dense component of the mixture is concentrated by thermal diffusion in the vicinity of the hot wall. The density gradient, which arises only because of the concentration gradient between the hot and cold walls, is then directed opposite to the thermally induced density gradient for these mixtures, and the magnitude of the concentration effect may be such as to retard, annul, or invert the normal velocity profile. The toluene-cyclohexane mixture is one in which the upward flow apparently occurs in the neighborhood of the cold wall and the downward flow in the neighborhood of the hot wall. The role played by the concentration gradient in altering the velocity profile and flow rate in the thermogravitational column has been termed *l'effet oublié*, or the *forgotten effect* by de Groot et al. (*4*).

A second inefficiency of the Clusius-Dickel apparatus arises when mixing takes place between the streams flowing countercurrent to each other in the column. It is clear that, in general, mixing of this type will reduce the amount of enrichment that can be obtained per unit length of column, and it is also evident that this type of mixing can readily occur in a thermogravitational column.

For these reasons the primary aim of this research project was the design, construction, and operation of a thermal diffusion column free from the ramifications of the forgotten effect and parasitic remixing. This was accomplished with a horizontal column in which two streams, one above the other and separated by a permeable membrane, moved countercurrently to each other. A vertical temperature gradient applied to the system provided the

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Edward Von Halle is with Union Carbide Nuclear Company, Oak Ridge, Tennessee.

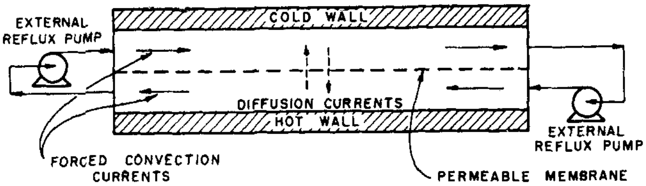

Fig. 1. Schematic diagram of the horizontal thermal diffusion column.

separating potential. The countercurrent flow was achieved with the aid of conventional pumps external to the column. These external pumps allowed the flow rate to be regulated independently of the other process variables, thus providing more flexibility in operation and permitting further economic optimization of the process. The important features of this horizontal thermal diffusion column are shown in Figure 1 for the special case of total reflux.

EXPERIMENTAL EQUIPMENT AND METHODS

The Horizontal Thermal Diffusion Column

The components of the column itself are the hot plate, the flow channel, the diffusion membrane, the cold plate, and the column supporting frame. An exploded drawing of the column is presented in Figure 2. The column was operated with the hot plate forming the lower boundary of the flow channel and the cold plate forming the upper boundary, as shown in the figure.

The hot plate consisted of a steel cavity retainer plate, 23½ in. long, 17⅞ in. wide, and 1⅞ in. thick, on which was mounted a smaller brass plate. Ten holes, ⅝ in. in diameter, were drilled horizontally through the steel plate to accommodate cartridge heaters. The brass plate was 15½ in. long, 15 in. wide, and 0.652 in. thick, and rested on the upper surface of the steel plate, centered between its edges. The lower half of the flow channel was formed by pouring a layer of thermosetting resin on the brass plate and machining the channel into the cured resin. The most satisfactory material found for the construction of the channel was Cycleweld C-17, a resin supplied by the Cycleweld Division of the Chrysler Corporation. Earlier models of the horizontal thermal diffusion column in which the flow channel had been machined in Formica and in Cycleweld C-14 resin had proved unsatisfactory: the former because of the absorption of the liquid mixture by the cellulose structure of the Formica, the latter because of the breakdown of the resin to brass bond at the temperature of the hot plate. The geometry of the flow channel is shown in Figure 3. It was 0.171 in. (0.434 cm.) in width and each half was 0.035 in. (0.089 cm.) in depth. The length of the flow channel was 904 in. (2,300 cm.) and consisted of sixty passes, each 15 in. long, separated by spacers each 0.072 in. wide.

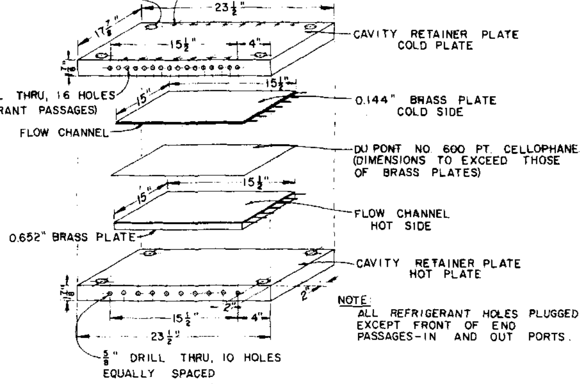

Fig. 2. Exploded drawing of the horizontal thermal diffusion column assembly.

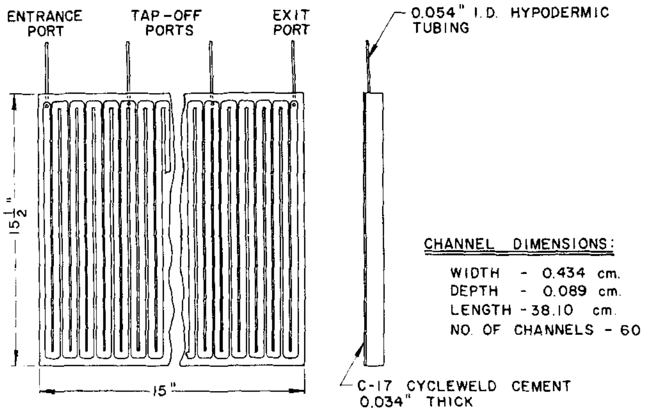

Fig. 3. Details of the flow channel.

The cold plate consisted of a similar steel cavity retainer plate with a brass plate 15½ in. long, 15 in. wide, and 0.144 in. thick centered between its edges and soldered to its lower surface. Sixteen holes, ⅜ in. in diameter, were drilled horizontally through the steel cavity retainer plate, plugged at the ends, and connected together from above, as shown in Figure 2, to form a continuous channel for the circulation of refrigerant. The upper half of the flow channel was a mirror image of the lower half and was fabricated in the same manner. The diffusion membrane was situated between the upper and lower half channels. Only one type of membrane was used in this work, P.T. 600 cellophane, supplied by the Du Pont Company. It is an unwaterproofed cellophane which was 0.0016 in. thick before use. Ten sampling ports were spaced at equal intervals along the channel length between the end reservoirs, five in the upper half channel and five in the lower.

