

The method described here could be extended to the study of mixtures of hydrocarbons and solvents used in extractive distillation. Since one must work at a temperature at which the samples have a high volatility, the method would be suitable over a wide range of temperature, the only limitation being the necessity of maintaining the temperature of the external tubings higher than the bath temperature.

Nomenclature

A_i^o = area of the chromatographic peak for a liquid sample
 A_i = area of the chromatographic peak for a vapor sample
 A, B, C, D = Redlich-Kister parameter
 K_i = vapor-liquid equilibrium constant
 k_i^o = chromatographic response factor for the liquid
 k_i = chromatographic response factor for the vapor
 x_i = mole fraction in liquid phase
 y_i = mole fraction in vapor phase

Greek Letters

$\alpha_{i,j}$ = relative volatility
 γ_i = liquid activity coefficient

π_i = vapor pressure of pure component
 σ = absolute deviation

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Thermal Diffusion: Separation in He-N₂ System with Temperature Gradient in Two Directions

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Separation in a nitrogen-helium system due to combined transverse and vertical temperature gradients was investigated experimentally using a conventional two-bulb system. The transverse gradients were obtained by using various metal inserts inside the tube connecting the two bulbs. Separation was greatly increased over that for simple vertical temperature gradient only. The separation was also strongly pressure dependent, with a maximum separation occurring at an optimum value of pressure. The effect of the width of the annular space was also studied, and an optimum value observed. An elementary analytical model was developed and gave a fair correlation with the observed experimental data and trends.

The separating effect due to thermal diffusion can be greatly enhanced through the use of a transverse temperature gradient, in which case the separation becomes the combined result of thermal diffusion and convection. Clusius and Dickel first reported this effect for a liquid separation column (1) and subsequently for gas mixtures (2, 3). These results promoted considerable research in the ensuing years (9-12). Furry et al. presented a rigorous theory for the separation column (4, 5), which was subsequently modified to a simpler form (8). These analytical and experimental results have been summarized by Grew and Ibbs (6), and in each case the temperature gradient was essentially one directional, i.e., in the transverse direction only. The present research

is concerned with a system involving temperature gradients in both the vertical and transverse directions.

Experimental Equipment and Procedures

The schematic diagram of the experimental equipment is shown in Figure 1. The basic test package consists of two copper cells approximately 95 cc in volume, connected by a 1-in. diameter stainless-steel tube 6 in. long. The lower cell was surrounded with 1/4-W carbon resistors and enclosed in a heat transfer can. Cooling was effected by immersing the can in a cryostat containing liquid nitrogen, and test tempera-

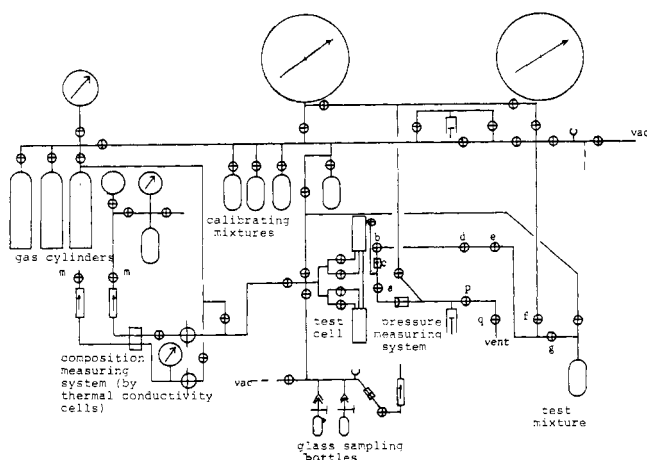


Figure 1. Schematic diagram

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Table I. Experimental and Calculated Results for Helium–Nitrogen Mixture with Vertical and Transverse Temperature Gradients

Mol composition, He (0.502), N₂ (0.498); top cell temperature (*T*₂), 273.0 K; bottom cell temperature (*T*₁); *f* = bottom cell mol fraction; *f*' = top cell mole fraction; insert diam (*d*); insert material: TS, tool steel; SS, stainless steel, BR, brass, AL, aluminum

