

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.**

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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

appear to be an effective means of reflux prevention, particularly with liquids of high boiling point. Thin-film rectification with respect to a more volatile component can occur on the outer body of the still above the reboiler while adaption of the compensating heater is critical to proper operation. Insufficient heat supplied by the heater coil means gradual condensation of vapors; excessive heat may lead to nonequilibrium total evaporation of the droplets sprayed on the walls. In the author's still, to reduce the heat losses, the entire vapor space is surrounded by a vacuum jacket, evacuated to a pressure below  $1 \mu$ . The vacuum jacket is further silvered to reduce radiation losses.

As Ellis has pointed out, Othmer still suffers from two main drawbacks, the presence of concentration gradient in the bulk of the reboiler liquid and imperfect mixing of the condensate with the reboiler liquid. In the design of this modified still, these drawbacks are completely eliminated by using a thermosyphon heat exchanger actuated on the temperature-induced density difference principle. This removes axial and radial concentration gradient in the reboiler and provides for accurate equilibrium composition. This is confirmed by the identical concentration of liquid samples drawn simultaneously from cocks  $K_1$  and  $K_2$ . The heating element of the reboiler is encased in a protecting pyrex tube to prevent the coil from any corrosive action of the reboiler liquid. It is important that the entire heating element be below the liquid level to avoid superheating of vapor. The reboiler is lagged with an asbestos-magnesia mixture.

Entrainment of liquid droplets into the vapor is prevented by providing a baffle to the vapor tube of the still. This has been confirmed by the following simple test. The reboiler is charged with 20% KCl solution, the condensate receiver filled with distilled water, and the system allowed to boil at a constant rate for 6 h, at the end of which the content of the condensate receiver is tested for chloride with silver nitrate solution. Chloride content in the condensate receiver solution is negligibly small.

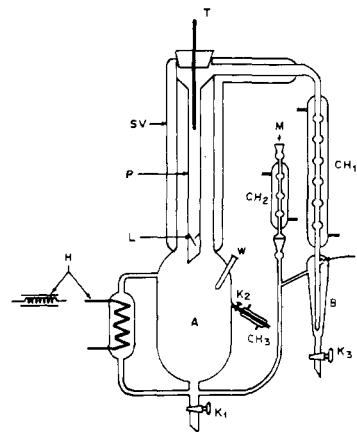
Development of concentration gradient in the condensate receiver is practically eliminated by dipping the condensate leading tube into the bottom of the receiver. For quick establishment of steady state, holdup of the receiver is minimized by making the receiver taper downward.

The equilibrium is attained within 45 min as indicated by the constancy of the equilibrium temperature recorded by a standard mercury thermometer. However, to obtain reliable results, it may be necessary to recirculate the vapor phase for about 2 h before the samples are drawn for analysis. Equilibrium data of the system ethanol-water, thus collected with the still at 760 mm Hg, are found to be in close agreement with the reported values of Carey and Lewis (7), as shown in Figure 2 and Table I. This fact confirms the experimental accuracy of the new equilibrium still.

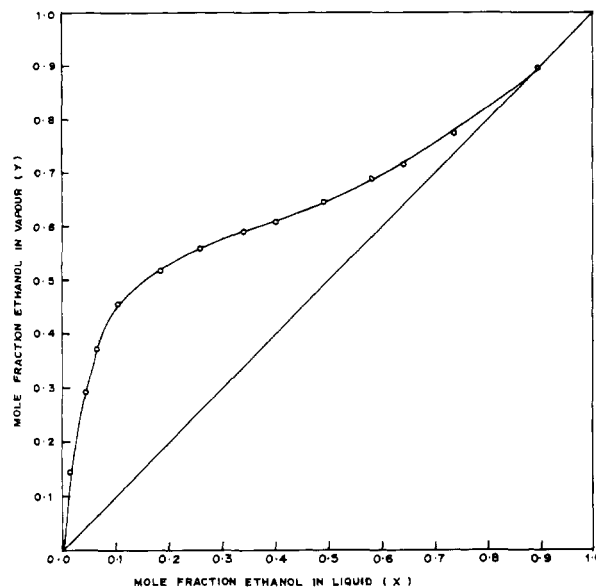
The apparatus can be used not only for miscible systems at subatmospheric and atmospheric pressures using a suitable type of cocks but also for partially miscible systems provided with a suitable mechanically stirred condensate receiver.

