mental data. Variations within the cell were ± 0.2°F. during circulation and ± 2 lb./sq.in.abs. during circulation, settling, and sampling.

Materials Used

The methane and *n*-hexane were of research grade with stated purity of 99.9%. The nitrogen was dry research grade with a purity of 99.85%. Independent analyses on the mass spectrometer and the gas chromatograph confirmed these purities.

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Correlations of Selectivity Parameters for Separations Extractions of Hydrocarbons with Fluorochemicals

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The equation ln $\beta^1_2 = \epsilon^1_2\, x_S^2/T$ adequately represents the variation of the separation factors for the extraction of hydrocarbon mixtures with fluorochemicals. The selectivity parameter ϵ^1_2 is a measure of the selectivity of a solvent for hydrocarbons 1 and 2 which is independent of the experimental conditions. With a given solvent it is possible to develop a correlation between ϵ_j^i for pairs of hydrocarbons and the heats of vaporization of these hydrocarbons. A group contributions method is also successful in correlating the selectivity parameters. The three fluorochemicals in these experiments, $(C_4F_9)_3N$, C_7F_{14}, and $C_8F_{16}O$, had essentially the same selectivity for hydrocarbon separation which one would expect on the basis of their essentially identical solubility parameters.

If we consider that, at equilibrium between two phases of a multicomponent system, the activity of each component must be the same in both phases, then, by definition

$$a_{1j} = x_{1j}\gamma_{1j} = a_{1i} = x_{1i}\gamma_{1i} \qquad (1)$$

For the two compounds to be separable by liquid-liquid extraction, the ratios of the distribution coefficients for the two compounds between the two phases must be different than unity.

$$(x_{1i}/x_{1j})/(x_{2i}/x_{2j}) = \beta_2^1 \neq 1 \qquad (2)$$

For convenience we may say that in order to extract component 1 from component 2, with a given solvent, $\beta_2^1 > 1$. This quantity β is sometimes called the selectivity (*16*), but it seems somewhat better to refer to the quantity ln β (or log β) as the selectivity (*1*), since with this definition a nonselective solvent has a selectivity of zero rather than one.

Substituting the first set of equations into the definition of the separation factor β one obtains

$$\beta_2^1 = (x_{1i}/x_{1j})/(x_{2i}/x_{2j}) = (\gamma_{1j}/\gamma_{1i})/(\gamma_{2j}/\gamma_{2i}) \qquad (3)$$

Here β is defined in terms of the activity coefficients of the two compounds to be separated in the two phases. If one considers the extraction of a mixture of hydrocarbons with a solvent, one phase *b* will be predominantly hydrocarbon and the other *a* will be predominantly solvent. To a reasonable approximation hydrocarbons form ideal mixtures and the activity coefficients of the hydrocarbons 1 and 2 in the predominantly hydrocarbon phase *b*, γ_{1b}, and γ_{2b} will be of the order of unity, as will be their ratio. This ratio also will be an insensitive function of the concentration of the solvent in the predominantly hydrocarbon phase *b*, so that

$$\beta_2^1 \cong 1/(\gamma_{1a}/\gamma_{2a}) \qquad (4)$$

That is, the separation factor is the inverse ratio of the activity coefficients of the two components to be separated in the predominantly solvent phase *a*.

Many equations can express the dependence of activity coefficients on concentration of single-phase binary mixtures; they are generally of the form

$$T \ln \gamma_{1j} = A_{1j} x_{2j}^2 F(x_2, x_1) \qquad (5)$$

although the temperature is not always explicity given. The lowest power of the concentration which can occur and satisfy the Gibbs-Duhem equation is x^2 (*9*) and this term is the only one occurring in the "zeroth approximation" of Guggenheim (*8*) for which random mixing is assumed, even with a nonzero energy of mixing. In the "quasichemical" treatment, which is a somewhat more complicated treatment involving only a single energy interaction term but no longer assuming complete randomness, a power series in mole fraction results (*8*). Further, if one considers the deviations from ideality to be due to association or complexes, then $\ln \beta$ is expressed as another power series in mole fractions involving these association complex equilibrium constants (*9*). In general, however, no precise physical significance can be attached to these coefficients in F(concentration), and the form and number of terms are determined by the presumed accuracy of the data.