The column was mounted on a rigid steel frame. The cold plate was held in a fixed position at the top of the frame; the hot plate was bolted to the piston of a hydraulic jack and was free to ride on four guide posts. By raising the jack the column could be closed uniformly and securely. The heat was supplied to the lower plate by ten Chromalox cartridge heaters inserted in the holes which had been drilled through the cavity retainer plate for this purpose. Each element was rated at 600 w. and 236 v. They were operated, however, at only one-fourth of their rated power. The upper plate was cooled by the circulation of Freon-12 through the zigzag passage in it. The Freon-12 pressure in the cold plate, which was the evaporator of the refrigeration system, was maintained at about 19 lb./sq.in.gauge by a pressure control valve located at the outlet from the plate. Since it was necessary for the column to run for relatively long periods of time without surveillance, solenoid switches were installed as a safety precaution which would cut off the compressor if the suction pressure dropped below its operating level and which would break the heating circuits if the temperature of the hot plate rose above a predetermined temperature. The temperatures of the hot and cold plates were determined by several strategically located copper-constantan thermocouples affixed to the brass plates.

It was necessary that the pumps used to provide the flow of the liquid mixture through the column meet the following requirements: steady and uniform flow at extremely low volumetric flow rates, low liquid holdup in the pumps, and no leakage of the process fluid. Sigmamotor T-6 pumps were therefore used to provide both the reflux at each end of the column and the product withdrawal. All connecting tubing was 0.054-in. I.D. stainless steel hypodermic tubing.

The concentrations of samples of the liquid mixture withdrawn from the column were determined from their refractive indices; the refractive index of a sample was measured with a Bausch and Lomb Abbe refractometer. The refractometer prisms were maintained at 25°C. by circulating water maintained at this temperature in a temperature controlled water bath.

Procedure

The cellophane sheet to be used as a diffusion membrane was washed with distilled water for 48 hr. to remove the plasticizer. Before being installed in the thermal diffusion column it was washed for about 1 hr. in an ethanol-water solution of the same concentration as that to be used to charge the column. After this pretreatment, the cellophane was placed in its position between the hot and cold plates and the column closed with the jack previously described. The upper and lower channels were then filled with the test solution with a gravity feed arrangement through the end reservoirs. When the column was completely filled, the cartridge heaters were turned on. When the temperature of the hot plate reached the desired value (after 15 to 20 min. of heating), the refrigeration system was turned on. Thirty minutes more were required for the temperature of the hot and cold plates to arrive within a few degrees of their steady state temperatures. At this point the reflux pumps were turned on and the time recorded at the start of the experiment.

The reflux pump which withdrew material from the cold half channel and returned it to the hot side will be designated as the B pump. This pump was set with a coarse control to deliver the desired flow. The other reflux pump, which will be designated as the T pump, was fitted with a fine control. The liquid level in the T pump reservoir was kept constant by the adjustment of this fine control. This method of operation required continuous observation and adjustment of the fine control during the first 12 hr. of each run. This was due to the presence of transient effects. The flow rates were determined by collecting portions of the throughput for a period of time after steady operation had been achieved and weighing them on an analytical balance. Small samples of the liquid mixture, about 0.25 ml., were withdrawn from the pump reservoirs at frequent intervals each day and the concentration of the sample determined from its refractive index.

THEORETICAL CONSIDERATIONS

The starting point for the theoretical developments which follow is the expression for the current of one component of a binary liquid mixture which results when the mixture is subjected to both concentration and temperature gradients. In the absence of a satisfactory formulation of the kinetic theory of liquids, it is expedient to adopt a modified form of the equation derived from the kinetic theory of gases for use in the case of liquid mixture. Thus it is assumed that the diffusive current can be expressed as the sum of two terms, the first due to the thermal gradient and the second due to the concentration gradient. The equation for the current of the one component across a surface at rest with respect to the mixture will be taken as

$$J = \rho[D'x(1-x)\,\mathrm{grad}\,T - D\,\mathrm{grad}\,x]\cdot\vec{n} \tag{1}$$

The convention will be adopted of taking as the specified component that constituent of the binary mixture which has the smaller molecular weight. It follows from this that when the light component tends to become concentrated in the warmer region of the system, the thermal diffusion coefficient for the mixture will be positive, and, conversely, when the component of greater molecular weight tends to become concentrated in the warmer region, the thermal diffusion coefficient for the mixture will be negative. In view of its semiempirical nature, Equation (1) is probably best regarded as simply the defining equation for the coefficient of thermal diffusion D'.

Generally in a well-designed thermal diffusion unit the temperature gradient, and hence the thermal diffusion, will be unidirectional. When one takes this direction as along the r axis, the current of specified component crossing a unit surface perpendicular to the r axis per unit time is

$$J_r = \rho\left[D'x(1-x)\frac{dT}{dr} - D\frac{dx}{dr}\right] \tag{2}$$

STEADY STATE DIFFUSION THROUGH A THIN MEMBRANE

As the experimental part of this investigation involved thermal diffusion through a thin membrane, it is necessary to obtain an equation for the current of specified component through a membrane across which both a concentration gradient and temperature gradient exist. The membrane itself will be considered as a collection of parallel cylindrical pores with diameters sufficiently large that no molecular sieve action is to be encountered. Furthermore, it will be assumed that no chemical interaction takes place between the membrane and either component of the liquid mixture.