<i>d</i> *10 ³ , in.	<i>P</i> , atm	<i>T</i> ₁ , K	<i>f</i> _{He}	<i>f</i> ' _{He}	<i>f</i> _{N₂}	<i>f</i> ' _{N₂}	ln <i>Q</i> , Ex
TS-800	3.0	120.0	0.404	0.704	0.596	0.296	1.26
TS-800	3.0	140.0	0.431	0.630	0.569	0.370	0.81
TS-800	3.0	160.0	0.449	0.582	0.551	0.418	0.54
TS-800	15.0	120.0
TS-800	20.0	120.0	0.364	0.724	0.636	0.276	1.52
TS-800	30.0	120.0	0.389	0.706	0.611	0.294	1.33
TS-800	40.0	120.0	0.428	0.654	0.572	0.345	0.95
TS-840	3.0	120.0	0.475	0.580	0.525	0.420	0.42
TS-760	3.0	120.0	0.384	0.651	0.616	0.349	1.10
TS-570	3.0	120.0	0.431	0.638	0.569	0.362	0.84
SS-800	3.0	120.0	0.426	0.608	0.574	0.392	0.74
BR-800	3.0	120.0	0.377	0.721	0.623	0.279	1.45
AL-800	3.0	120.0	0.347	0.744	0.653	0.256	1.70
AL-800	15.0	120.0	0.289	0.894	0.711	0.106	3.03
AL-800	30.0	120.0	0.321	0.867	0.679	0.133	2.62

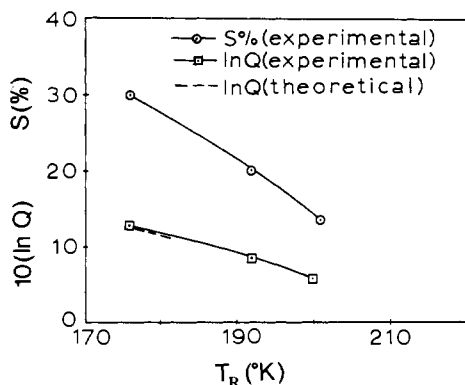


Figure 2. Separation ($S\% = 100 (f'_{He} - f_{He})$) and log separation factor [$\ln Q = (f'_{He}/f_{He})/(f'_{N_2}/f_{N_2})$] vs. log mean temperature $T_R = T_2 T_1 / T_2 - T_1 \ln T_2 / T_1$ (K). Mol composition: He (0.502), N₂ (0.498); pressure, 3 atm; $T_2 = 273$ K; insert material, tool steel (diam 0.800 in.)

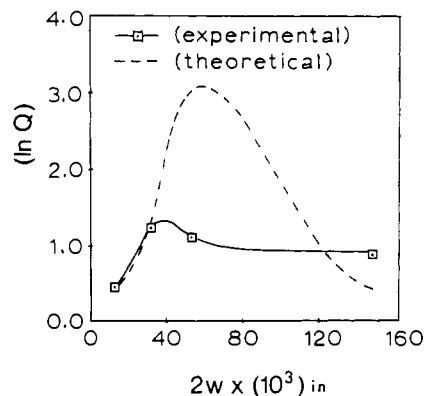


Figure 3. Log separation factor [$\ln Q = (f'_{He}/f_{He})/(f'_{N_2}/f_{N_2})$] vs. width of annular space $2w$ (in.). Mol composition: He (0.502), N₂ (0.498); T_1 , 120 K; T_2 , 273 K; pressure, 3 atm; insert, tool steel (diam 0.840, 0.800, 0.760, 0.570 in.)

tures were maintained by varying electrical power supplied to the resistors from a temperature controller. The upper cell was immersed in a water–ice mixture to maintain its temperature.