#### Liquid-Vapor Equilibrium of Propionic Acid-Carbon Tetrachloride System at 710 mm Hg

Separation of propionic acid from its aqueous solution cannot be effected by fractional distillation due to the formation of azeotropic mixture. This can be accomplished through the liquid-liquid extraction using carbon tetrachloride (9) as solvent. The design of the distillation column for subsequent recovery of propionic acid from the solvent phase requires isobaric phase equilibrium data. As no such data are available in the literature, the present investigation was undertaken to provide liquid-vapor equilibrium data of the system pro-



**Figure 1.** Improved adiabatic vapor-liquid equilibrium still  
A, boiling flask; B, condensate receiver; CH<sub>1</sub>, CH<sub>2</sub>, CH<sub>3</sub>, coolers; K<sub>1</sub>, K<sub>2</sub>, K<sub>3</sub>, cocks; P, vapor tube; H, electric heater; S, slot opening; L, baffle; SV, silvered vacuum jacket; T, thermometer; M, to manostat; W, thermowell



**Figure 2.** X-Y diagram for ethanol-water system at 760 mm Hg. Solid line, data of Carey and Lewis (7); circles, experimental data of author

**Table I.** Experimental Equilibrium Data for System Ethanol-Water at 760 mm Hg

$T, ^\circ\text{C}$	$x_{\text{alc}}$	$y_{\text{alc}}$	$X_{\text{alc}}$	$Y_{\text{alc}}$	$\gamma_{\text{alc}}$	$\gamma_{\text{water}}$
96.10	3.75	29.85	0.0150	0.1425	4.963	1.026
92.20	10.52	51.13	0.0439	0.2901	3.939	1.047
90.45	14.91	59.96	0.0641	0.3690	3.629	1.398
86.10	23.11	68.14	0.1051	0.4552	3.189	1.023
83.51	36.97	73.30	0.1863	0.5171	2.275	1.104
82.25	47.47	76.43	0.2610	0.5589	1.844	1.163
81.30	57.15	78.68	0.3425	0.5901	1.538	1.260
80.65	63.31	79.93	0.4025	0.6085	1.383	1.360
79.90	71.31	82.33	0.4925	0.6454	1.233	1.496
79.20	78.14	85.07	0.5825	0.6902	1.147	1.635
78.83	82.12	86.58	0.6421	0.7160	1.095	1.778
78.40	87.90	89.80	0.7394	0.7753	1.057	1.971
78.12	95.61	95.61	0.8950	0.8950	1.010	2.303

propionic acid-carbon tetrachloride at 710 mm Hg using the author's improved equilibrium still.

**Materials.** Carbon tetrachloride. Analar grade carbon tetrachloride from BDH Ltd., London, containing 0.0015% non-volatile matters, 0.0025% absorbed oxygen, 0.005% carbon disulfide and 0.02% water as impurities, was used.

**Propionic acid.** Reagent grade propionic acid from Naarden Chemical Co., Holland, was used. The purity was 99.5% as determined by titration with standard alkali.

The physical properties of these chemicals together with the literature values are given in Table II.

**Experimental procedure.** The basic equilibrium data were obtained at 710 mm Hg using the author's equilibrium still as shown in Figure 1. The still was charged with 250 cc of mixture. The drying tower, filled with anhydrous silica gel, was connected to the still to prevent absorption of moisture by the mixture. The cooling water to the condensers was turned on. The reboiler electric heater voltage was adjusted to obtain 8 ml/min distillation rate. At this rate the entrainment was nil as tested earlier. The equilibrium was attained within 1 h as indicated by the constancy of the equilibrium vapor temperature, recorded by the standard mercury thermometer. However, the vapor phase was recirculated for 2½ h before samples were simultaneously drawn from cocks K<sub>2</sub> and K<sub>3</sub> for analysis. The reboiler was then filled with a new mixture, and the entire experimental procedure was repeated.