Let the temperature on the warm side of the membrane be maintained at T_2 and the concentration at x_2, the temperature on the cold side at T_1 and the concentration at x_1. Since the temperature difference $T_2 - T_1$ and the concentration difference $x_2 - x_1$ across the membrane are usually small, it follows that a satisfactory expression for the current of specified component through the membrane J_m is given by

$$J_m = \sigma\rho\left(D'\frac{\Delta T_m}{\delta}q - D\frac{x_2 - x_1}{\delta}\right) \tag{3}$$

where q is the mean value of the product $x(1-x)$ over the concentration interval under consideration. For the simple model of the membrane employed, it is evident that σ, which is the fraction of the membrane surface available for diffusion, is also equal to the fraction of the total membrane volume occupied by the liquid mixture. When the diffusion through the membrane is accompanied by a net flow of N moles per unit area per unit time of material from the cold to the hot side of the membrane, as shown in Figure 4, the current of specified component through the membrane is given by

$$J_m = \sigma\rho D'\frac{\Delta T_m}{\delta}q - N\frac{x_2 - x_1 e^{\frac{N\delta}{\sigma\rho D}}}{e^{\frac{N\delta}{\sigma\rho D}}} \tag{4}$$

which reduces to

$$J_m = Nx_1 + \sigma\rho\left(D'\frac{\Delta T_m}{\delta}q - D\frac{x_2 - x_1}{\delta}\right) \tag{5}$$

when

$$N << \frac{\sigma\rho D}{\delta}$$

THEORY OF THE HORIZONTAL THERMAL DIFFUSION COLUMN

The theory is based upon the following assumptions:

1. Purely laminar flow of the liquid mixture exists in each channel, and consequently neither vertical nor longitudinal mixing may occur.
2. Variations of the density and thermal conductivity of the liquid are negligible.
3. The diffusion coefficients are constant.
4. The current of specified component through the membrane is given by Equation (5).

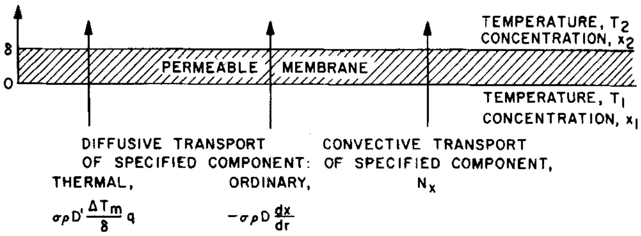

Fig. 4. Diffusion through a thin membrane.

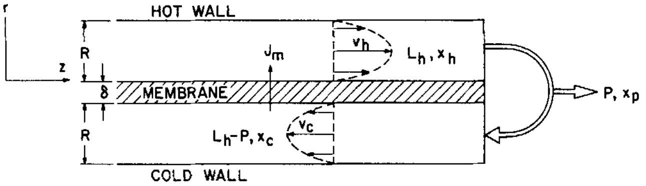

Fig. 5. Simple model of the flow pattern in the horizontal thermal diffusion column.

Two additional assumptions are made to simplify the hydrodynamical problem in the column: that the width of the flow channel is sufficiently greater than its depth so that the distortion of the velocity profile due to the effect of the side walls may be neglected; and that the effect of the variation of the viscosity of the liquid on the velocity profile is negligible. The steady state velocity profile for the convective flow through the column is readily obtained by virtue of these simplifying assumptions. The equation

$$\frac{dp}{dz} = \frac{d}{dr}\left(\mu \frac{dv}{dr}\right) = \mu \frac{d^2v}{dr^2} \qquad (6)$$

where v is the linear velocity of the fluid in the z direction, is derived by setting the net unbalanced force on an element of fluid in the channel equal to zero. Since dp/dz is essentially independent of r, the velocity profile is obtained immediately from Equation (6) by quadrature. The constants of integration are evaluated from the boundary conditions. Since the velocity must vanish at the membrane ($r = 0$) and at the wall ($r = R$), the velocity profile in the upper (hot) channel is given by

$$v_h = \frac{1}{2\mu}\frac{dp}{dz}(r^2 - Rr) \qquad (7)$$

The average velocity in the hot channel $\bar{v}_h$ can be expressed by

$$\bar{v}_h = \frac{1}{R}\int_0^R v_h dr = -\frac{1}{12\mu}\frac{dp}{dz}R^2 = \frac{L_h}{\rho R b} \qquad (8)$$

where L_h is the molar flow rate in the hot channel. The laminar flow velocity profile may therefore be written in the form

$$v_h = \frac{6L_h}{\rho b R^3}(Rr - r^2) \qquad (9)$$

The coordinate system used is shown in the schematic representation of the product withdrawal end of the horizontal thermal diffusion column in Figure 5.

If longitudinal back diffusion is neglected, the equation of continuity which must be satisfied within the body of the liquid mixture in each channel is

$$\frac{\partial(\rho x)}{\partial t} = -\frac{\partial}{\partial r}(J_r) - \frac{\partial}{\partial z}(\rho v x)$$
$$= \frac{\partial}{\partial r}\left[\rho D' \frac{\Delta T_R}{R} x(1-x) - \rho D \frac{\partial x}{\partial r}\right] - \rho v \frac{\partial x}{\partial z} \qquad (10)$$

For the steady state case this reduces to

$$\frac{\partial}{\partial r}\left[\rho D' \frac{\Delta T_R}{R} x(1-x) - \rho D \frac{\partial x}{\partial r}\right] = -\rho v \frac{\partial x}{\partial z} \qquad (11)$$

Equations (9) and (11) will now be used to obtain an expression for the transport of the specified component in the positive direction (toward the product withdrawal end) in the column. The transport of specified component in the $+z$ direction in the hot channel is given by

$$\tau_h = L_h \bar{x}_h = \rho b \int_0^R v_h x dr \qquad (12)$$

The velocity v_h in the channel is given as a function of r by Equation (9); $x(r)$ is obtained from Equation (11) as follows. Equation (11) may be integrated with respect to the variable r to yield an expression for $\partial x/\partial r$. When one notes that the diffusive current, the quantity in brackets in Equation (11), must vanish at the boundary at $r = R$, the result of the integration is

$$\rho D' \frac{\Delta T_R}{R} x(1-x) - \rho D \frac{\partial x}{\partial r} = \int_r^R \rho v_h \frac{\partial x}{\partial z} dr' \qquad (13)$$