The transverse temperature gradient was established by the use of various cylindrical metal inserts, installed inside the tube connecting the two cells. Four sets of thermocouples bonded into holes drilled in the inserts were used to measure the temperature distribution along the inserts. Four thermocouples located on the connecting tube wall were used to estimate the corresponding temperature distribution inside the connecting tube.

Each cell contained two 0.004-in. i.d. capillary sampling tubes, and the test samples were collected in evacuated glass bottles. Nearly equal volumes of samples were withdrawn from each tube. Composition analysis was performed on a Bendix TOF mass spectrometer. Pressure in the test cells was measured by a differential pressure indicator and 16-in. calibrated Heise gages. Test and calibrating mixtures were stored in high-pressure cylinders.

The operating procedures are described in a previous work (7), with the accuracy of the results estimated as follows: temperatures, ± 0.1 K; pressure, $\pm 1\%$; composition, ± 0.5 vol %.

Analytical Model

Because of uncertainties in the actual flow pattern in the annular space and the relatively short column (resulting in significant end effects), the treatment of the rigorous theory of separating columns (4, 5) would appear superfluous. Consequently, the results of this work have been compared with a simplified analytical model based on the analysis by Jones and Furry (8), with the addition of a contribution due to a superimposed vertical temperature gradient. The effects of the two gradients have been assumed to be mutually uncoupled. In the resulting model, the separation factor is given by:

$$\ln Q = \left(\frac{\frac{v \Delta \bar{T}_h}{2 \bar{T}_h} \alpha_h + 2 D \frac{\Delta \bar{T}_v \alpha_v}{\bar{T}_v}}{\frac{v^2 w^2}{D} + 2 D} \right) \times 1$$

where v = convective velocity; \bar{T}_h = mean horizontal temperature of mixture in annular space of connecting tube; $\Delta \bar{T}_h$ = mean horizontal temperature difference between walls of annular space; α_h = thermal diffusion factor based on \bar{T}_h ; D = concentration diffusion coefficient for mixture (based on mean system temperature); $\Delta \bar{T}_v$ = mean vertical temperature difference in annular space; \bar{T}_v = mean vertical temper-

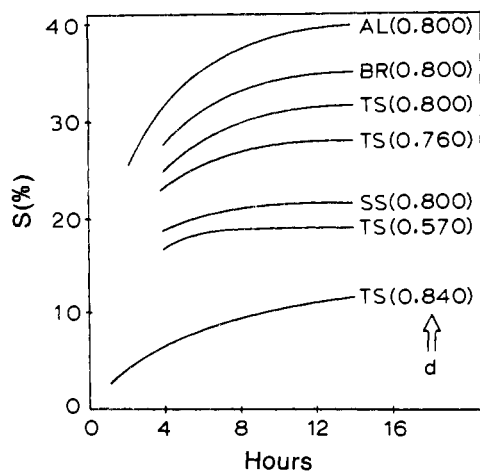


Figure 4. Separation ($S\%$) vs. time (h)
Mol composition, He (0.502), N_2 (0.498); top cell temperature (T_2), 273.0 K; bottom cell temperature (T_1), 120.0 K; pressure, 3 atm; diam of Insert (d), in.

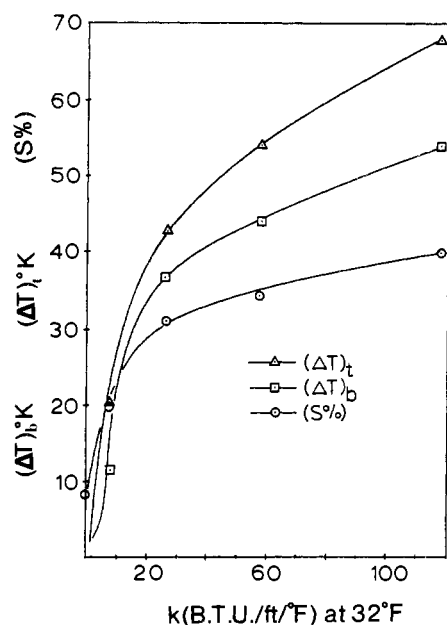


Figure 5. Temperature difference across top of annular space (ΔT_t) vs. temperature difference across bottom of annular space (ΔT_b) and separation ($S\%$)
Thermal conductivity of insert material (k); top cell temperature, 273 K; bottom cell temperature, 120 K; mol composition, He (0.502), N_2 (0.498); pressure, 3 atm

ature; α_v = thermal diffusion factor based on \bar{T}_v ; l = length of annular space; and w = width of annular space.