The weight % fatty acid in each of the samples was determined by titrating against standard sodium hydroxide solution using phenolphthalein. Prior to titration, ethanol was added to each sample to maintain homogeneity during titration.

**Treatment of data.** The liquid-phase activity coefficient of a component, when equilibrium is established between a nonideal liquid solution and an ideal gas mixture, is given by

$$\gamma_i = \frac{P_i}{x_i p_i^\circ} = \frac{y_i \pi}{x_i p_i} \quad (1)$$

Because of the extensive vapor-phase association of propionic acid, the activity coefficient of the propionic acid-carbon tetrachloride system cannot be calculated by the above equation. This case requires modified techniques for correlating and checking the thermodynamic consistency of equilibrium data. In this case,  $\gamma_i$  in Equation 1 should be termed as the coefficient of deviation from Raoult's law, which will be symbolized as  $\Delta_i$ . Assuming vapor-phase nonideality is due solely to association, Hansen et al. (6) developed the following relationship for the calculation of the fugacity of the fatty acid which associates in the vapor phase.

$$\ln \frac{f_A}{P_A} = \int_0^{P_A} \left( \frac{1}{P_1 + 2P_2 + 3P_3} - \frac{1}{P_A} \right) dP_A \quad (2)$$

$$= \int_0^{P_A} \left( \frac{1}{P_1 + 2K_2 P_1^2 + 3K_3 P_1^3} - \frac{1}{P_A} \right) dP_A \quad (3)$$

$$= \int_0^{P_A} \left( \frac{1}{P_1} \frac{dP_A}{dP_1} - \frac{1}{P_A} \right) dP_A = \ln \frac{P_1}{P_A} \quad (4)$$

whence

$$f_A = P_1 \quad (5)$$

Table II. Physical Properties of Chemicals

Reagent	Bp, °C, 760 mm Hg	Density at 30 °C, g/ml	Refractive index at 30 °C	Ref
Propionic acid	141.0 (140.99)	0.98255 (0.9826)	1.3826 (1.3827)	(2)
Carbon tetrachloride	76.5 ± 0.1 (76.5)	1.5746 (1.5745)	1.45407 (1.45409)	(2)

The value of  $P_1$ , the partial pressure of the monomer, can be obtained by solving the following expression, derived from the definitions of  $x$  and  $K$ .

$$K_3(3 - 2x_A)P_1^3 + K_2(2 - x_A)P_1^2 + P_1 - x_A \pi = 0 \quad (6)$$

The data of Taylor and Bruton (12) are adopted for the equilibrium association constant of propionic acid. According to Taylor and Bruton, trimer formation is negligible and the equilibrium constant for dimer formation for the temperature range of 50–150 °C is given by

$$\log K_2 = \frac{3316}{T} - 10.834 \quad (7)$$

The activity coefficients were then calculated from Equations 5 and 6 and the main equation

$$\gamma_i = \frac{f_i}{x_i p_i} \quad (8)$$

vapor pressure ( $p_i^\circ$ ) used in Equation 8 was taken from smooth plots of data reported for carbon tetrachloride (7) and for propionic acid (3).

### Sample Calculation

Considering an equilibrium temperature of 93.4 °C at vapor pressure of carbon tetrachloride ( $p_1^\circ$ ) = 1235 mm Hg. At 93.4 °C vapor pressure of propionic acid ( $p_2^\circ$ ) = 135.2 mm Hg. From Equation 7,  $K_2$  = 0.0163. Raoult's law deviations ( $\Delta_i$ ) are calculated from Equation 1 as follows:

$$\Delta_1 (\text{for CCl}_4) = \frac{Y_1}{X_1 p_1} = \frac{0.8314 \times 710}{0.2169 \times 1235} = 2.204$$