A second integration gives

$$x(r) = x_h(0) + \frac{D'}{D}\frac{\Delta T_R}{R}\int_0^r x(1-x)\, dr$$
$$- \frac{1}{D}\int_0^r dr' \int_{r'}^R v_h \frac{\partial x}{\partial z} dr'' \qquad (14)$$

where $x_h(0)$ is the concentration of the specified component adjacent to the membrane in the hot channel. This expression for $x(r)$ is then inserted into Equation (12) to obtain the expression for the transport. Clearly, use has been made of the assumed independence of ρ, D', and D of the coordinate r. Since the maximum variation of the concentration of the specified component in the r direction is limited to a very small value, it is reasonable to assume that the product $x(1 - x)$ and the derivative $\partial x/\partial z$ are also essentially independent of r. Therefore, one may set

$$x(1-x) = \bar{x}_h(1-\bar{x}_h) = \bar{x}_c(1-\bar{x}_c) \text{ and } \frac{\partial x}{\partial z} = \frac{d\bar{x}_h}{dz} \qquad (15)$$

and write the equation for the transport in the form

$$\tau_h = L_h \bar{x}_h = \rho b \left[x_h(0) \int_0^R v_h dr \right.$$
$$+ \frac{D'}{D}\frac{\Delta T_R}{R}\bar{x}_c(1-\bar{x}_c)\int_0^R v_h r dr$$
$$\left. - \frac{1}{D}\frac{d\bar{x}_h}{dz}\int_0^R v_h dr \int_0^r dr' \int_r^R v_h dr'' \right] \qquad (16)$$

The integrals in Equation (16) are easily evaluated with Equation (9) used to express v_h as a function of r, and the transport of the specified component in the $+z$ direction in the upper channel is found to be

$$\tau_h = L_h \bar{x}_h = L_h x_h(0) + \frac{L_h}{2}\frac{D'}{D}\Delta T_R \bar{x}_c(1-\bar{x}_c)$$
$$- \frac{13}{35} R \frac{L_h^2}{\rho D b}\frac{d\bar{x}_h}{dz} \qquad (17)$$

In a similar manner the transport of the specified component in the $+z$ direction in the lower (cold) channel is found to be

$$\tau_c = -L_c \bar{x}_c = -L_c x_c(0) + \frac{L_c}{2}\frac{D'}{D}\Delta T_R \bar{x}_c(1-\bar{x}_c)$$
$$- \frac{13}{35} R \frac{L_c^2}{\rho D b}\frac{d\bar{x}_c}{dz} \qquad (18)$$

The total net transport of the specified component in the $+z$ direction in the column is the sum of τ_h and τ_c. For steady state conditions this net transport must equal the withdrawal rate $P x_P$. Adding Equations (17) and (18) and making use of the material balance relationships

$$L_h \frac{d\bar{x}_h}{dz} = L_c \frac{d\bar{x}_c}{dz} \text{ and } L_h - L_c = P \tag{19}$$

one obtains for the net transport Equation (20):

$$\tau_h + \tau_c = Px_P = L_h[x_h(0) - x_c(0)] + P\bar{x}_c + L_h \frac{D'}{D} \Delta T_R \bar{x}_c(1-\bar{x}_c) - \frac{26}{35} R \frac{L_c L_h}{\rho D b} \frac{d\bar{x}_c}{dz} \tag{20}$$

An expression for the concentration difference across the membrane, $x_h(0) - x_c(0)$, is obtained by taking a material balance around a differential element of length of the cold channel. When Equation (5) is used to evaluate J_m, the current of specified component through the membrane, one obtains the relation

$$L_c \frac{d\bar{x}_c}{dz} = b\rho\sigma \left[D' \frac{\Delta T_m}{\delta} \bar{x}_c(1-\bar{x}_c) - D \frac{x_h(0) - x_c(0)}{\delta} \right] \tag{21}$$

The expression for $x_h(0) - x_c(0)$ obtained from Equation (21) is introduced into Equation (20) to give the desired form of the transport equation:

$$\tau_h + \tau_c = Px_P = P\bar{x}_c + L_h \frac{D'}{D} (\Delta T_R + \Delta T_m)\, \bar{x}_c(1-\bar{x}_c) - \left(\frac{\delta}{\sigma} + \frac{26}{35} R \right) \frac{L_h L_c}{b\rho D} \frac{d\bar{x}_c}{dz} \tag{22}$$

The longitudinal back diffusion which was neglected when Equation (10) was written may now be taken into account by the addition of the term $- 2Rb\rho D(d\bar{x}_c/dz)$ to the above expression for the transport of the specified component. The gradient equation for the case in which the convective flow in the column is laminar is therefore

$$\left[\frac{L_h - P}{b\rho D} \left(\frac{\delta}{\sigma} + \frac{26}{35} R \right) + \frac{2Rb\rho D}{L_h} \right] \frac{d\bar{x}_c}{dz} = \frac{D'}{D} (\Delta T_R + \Delta T_m)\, \bar{x}_c(1-\bar{x}_c) - \frac{P}{L_h} (x_P - \bar{x}_c) \tag{23}$$

where the modification for back diffusion has been included. By analogy with other separation processes the gradient equation may be written in the form

$$S \frac{d\bar{x}_c}{dz} = \psi \bar{x}_c(1-\bar{x}_c) - \frac{P}{L_h} (x_P - \bar{x}_c) \tag{24}$$

where

$$S = \frac{\delta(L_h - P)}{\sigma b \rho D} \left(1 + \frac{26}{35} \frac{\sigma}{\delta} R \right) + \frac{2Rb\rho D}{L_h} \tag{25}$$

and

$$1 + \psi = 1 + \frac{D'}{D} (\Delta T_R + \Delta T_m) \tag{26}$$

The quantity S has the dimension of length and is called the *stage length*; the dimensionless quantity $(1 + \psi)$ is called the *separation factor* of the separation process.

EXPERIMENTAL RESULTS AND DISCUSSION

Experiments were conducted on the separation of water-ethyl alcohol mixtures in the horizontal thermal diffusion column both at total reflux and with continuous product withdrawal. The experimental conditions for some typical runs are shown in Table 1. In runs 5 through 9 a reservoir of large capacity (about 15,000 cc.) was connected to the lower end of the column. Thus, in these runs, called *infinite reservoir operation*, the concentration at the lower end of the column was maintained at a constant value throughout the course of the experiment. Table 2 presents the concentration gradients in the column after steady state conditions had been attained. A typical steady state concentration gradient for total reflux operation is shown graphically in Figure 6. It is clear from these data that separation of the water-ethyl alcohol mixtures was effected by the horizontal thermal diffusion column.