For weakly interacting hydrocarbon-solvent systems one may reasonably expect that the activity coefficients of the hydrocarbons in the predominantly solvent phase a, and hence the selectivity, are determined primarily by the total concentration of hydrocarbons in phase a and to a much smaller extent by the distribution of hydrocarbon components. In an analogy to Equation (5), one would then postulate for a multicomponent system of hydrocarbons and solvent that

$$T \ln (\gamma_{2a}/\gamma_{1a}) = T \ln \beta_2^1 = \epsilon_2^1(1 - x_{HC})^2 F(x_{HC}, 1 - x_{HC}) = \epsilon_2^1 x_s^2 F(x_s, x_{HC}) \quad (6)$$

in which ϵ_2^1 is the selectivity parameter, a constant depending only upon the two compounds being separated and the solvent, and $F(x_s, x_{HC})$ is some function of the solvent concentration and total hydrocarbon concentration.

The simplest equation which one might expect to be a reasonable fit to the relatively imprecise selectivity data is

$$\ln \beta_2^1 = \epsilon_2^1 x_s^2/T \quad (7)$$

This equation contains one parameter ϵ_2^1, which depends on the two components to be separated and the solvent. It would be a good measure of the selectivity of the solvent for that pair of compounds and one which is independent of the experimental conditions. The equation is not valid over the entire two-phase region, since it does not vanish at the critical point of the mixture. This error, however, would not be serious except very near the miscibility temperature.

Theories of solutions are not sufficiently advanced at present to enable one to calculate ratios of activity coefficients precisely from first principles. Furthermore, the equation determining the selectivity parameter ϵ_j^i (which will be shown later to represent the data adequately) is probably satisfactory because of several compensating errors and is not directly calculable from any present solution theory. The requirement that Equation (7) be adequate to express the selectivity data is the ill-defined one that the two activity coefficients be expressible as similar, although arbitrary, functions of concentration and temperature. However, for "chemically similar compounds" one can expect a correlation for ϵ_j^i values in the same solvent with properties of the compounds i and j.

The Hildebrand-Scatchard (*9*) theory of solutions is sufficiently inclusive to give a correct qualitative description of many nonideal solutions, even though the assumptions and approximations made in the development of the theory cannot be correct. It has the further advantage of a simple form of the equation for the activity coefficients in binary mixtures, which uses only two parameters, δ and V. The limiting ratio of the activity coefficients of two compounds in homogeneous solution in a solvent at zero concentration of these compounds is given by (*9*)

$$\underset{\substack{x_i, x_j \to 0 \\ x_s \to 1}}{RT \ln(\gamma_{1j}/\gamma_{2j})} = V_1(\delta_1 - \delta_s)^2 - V_2(\delta_2 - \delta_s)^2$$
$$= V_2[(\delta_1 - \delta_2)(\delta_1 + \delta_2 - 2\delta_s) + \rho(\delta_1 - \delta_s)^2] \cong R\epsilon_2^1 \quad (8)$$

To the extent that (7) holds and the Hildebrand-Scatchard theory is adequate to describe the systems, there should be a rough correlation between ϵ_2^1 and $(\delta_1 - \delta_2)$ which should be influenced by appreciable differences in molar volumes of the two compounds.

Other efforts have been made to generalize extraction data or correlate activity coefficients with solution theories. Alders (*1*) mentioned the quantity "selective power," defined as the separation factor divided by the difference in solvent mole fractions in the extract and raffinate phase. For *n*-heptane–aniline–toluene systems he showed that the selective power thus defined is reasonably constant over the two-phase area. He also noted that the selective power generally increases as the temperature decreases.

Several years ago, Francis (*7*) discussed the selectivities of an extensive series of hydrocarbons in terms of differences in critical solution temperatures with the solvents. He did not, however, make a comparison of an experimental selectivity with his correlation.

In the past several years workers from the Shell Development Laboratories have studied activity coefficients for many hydrocarbons and related compounds in solvents and have developed correlations for the limiting values of activity coefficients in terms of contributions of different interacting structural groups of the molecules (*2, 5, 6, 11, 12, 14, 17*). Prausnitz and Anderson (*13*) have treated solvent selectivity for extractive distillation by a modification of Hildebrand-Scatchard solution theory, which includes specific solvent-hydrocarbon complexes.

This paper is a study of the selectivities of certain fluorochemicals for separations of several hydrocarbons and an interpretation of these selectivities in terms of properties of the separate components. Fluorochemicals were chosen for these experiments, since fluorochemical-hydrocarbon mixtures provide examples of highly nonideal solutions without involving strong complexing between solvent and solute.