Similarly  $\Delta_2$  (for propionic acid) = 1.131.  $P_1$ , the propionic acid monomer partial pressure, is calculated from Equation 6. Substitution of the value of  $K_2$  in Equation 6 gives

$$0.0163(2 - 0.7831)P_1^2 + P_1 - 0.7831 \times 710 = 0$$

This equation is solved quadratically to give

$$P_1 = 144.1 \text{ mm Hg}$$

From Equation 5,  $P_1 = f_A$  (or  $f_2$ ). Substitution of the value of  $f_A$  (or  $f_2$ ) in Equation 8 gives

Activity coefficient for propionic acid ( $\gamma_2$ ) =

$$\frac{f_2}{x_2 p_2^\circ} = \frac{144.1}{0.7831 \times 135.2} = 1.360$$

and

Activity coefficient for carbon tetrachloride ( $\gamma_1$ ) =

$$\frac{710 - 144.1}{0.2169 \times 1235} = 2.112$$

### Calculation of Herington Test Parameters

$$D = \frac{100 \times I}{\Sigma} = \frac{100 \times 3.0}{52} = 5.77$$

and

$$J = \frac{150 \Theta}{T_{\min}} = \frac{150 \times 64.2}{347.8} = 27.69$$

### Results and Discussion

The experimental equilibrium temperature, the liquid and vapor mole fractions, vapor pressures of propionic acid, calculated values of the coefficient of deviation from Raoult's law, and the activity coefficients are listed in Table III. The

Table III. Equilibrium Data for System Propionic Acid–Carbon Tetrachloride at 710 mm Hg

Temp, °C	$x_1$	$y_1$	$X_1$	$Y_1$	$\Delta_1$	$\Delta_2$	$\gamma_1$	$\gamma_2$	$p_2^\circ$ , mm Hg	$f_A$ , mm Hg	$K_2$
74.8	94.12	99.45	0.8853	0.9886	1.102	1.206	1.076	3.656	58.5	24.53	0.0502
76.0	85.82	99.02	0.7446	0.9800	1.263	0.8580	1.214	2.511	64.8	41.57	0.0464
78.4	72.57	98.19	0.5602	0.9632	1.643	0.8194	1.553	1.985	72.5	63.28	0.0399
81.4	61.57	97.14	0.4356	0.9423	1.760	0.8810	1.652	1.760	82.4	81.83	0.0332
84.4	52.76	95.69	0.3497	0.9143	1.933	0.9872	1.820	1.602	94.8	98.72	0.0276
86.2	49.98	95.03	0.3249	0.9020	2.101	1.012	1.841	1.543	101.9	106.1	0.0250
90.0	42.15	92.75	0.2598	0.8604	2.095	1.607	2.003	1.419	120.0	126.0	0.0200
93.4	36.50	91.11	0.2169	0.8314	2.204	1.131	2.112	1.360	135.2	144.1	0.0163
99.0	28.14	87.72	0.1587	0.7747	2.432	1.137	2.368	1.241	167.2	174.5	0.0120
105.1	22.87	81.82	0.1250	0.6844	2.288	1.219	2.370	1.124	210.1	206.5	0.00863
110.8	17.45	76.03	0.0924	0.6043	2.309	1.063	2.525	1.001	265.0	240.7	0.00639
115.8	12.88	69.08	0.0710	0.5182	2.253	1.132	2.689	0.8966	325.2	270.9	0.00495
121.0	8.91	58.01	0.0450	0.3996	2.416	1.131	3.445	0.8097	395.0	305.4	0.00382
123.8	7.66	52.17	0.0384	0.3443	2.274	1.113	3.598	0.7720	435.2	323.1	0.00332
125.6	5.90	46.95	0.0293	0.2989	2.492	1.110	4.402	0.7491	462.0	335.9	0.00304
127.3	5.59	41.65	0.0277	0.2560	2.191	1.109	4.392	0.7251	490.2	345.6	0.00281
128.9	3.44	36.23	0.0168	0.2149	2.839	1.091	6.543	0.7009	519.8	358.3	0.00260
132.0	2.91	25.20	0.0142	0.1398	2.118	1.076	7.115	0.6639	575.2	376.5	0.00225
134.3	0.78	13.12	0.0037	0.0678	3.771	1.073	24.82	0.6369	619.5	393.2	0.002028