$$\ln Q = (f'_{He}/f_{He})/(f'_{N_2}/f_{N_2})$$

Results and Discussion

The experimental and calculated results are shown in Table I. The plot of experimental results in Figure 2 indicates the variation in separation factor with the log mean temperature T_r . Figure 3 demonstrates the existence of a maximum separating effect with width. However, the temperature difference across the annular space also increased with the width. Since the convection velocity is proportional to the temperature difference and to the square of the width, these two effects change the (velocity)² term in the expression for

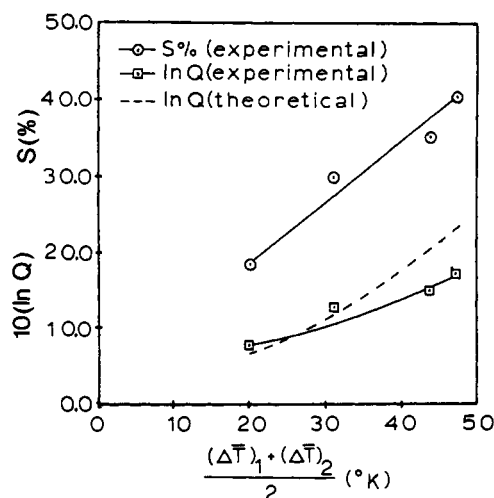


Figure 6. Separation ($S\%$) and log separation factor ($\ln Q$) vs. average temperature difference in annular space $(\Delta \bar{T})_1 + (\Delta \bar{T})_2/2$
Mol composition, He (0.502), N_2 (0.498); T_1 , 120 K; T_2 , 273 K; pressure, 3 atm; diam of inserts (0.800 in.)

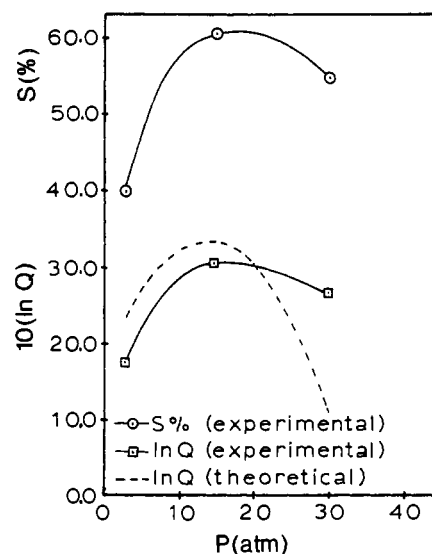


Figure 7. Separation ($S\%$) and log separation factor ($\ln Q$) vs. pressure (atm)
Mol composition, He (0.502), N_2 (0.498); T_1 , 120 K; T_2 , 273 K; insert material, aluminum (diam, 0.800 in.)

the separation factor rapidly. In the theoretical expression for $\ln Q$, $\ln Q$ is a maximum when $v^2 w^2/D = 2D$, with respect to a variation in v .

Figure 4 indicates an exponential approach to the steady state. The case of TS (0.840) with an annular width of 0.013 in. (the smallest width) shows a slower response. This response indicates possible mixing of the two halves of the streams in the annular space to a greater extent than in the other cases with larger widths.

The influence of the thermal conductivity of the insert material is also seen in Figure 4 and also in Figures 5 and 6 (the effect of thermal conductivity being reflected in the temperature gradients across the annular space). Transverse temperature gradients increase with thermal conductivity of the insert material, and the separation increases accordingly.