To establish the validity of the theory of the horizontal thermal diffusion column proposed, it is necessary to determine quantitatively the values of the separation factor and the stage length from the experimental results. It is not possible to evaluate both ψ and S from steady state total reflux gradients alone; only the value of the ratio ψ/S can be obtained. Therefore, in addition to the steady state total reflux data, one requires information either on the rate of approach of the column to the steady state or on the separation attained under the condition of continuous product withdrawal. For reasons which are given later it was not possible to use the transient state data in this respect. A value for the stage length was, therefore,

TABLE 1. EXPERIMENTAL VALUES OF COLUMN VARIABLES

Run	Product withdrawal rate, g.-moles/hr.	T pump flow rate, g.-moles/hr.	B pump flow rate, g.-moles/hr.	T_h, °C.	T_c, °C.	Duration of expt., hr.
1-C	None	0.402	0.656	52.9	−3.6	264
2-C	None	0.872	0.756	41.1	−4.8	67
3	None	0.511	0.839	49.3	−4.2	162
4	None	0.304	0.367	59.1	−3.6	96
5-A	None	0.377	0.661	51.9	−3.1	576
6	0.0555	0.525	0.689	55.9	−2.0	166
7	0.1392	0.564	0.661	51.9	−3.1	115
8	0.2066	0.638	0.661	52.4	−3.2	49
9	0.4592	0.900	0.661	52.4	−3.2	46

TABLE 2. STEADY STATE COLUMN CONCENTRATION GRADIENTS

Run		T-Reservoir	Sampling points 1	2	3	4	5	B-Reservoir
1-C	Mole % H_2O	72.1	74.9	77.3	79.0	80.4	81.8	82.9
2-C	Mole % H_2O	99.2	98.4	97.2	95.7	94.0	92.4	90.8
3	Mole % H_2O	67.3	70.1	72.8	74.9	76.6	78.0	79.4
4	Mole % H_2O	21.0	—	23.5	—	26.4	—	28.0
5-A	Mole % H_2O	63.9	68.1	70.8	72.8	74.4	75.7	76.9
6	Mole % H_2O	70.4	72.8	74.4	75.5	76.2	76.6	76.9
7	Mole % H_2O	72.8	74.7	75.7	76.2	76.6	76.9	76.9
8	Mole % H_2O	74.0	75.6	76.8	76.9	76.9	76.9	76.9
9	Mole % H_2O	75.5	76.9	76.9	76.9	76.9	76.9	76.9

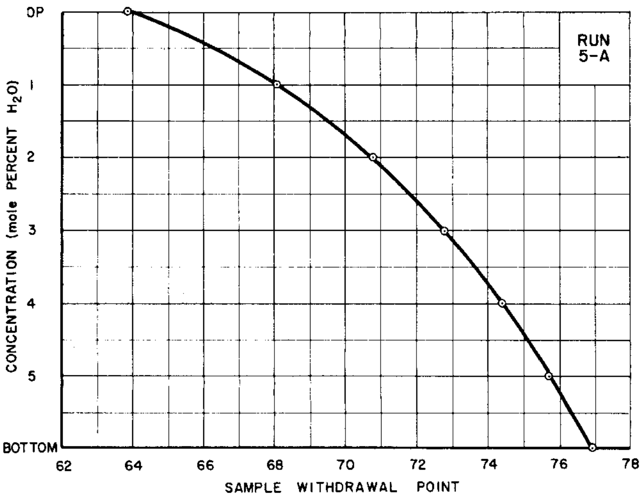

Fig. 6. Steady state concentration gradient for column at total reflux.

calculated by utilizing the information obtained from runs 5 through 9 in which the product rate was varied.

Calculation of the Value of the Stage Length

It follows from Equation (24) that in the case of a column with continuous product withdrawal, ψ and S must satisfy the relationship

$$\int_{x_B}^{x_P} \frac{dx}{\psi x(1-x) - \dfrac{P}{L}(x_P - x)} = \int_0^z \frac{dz}{S} \qquad (27)$$

for each experimental run. In principle, the values of ψ and S are determined by solving simultaneously two equations of the form of Equation (27) representing two runs in which the values of P are different.

In the case under consideration the problem was further complicated by the fact that the flow L varied along the column length. The following analytical procedure was therefore adopted. First, since L could only be measured at the two ends of the column, it was assumed that L varied linearly with distance along the column length. The gradient equation could then be written in the form

$$\frac{dx}{dz} = \frac{\psi x(1-x)}{S} - \frac{P(x_P - x)}{S(A + Bz)} \qquad (28)$$

in which the flow L has been replaced by the linear expression $A + Bz$. Since, under the experimental conditions of runs 5 through 9, the contribution to the stage length of the longitudinal back diffusion term should be negligible, the stage length was expressed by

$$S = S_0(A + Bz - P) \qquad (29)$$

The quantity S_0, termed the *reduced stage length,* may therefore be interpreted as the stage length in a column at total reflux in which the flow L is unity. Similarly, the quantity ψ was corrected for variations in the temperature difference ΔT by the relationship

$$\psi = \psi_0 \frac{\Delta T}{55} \qquad (30)$$

Thus, $1 + \psi_0$ is the value of the separation factor corresponding to an overall temperature difference of 55°C. between the hot and cold walls. For a series of runs in which the values of the concentration are restricted to a relatively small range, ψ_0 and S_0 may be regarded as constants which depend only on the geometry of the column and the physical properties of the liquid mixture.

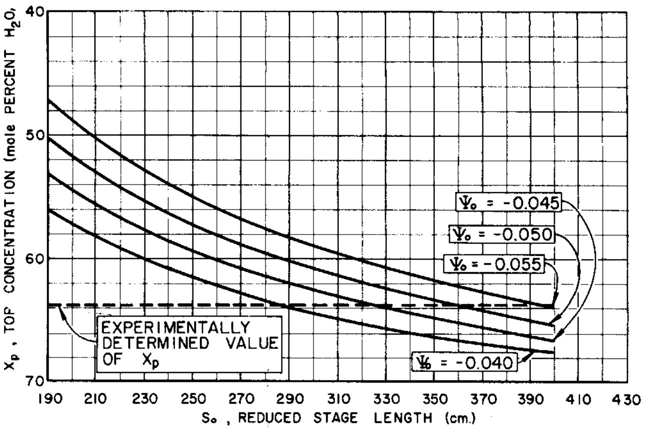

Fig. 7. Results of numerical integration for run 5-A.