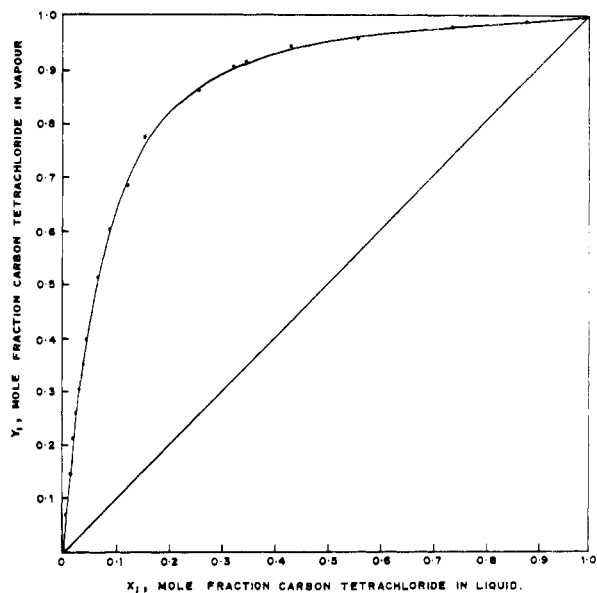


Figure 3. X-Y diagram for propionic acid-carbon tetrachloride system

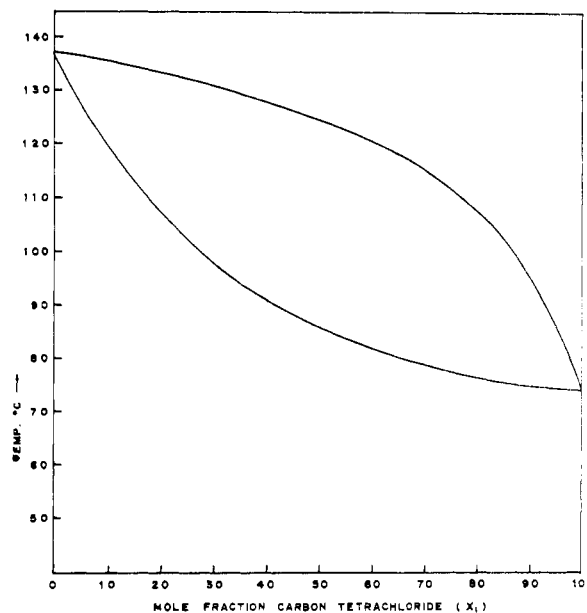


Figure 5. Temperature-composition curve for propionic acid-carbon tetrachloride system

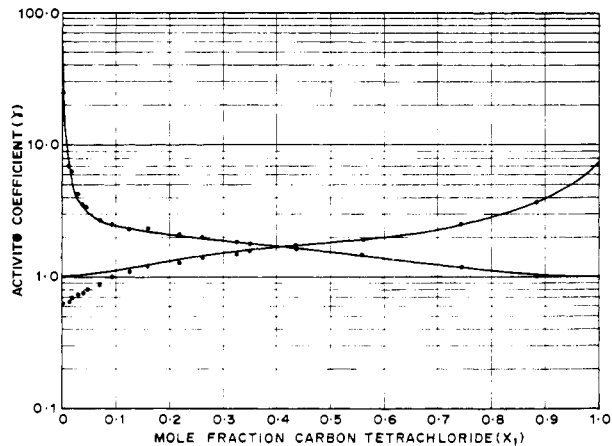


Figure 4. Activity coefficient-composition curve for propionic acid-carbon tetrachloride system at 710 mm Hg

experimental liquid-vapor equilibrium curve is shown in Figure 3. The activity coefficient-composition plot is given in Figure 4. The boiling point-composition diagram is presented in Figure 5.