EXPERIMENTAL

Approximately equal volumes of the hydrocarbon mixture and fluorochemical were placed in a flask equipped with stopcocks through which samples of both layers could be withdrawn with a syringe. Two liquid phases were stirred for about 15 to 30 min. to insure equilibrium and then allowed to settle for 5 to 10 min. to be reasonably certain that complete separation had been attained. The temperature was maintained constant within ± 0.1°C. during these operations. Samples of each phase were transferred to small vials sealed with rubber serum caps to prevent loss by vaporization. The samples were analyzed by gas chromatography within about 1 hr. after transference since it was observed that even in the closed vials loss of hydrocarbon from the fluorochemical phase occurred after a few hours. The gas chromatography column was frequently calibrated with different blends of fluorochemical and hydrocarbon mixtures in the concentration range of the samples to be analyzed. Good reproducibility in introducing the samples was obtained by using the Chaney adaptation of the Hamilton Micro-syringe.

Phillips Pure or Research grade hydrocarbons were used. The fluorochemicals were a perfluoro cyclic ether, $C_8F_{16}O$ (purity estimated at 92% by gas chromatography); a fluorinated amine, $(C_4F_9)_3N$ (purity estimated at 95% by gas chromatography) from the Minnesota Mining and Manufacturing Company; and a sample of perfluoromethyl cyclohexane ($\sim$ 80%) from the Halocarbon Products Corporation. These fluorochemicals were purified by refluxing with concentrated $H_2SO_4 + K_2Cr_2O_7$ to remove any hydrogen containing impurities and then distilled very carefully.

DATA AND RESULTS

Table 1 shows representative data for the extraction of a mixture of 2,3-dimethyl butane (2,3DMB) and *n*-hexane ($n - C_6$) with $C_8F_{16}O$. The concentration of fluorochemical in the predominantly hydrocarbon phase was less than 3 mole percent. Fluorochemical-hydrocarbon systems have very unsymmetrical two-phase envelopes when expressed in terms of mole fraction (*10*). β_{exp} is the experimental separation factor determined from the ratios of the concentrations of the two compounds in the two phases (*2*). The values of ϵ are calculated from Equation (7); the average deviation of the values for ϵ in Table 1 is 2%, and the average deviations for practically all pairs of compounds were less than 10%. The values of β_{calc} are calculated with the average value of ϵ; the agreement of the experimental values of the separation factors, which are probably good to within a few percent, and those calculated from the equation with the average value of ϵ, is good. Similar experiments were performed for several binary hydrocarbon mixtures. The accuracy of the measurements never warranted any more terms in the equation.

It is apparent from Equation (7) that the major portion of the variation of separation factor with temperature of extraction is the result of the change of the concentration of the hydrocarbons in the solvent phase, since the temperature coefficient for β at constant composition is 0.2%/°K. at $x_s = 1$ and 0.1%/°K. at $x_s = 0.7$.

Table 2 lists $\epsilon_j{}^i$ values for a few pairs of hydrocarbons determined with this solvent. The abbreviations are illustrated by (1) cyclohexane-benzene, (2) 2,2,4-trimethylpentane-*n*-octane, and (9) *n*-heptane-methylcyclohexane. One may obtain an internal consistency check on the data, since $\epsilon_b{}^a = \epsilon_c{}^a - \epsilon_c{}^b$ and $\epsilon_j{}^i = -\epsilon_i{}^j$:

$$\epsilon_{2,3,4TMP}^{2,2,4TMP} = \epsilon_{n-C8}^{2,2,4TMP} - \epsilon_{n-C8}^{2,3,4TMP} = 209 - 146 = 63 \qquad (9)$$

This value is to be compared with the experimental value of 65 ± 2; and (9) should equal (8) minus (7). The agreement is good for these and all of the other checks for data not presented in Table 2.

Extractions of mixtures of four hexanes: 2,2-dimethylbutane (2,2DMB), 2,3-dimethylbutane (2,3DMB), 3-methylpentane (3MP), and *n*-hexane (*n*C6), gave values for the respective $\epsilon_j{}^i$'s which were always within the experimental error of the values determined for binary pairs. This observation verifies the earlier supposition that the selectivity is relatively insensitive to the distribution of hydrocarbons in the solvent phase and is determined primarily by the total hydrocarbon concentration in the solvent phase. The $\epsilon_j{}^i$ values for each pair of hydrocarbons were the same whether determined by extraction of a binary or multicomponent mixture.

Also shown in Table 2 are the values of $\epsilon_j{}^i$ calculated from Equation (8) with $\delta_s = 5.9$. The agreement is only to the order of magnitude, but this is the best agreement which can be expected if one considers the approximations which were used in developing both Equations (7) and (8). Furthermore, since the solubility parameter theory does not adequately represent binary mixtures of fluorochemicals and hydrocarbons (*9, 15*), one would hardly expect it to give an accurate quantitative representation of these two-phase multicomponent mixtures. However, the theory is qualitatively correct and the heats of vaporization and molar volumes are acceptable, although indirect, measures of molecular size and interactions. Thus, with this theory as a guide, an empirical correlation should be obtained between these selectivity parameters for pairs of hydrocarbons and differences in these physical properties of the pair.