Figure 7 demonstrates the influence of pressure. This is in agreement with the theory in as far as a maximum separating effect is predicted. Transverse temperature gradients were influenced only very slightly by pressure, and the change in the separation factor can be assumed to be due principally to the effect of pressure.

The assumption is made in developing the theoretical equations that two cells exist due to the crossing of the temperature fields in the annular space. With higher transverse temperature gradients, there would be a tendency for more cells to be formed with secondary flows. This would decrease the separating effect.

It is not very clear what the flow pattern is, at the point where the transverse temperature gradient is zero. Due to the steady reduction of the gradient on both sides of this point, the flows are decelerated and may be reversed. Some mixing of the helium-rich and nitrogen-rich streams in this region seems probable.

Thermal diffusion would occur in each cell, due to the difference in temperature between the end of the rod and the wall of the cell. However, these differences also cause convection currents in the cell as indicated by the fact that the composition of samples from the pair of sampling tubes in each cell was essentially the same. Since it is obvious that

the measured separating factor is sometimes greater than the calculated values, that it is frequently less cannot be attributed to mixing losses alone. The assumptions of the development are very simplifying, and the values of the properties of the mixture are based on very approximate temperatures and compositions. This elementary theory qualitatively indicates the effects of certain factors to be considered in the design of thermal diffusion separation systems with reasonable accuracy.

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Study of Liquid-Vapor Equilibrium in Improved Equilibrium Still

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The design and operation of an improved adiabatic equilibrium still are described. The experimental accuracy of the new still is confirmed. Isobaric liquid-vapor equilibrium values are determined for the carbon tetrachloride-propionic acid system at 710 mm Hg by use of the equilibrium still. Experimental data are verified by the Herington criterion by taking into account the association of propionic acid in the vapor phase.

The design and operation of stage-wise or differential contacting equipment such as a distillation column require reliable liquid-vapor equilibrium data. There are few ideal solutions whose equilibrium relationships can be computed from Raoult's law and gas laws, but by far the large number of systems of industrial importance are nonideal; prediction of the equilibrium composition of such mixtures from theoretical considerations has not been safe. It has been the general practice to determine such basic equilibrium data experimentally. There are various types of equilibrium stills in vogue to determine equilibrium data. In designing and operation of these stills the most common sources of error are due to partial condensation of equilibrium vapor or superheating of vapor in the vapor jacket, occurrence of concentration gradient in the boiling liquid, imperfect mixing of cold condensate with boiling liquid, entrainment of liquid droplets with the vapor, and the presence of concentration gradient in the condensate receiver. The most important stills are those of Othmer (17), Carey and Lewis (7), Jones et al. (10), Gillespie (5), Ellis (4), and many others based on these designs.

Although these stills have been used with some degree of success, certain sources of error (mentioned above) appear to be inherent in each type, and there is a real need for an apparatus which is not only free from many of the usual sources of error, but also simple in design, construction, and operation. Mostly isobaric data are used for the design purpose of industrial contacting equipment, whereas isothermal data provide information on interactions in solutions. The most satisfactory and useful still for obtaining adiabatic data is Othmer's. Othmer's apparatus and those based on it are simple in design and construction and need very little attention during operation, whereas other types require accurate fabrication and very careful attention during their operation.

The present paper deals with the design and operation of an improved adiabatic equilibrium still and the collection of liquid-vapor equilibrium data with this still, for the system propionic acid-carbon tetrachloride at 710 mm Hg—not so far reported in the literature.

Description and Operation of Improved Equilibrium Still

The new still, shown in Figure 1, is the modified version of the Othmer still, and, as such, the essential features of the latter still are retained in its design. The still is modified to prevent or minimize as far as possible the errors due to the different sources listed earlier.

Various methods have been adopted to prevent refluxing of vapor condensate in the vapor space of the still. It is not possible to reduce the heat losses to a practicable limit by insulation alone. This is done either by jacketing the vapor line with the same vapor or by using some form of external compensating heater. However, vapor jacketing alone does not