The experimental data collected, being isobaric, cannot be tested by the Van Laar equation fitting since the standard states for activity coefficient are temperature dependent. Application of the Herington criterion for verification of such isobaric data seems to be possible. According to the Herington generalization (7), the data are supposed to be thermodynamically consistent if  $D - J$  is less than 10, where  $D = 100 / \Sigma$  and  $J = 150 \Theta / T_{\min} \cdot D$  for the system propionic acid-carbon tetrachloride is determined using the curve given in Figure 6.

Results of applying the Herington test to the data are presented in Table IV. Accordingly, the data appear to be inconsistent for the calculations based on the deviations from Raoult's law and consistent for the calculations based on the

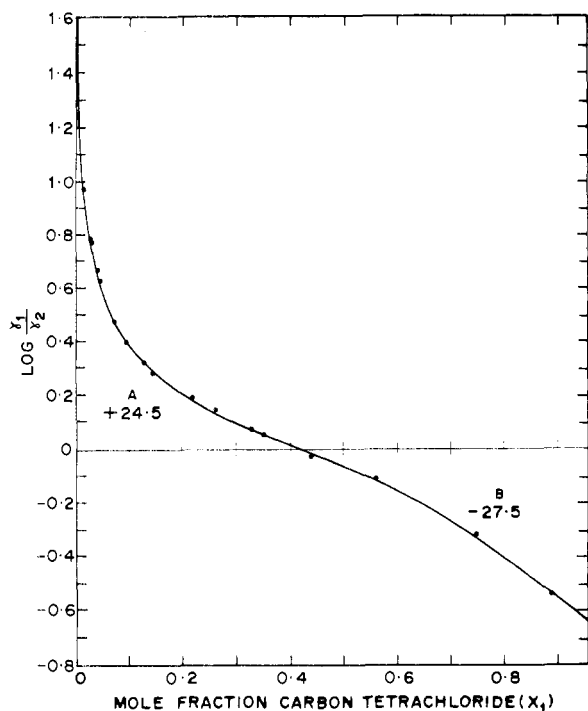


Figure 6. Redlich and Kister plot for propionic acid-carbon tetrachloride system at 710 mm Hg

Table IV. Herington Test Data for System Propionic Acid-Carbon Tetrachloride

$D\Delta$	$D$	$J$	$D\Delta - J$	$D - J$
85.43	5.77	27.69	+57.74	-21.92

assumption of vapor-phase association of propionic acid. The latter findings could have been proved conclusively from exact knowledge of association constants since there is no reason to believe that with a recirculation type of still the residence time falls short for the vapor to attain association equilibrium.

## Acknowledgment

Thanks are extended to Niranjan Singh for his helpful suggestions in the fabrication of the apparatus.

## Nomenclature

- $f_A$  = fugacity of fatty acid  
 $K$  = equilibrium constant  
 $K_2, K_3$  = dimerization and trimerization equilibrium constants, respectively  
 $p^\circ$  = vapor pressure of pure component, mm Hg  
 $P$  = partial pressure, mm Hg  
 $T$  = temperature, K  
 $X$  = mole fraction in liquid  
 $Y$  = mole fraction in vapor  
 $x$  = weight % in liquid  
 $y$  = weight % in vapor  
 $\gamma$  = activity coefficient defined by Equation 8  
 $\Delta$  = coefficient of deviation from Raoult's law defined by Equation 1  
 $\pi$  = total pressure, mm Hg  
 $I$  = algebraic sum of areas  $A$  and  $B$  in Figure 6  
 $\Sigma$  = sum of the magnitudes of areas  $A$  and  $B$  in Figure 6  
 $\Theta$  = overall range of boiling points of the system at 710 mm Hg  
 $T_{\min}$  = lowest measured boiling temperature, K

## Subscripts

- $A$  = fatty acid  
 $1$  = carbon tetrachloride  
 $2$  = propionic acid  
 $i$  =  $i$  component

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