Equation (28) was then integrated by using the values for A, B, P, ΔT, and x_B corresponding to run 5-A and with a series of arbitrary values for S_0 and ψ_0. The integration was performed numerically with an IBM 704 electronic data processing machine with the Runge-Kutta procedure. The integration yielded a value of x_P corresponding to each pair of values of ψ_0 and S_0 used. The results of these calculations are shown in Figure 7. The calculations were then repeated with the use of the experimental values corresponding to run 6. The pairs of values of ψ_0 and S_0 which yielded a value of x_P equal to the experimentally obtained values, 63.9 mole % water for run 5-A and 70.4 mole % water for run 6, were then selected. These values of ψ_0 are plotted against the corresponding values of S_0 in Figure 8. The coordinates of the point of intersection of the two curves are, therefore, the true values of ψ_0 and S_0 for the horizontal thermal diffusion column under the experimental conditions of runs 5-A and 6. By this method it was determined that ψ_0 has the value −0.049 and that S_0 has the value 350 cm. when the concentration of the water-ethyl alcohol mixture in the column is in the neighborhood of 70 mole % water. These values are corroborated by the experimental results of runs 7, 8, and 9.

Calculation of the Soret Coefficient for Water-Ethyl Alcohol Mixtures

The value of the Soret coefficient for water-ethyl alcohol mixtures was obtained as a function of the concentration of the mixture by the following procedure which utilizes both the value of S_0 calculated above and the results from the total reflux runs. The value of the ratio ψ_0/S_0 was

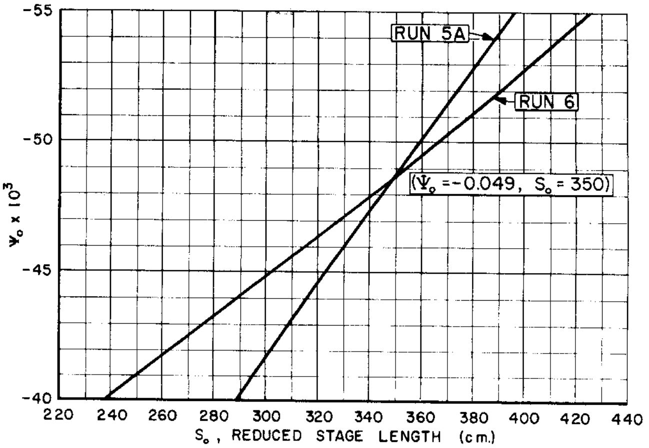

Fig. 8. Determination of S_0 and ψ_0 from the experimental results.

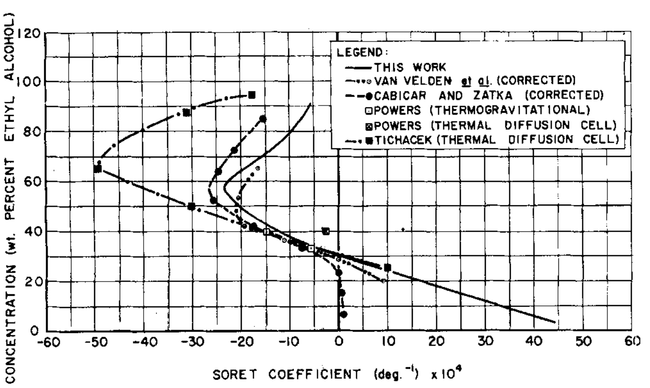

Fig. 9. Values of the Soret coefficient for water-ethyl alcohol mixtures computed from the experimental work of the various investigators.

determined as a function of the concentration of the mixture by means of the relationship

$$\frac{\psi_0}{S_0} = 55\frac{L}{\Delta T}\frac{1}{x(1-x)}\frac{\Delta x}{\Delta z} \qquad (31)$$

which is valid for total reflux operation at steady state conditions and the measured steady state, total reflux concentration gradients. The reduced stage length was obtained as a function of the concentration of the mixture by means of the relation

$$\rho D S_0 = \text{constant} \qquad (32)$$

which follows from the theory when the ratio of the thickness of the membrane to its fraction of free area δ/ϕ is independent of the concentration of the diffusing mixture. The Soret coefficient D'/D was then computed from the equation

$$\frac{D'}{D} = \frac{1}{55}\frac{2R+\delta}{R+\delta}\left(\frac{\psi_0}{S_0}\right)S_0 \qquad (33)$$

The use of Equation (33) to evaluate the Soret coefficient presumes the validity of the laminar flow model for the convective flow in the horizontal thermal diffusion column and applies, in particular, to the case in which the thermal conductivity of the swollen membrane is the same as that of the liquid mixture. The thickness of the swollen membrane was measured and found to be approximately 0.0077 cm.; it was independent of the concentration of the mixture provided that the membrane had been pretreated by swelling in distilled water. The values of the Soret coefficient obtained from this work are shown in Figure 9 along with those which have been obtained by other investigators.

The enrichment obtained in runs 5 through 9 is shown as a function of the product withdrawal rate in Figure 10. The curve represents the value of the enrichment calculated with Equations (27) through (30) and with the values of ψ_0/S_0 calculated from the total reflux gradients. The agreement between theory and experiment is satisfactory.

Discussion of Results

The values of the Soret coefficient calculated from this work and from the experimental results of van Velden et al. (5), from the thermogravitational work of Powers (6), and from the work of Cabicar and Zatka (7) are seen from Figure 11 to be in remarkably good agreement in the concentration range from 30 to 60 wt. % ethyl alcohol. It should be pointed out that in none of these investigations was the experimental accuracy such that the Soret coefficients could be computed to better than ±10%. There has not been sufficient experimental work conducted with concentrations which exceed 60% to define the Soret coefficient very well in this range. All the experimental results indicate that the Soret coefficient remains negative throughout this concentration range, approaching some small value as a limit as the concentration of alcohol approaches 100%. In the range of concentrations from 0 to 30% alcohol, however, there is substantial disagreement as to the value of the Soret coefficient. It is our opinion that in this range the values calculated from this work are the most accurate because the horizontal thermal diffusion column is exempt from the operational instability and theoretical uncertainty which arise when the more dense component is concentrated in the region of the hot wall.

In the concentration range from 5 to 15% alcohol, and with thermogravitational columns with small wall spacings (about 0.025 cm.) used, Korching and Wirtz, van Velden et al., and Cabicar and Zatka all obtained negligibly small enrichments. Two of these groups attributed this phenomenon to a vanishing Soret coefficient over this concentration range; van Velden et al., conversely, attributed it to a very high value of the Soret coefficient and the emergence of the forgotten effect. For the forgotten effect to cause a change in the direction of the separation in a thermogravitational column, $(\partial\rho/\partial x)(\partial x/\partial r)$ must be of opposite sign and larger in magnitude than $(\partial\rho/\partial T)$ $(\partial T/\partial r)$. In the case of small plate spacings this condition implies that

$$\frac{D'}{D} > \frac{1}{x(1-x)}\frac{(\partial\rho/\partial T)}{(\partial\rho/\partial x)} \qquad (34)$$

Therefore, if the forgotten effect were responsible for the inversion of the separation effect observed by van Velden and co-workers at small plate spacings, it follows that the Soret coefficient of the mixture must exceed 270 × 10^{-4} deg.$^{-1}$ when the concentration of the alcohol is 12%, 300 × 10^{-4} deg.$^{-1}$ when the alcohol concentration is 9.5%, and 580 × 10^{-4} deg.$^{-1}$ when the alcohol concentration is 4% in the water-ethyl alcohol mixture.

The values found in this work for the Soret coefficient of water-ethyl alcohol mixtures with alcohol content between 5 and 15 wt. % confirm neither the very low values of Korsching and Wirtz and of Cabicar and Zatka nor the very high values hypothesized by van Velden et al. Therefore, it is concluded that the metastable equilibrium situation which is set up in a thermogravitational column

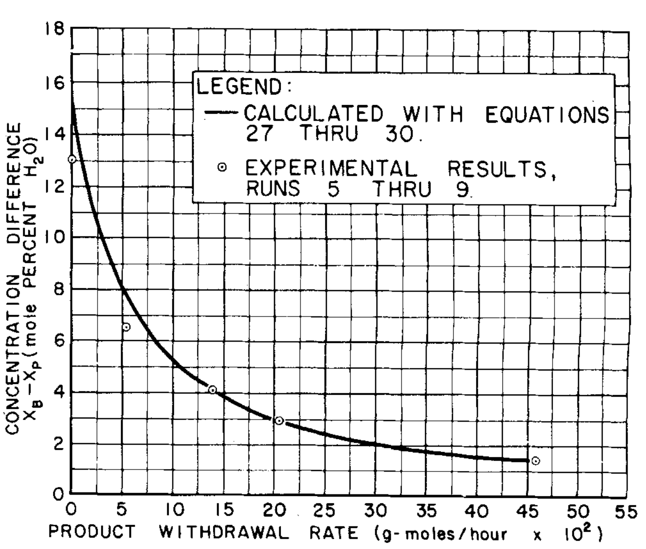

Fig. 10. The enrichment obtained with the horizontal thermal diffusion column vs. the product withdrawal rate.

when the solution in the upper portions of the column is of greater density than the solution in the lower portions of the column causes theoretically unpredictable fluctuations in the velocity profile in the column which make it impossible to interpret the separation data and subsequent calculation of the Soret coefficient.

Validity of the Theory

Several aspects of the theory, although apparently satisfactory, still remain in need of quantitative confirmation. This is due in part to the appearance of a thermo-osmotic effect during the operation of the column.

Thermo-osmosis, in the case under consideration, causes a net transport of solution through the cellophane membrane from the hot region to the cold. This current is in the direction opposite to that predicted by kinetic theory for gases. Riehl (*9*), who was the first to employ a cellophane membrane in a single-stage thermal diffusion cell, also observed this phenomenon.

The presence of a large thermo-osmotic effect has several disturbing consequences. In the first place, since approximately 1 hr. was allowed for the column to attain its operating temperature before the reflux pumps were started, an appreciable flow had already taken place prior to experimental time zero. Second, even though the membranes were washed in distilled water for 48 hr. prior to their use, transient thermo-osmotic effects, similar to those discussed by Alexander and Wirtz (*10*), were observed during the initial periods of operation with each new membrane. The transient effect introduced a control problem and made it difficult to maintain the inventories in the reservoirs at a constant level with the manual system of flow control employed. As a result of these two consequences of the thermo-osmotic effect it was not possible to use the unsteady state concentration measurements taken during the course of operation of the horizontal thermal column for the purpose of evaluating with precision the values of the Soret coefficient.

The theoretical implications of the thermo-osmotic effect are also disturbing. It has been assumed in this work that there is no chemical interaction between the membrane and the solution. The large thermo-osmotic effect observed during the operation of the horizontal thermal diffusion column does, however, indicate the existence of an interaction of some nature between the membrane and the solution. It is not possible, at the present time, because of the lack of knowledge concerning the mechanism of the thermo-osmotic effect, to ascertain whether the separation performance of the column is affected by it. This, perhaps, may best be decided by constructing and operating a column employing a membrane of inorganic material which would not exhibit any thermo-osmotic effects.

Although there may be some doubt as to the validity of the assumption of no chemical interaction between the membrane and the solution on which the theory of the horizontal thermal diffusion column was based, the theory appears quite satisfactory on an ad hoc basis. It led to values of the Soret coefficient which agree quite well with those obtained by previous investigators in the range where their results are judged to be valid.

Comparison Between the Efficiency of the Horizontal Thermal Diffusion Column and That of the Vertical Thermogravitational Column

A comparison of the horizontal thermal diffusion column with the conventional thermogravitational column indicates that a horizontal thermal diffusion column with a negligibly thick membrane would require 4.0% more power than the thermogravitational column. In addition, the capital cost of the horizontal thermal diffusion plant would be somewhat greater owing to the cost of the reflux pumps. In return for this additional expense, the horizontal thermal diffusion column offers a flexibility in the control of the convective flow entirely lacking in the thermogravitational column. Furthermore, in those cases where tne forgotten effect is present, such as in water-ethyl alcohol mixtures of low alcohol content, it appears that the horizontal thermal diffusion column will effect separations of which the vertical thermogravitational column is incapable.

NOTATION

A, B = constants in linear representation of the flow L, Equation (28), Mt^{-1} and ML^{-1} —1, respectively
b = width of channel in the thermal diffusion column, Equation (8), L
D = coefficient of ordinary diffusion, Equation (1), L^2t^{-1}
D' = coefficient of thermal diffusion, Equation (1), $L^2t^{-1}T^{-1}$
J = current of specified component, Equation (1), $ML^{-2}t^{-1}$
J_m = current of specified component through membrane, Equation (3), $ML^{-2}t^{-1}$
J_r = current of specified component in r direction, Equation (2), $ML^{-2}t^{-1}$
L = molar convective flow in hot channel of the thermal diffusion column, Equation (27), Mt^{-1}
L_c = molar convective flow in cold channel of the thermal diffusion column, Equation (18), Mt^{-1}
L_h = molar convective flow in hot channel of the thermal diffusion column, Equation (8), Mt^{-1}
N = net flow through membrane, Equation (4), $ML^{-2}t^{-1}$
$\vec{n}$ = unit vector, Equation (1), L
P = product withdrawal rate, Equation (19), Mt^{-1}
p = pressure, Equation (6), $ML^{-1}t^{-2}$
q = mean value of the product $x(1 - x)$ over the concentration interval under consideration, Equation (3), dimensionless
R = depth of channel in the thermal diffusion column, Equation (7), L
r = coordinate in direction of temperature gradient, Equation (2), L
S = stage length, Equation (24), L
S_0 = reduced stage length (stage length per unit flow), Equation (29), $M^{-1}Lt$
T = temperature, Equation (1), T
ΔT = overall temperature difference between the hot and cold walls of thermal diffusion column, Equation (3), T
ΔT_m = temperature difference across the membrane, $T_2 - T_1$, Equation (3), T
ΔT_R = temperature difference across the channel of the thermal diffusion column, Equation (1), T
t = time, Equation (10), t
v = convective velocity in the thermal diffusion column, Equation (6), Lt^{-1}
v_h = convective velocity in hot channel of the thermal diffusion column, Equation (7), Lt^{-1}
$\overline{v}_h$ = average convective velocity in the hot channel, Equation (8), Lt^{-1}
x = mole fraction of specified component, Equation (1), dimensionless
x_B = mole fraction of specified component at the bottom of the column, Equation (27), dimensionless
x_c = mole fraction of specified component in the cold channel, Equation (18), dimensionless
$\overline{x}_c$ = average mole fraction of specified component in the cold channel, Equation (15), dimensionless

x_h = mole fraction of specified component in the hot channel, Equation (14), dimensionless
$\bar{x}_h$ = average mole fraction of the specified component in the hot channel, Equation (12), dimensionless
x_P = mole fraction of specified component in the product, Equation (20), dimensionless
Z = length of channel in the thermal diffusion column, Equation (27), L
z = coordinate of channel length of the thermal diffusion column, Equation (6), L

Greek Letters

δ = thickness of membrane, Equation (3), L
μ = coefficient of viscosity, Equation (6), $ML^{-1}t^{-1}$
ρ = molar density, Equation (1), ML^{-3}
σ = fraction of membrane surface open to diffusion, Equation (3), dimensionless
τ_c = transport of specified component in the $+z$ direction in the cold channel, Equation (18), Mt^{-1}
τ_h = transport of specified component in the $+z$ direction in the hot channel, Equation (12), Mt^{-1}
$1 + \psi$ = stage separation factor, Equation (26), dimensionless
ψ_0 = coefficient in representation of ψ, Equation (29), dimensionless

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The Phase and Volumetric Relations in the Helium—*n*-Butane System: Part I.

Phase and Volumetric Behavior of Mixtures of Low Helium Concentration

ALLAN E. JONES and WEBSTER B. KAY
Ohio State University, Columbus, Ohio

The *P-V-T-x* phase relations of helium–*n*-butane system were measured in the region of low helium content (up to 10.4 mole % helium). The system exhibits the *gas-gas* equilibrium originally predicted by Kamerlingh-Onnes and Keesom. The term *gas-gas* equilibrium is applied because the critical temperatures of the mixtures are higher than the critical temperature of either component. This behavior is quite unlike that observed in most binary systems, in which the critical temperature of the mixtures lie between those of the pure compounds. As a consequence of the shape of the critical locus curve, the system exhibits isothermal retrograde condensation of the second kind.

Some recent investigators of phase equilibria in binary fluid mixtures have reported the existence of a so-called *gas-gas* equilibrium. Krichevskii and co-workers (*10, 12*) apparently were the first to observe this phenomenon and to study it extensively, although Kamerlingh-Onnes and Keesom (*6*) had predicted many years before that it was possible for a fluid mixture to separate into two phases at temperatures above the critical temperature of either component. Kamerlingh-Onnes and Keesom speculated that both phases should have the properties of gases at such temperatures, and hence gave the name gas-gas equilibrium to this phenomenon. This argument was accepted by Krichevskii and co-workers and they have applied the title gas-gas equilibrium to their experimental observations.

Although the accuracy of this nomenclature has been sharply attacked (*11, 15*), there is no doubt that there are binary fluid mixtures which exhibit two phases in equilibrium at temperatures above the critical temperatures of both pure components. There are two classes of mixtures which exhibit this behavior, both composed of compounds which differ greatly in their critical temperatures. The first class consists of mixtures having one polar and one nonpolar component such as ammonia-nitrogen (*10*). The second class is composed of mixtures containing helium and a heavier compound, either polar or nonpolar (*13*). The distinguishing feature of the latter type is that the critical locus curve (the locus of critical points in *P-T-X* space), when plotted in *P-T* coordinates, leaves the critical point of the less volatile component with a