For these data a plot of $\epsilon_j{}^i$ vs. $\delta_j - \delta_i$ gave a reasonably straight line, but a slightly better fit to the data was given by a plot of $\epsilon_j{}^i$ against the differences in heats of

TABLE 1. EXTRACTION OF 50 WEIGHT PERCENT 2,3DMB AND 50 WEIGHT PERCENT nC_6 WITH $C_8F_{16}O$

t, °C.	x_{HC}	β_{exp}	ϵ	β_{calc}
—50.5	0.061	1.51	105	1.51
—40.7	0.084	1.45	104	1.46
—29.7	0.113	1.41	105	1.40
—19.4	0.167	1.34	106	1.33
—9.1	0.228	1.28	107	1.26
+1.3	0.293	1.20	99	1.21
			104 ± 2 (average deviation)	

TABLE 2. SELECTIVITY PARAMETERS FROM EXTRACTIONS WITH $C_8F_{16}O$

		ϵ_j^i					
		Exp.	Calc. (8)	Group contr.	$\delta_j - \delta_i$	$\Delta H_{v,j} - \Delta H_{v,i}$	ρ
1	C6H12 C6H6	114 ± 3	268	—	0.96	195	—0.178
2	2,2,4TMP *n*C8	209 ± 9	153	185	0.70	1519	—0.025
3	2,3,4TMP *n*C8	146 ± 6	74	141	0.29	903	+0.024
4	2,2,4TMP 2,3,4TMP	65 ± 2	79	44	0.41	616	—0.038
5	2,3DMB 3MP	46 ± 3	22	—	0.16	275	—0.005
6	2,2DMB 2,3DMB	44 ± 2	30	—	0.26	343	—0.019
7	2,2,4TMP *n*C7	110 ± 2	113	78	0.58	339	—0.112
8	2,2,4TMP MCH	93 ± 3	213	95	0.97	55	—0.227
9	*n*C7 MCH	—17 ± 3	94	—	0.39	—284	—0.130
10	*n*C8 *n*C9	107 ± 3	115	—	0.10	1184	+0.099

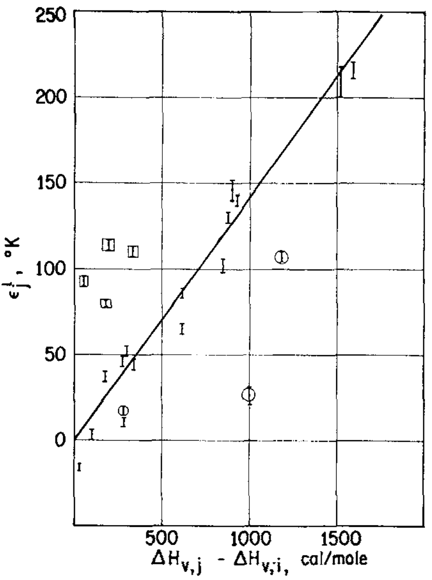

Fig. 1. The energy parameter $\epsilon_j{}^i$ for a pair of hydrocarbons from extraction with $C_8F_{16}O$ vs. difference in heat of vaporization for the same pair.

vaporization (Figure 1). The points $\boxed{\mathrm{I}}$ and Ⓘ, which are well off the line, refer to mixtures of unequal volumes and are not expected to fit this simple picture. The effect of the differences in volume is consistent, since for the points Ⓘ $V_j > V_i$ and for the points $\boxed{\mathrm{I}}$ $V_j < V_i$. The equation

$$\epsilon_j^{\,i} = 0.142\ (\Delta H_{v,j} - \Delta H_{v,i}) - 250\,\rho \qquad (10)$$

fits the complete set of data with an average deviation of ± 17°K. for $\epsilon_j^{\,i}$ and gives the wrong sign for only one pair: paraxylene (PX) and ethylbenzene (EB).

For extractions of mixtures of 2,3 dimethylbutane, n-hexane, and benzene at constant temperature, there is perhaps a slight increase in $\epsilon_{n\text{-}C_6}^{2,3DMB}$ with increasing concentration of benzene in the hydrocarbon phase. The total concentration of hydrocarbon in the predominantly fluorochemical phase decreases markedly with increasing benzene concentration in the hydrocarbon phase, since benzene is much less soluble in fluorochemicals than the hexanes. This apparent increase of 7% in $\epsilon_{n\text{-}C_6}^{2,3DMB}$ with an increase in benzene concentration from 50 to 90 weight percent is approximately the same as the experimental error. One may consider this value as being constant and further confirmation of Equation (7). However, this increase, if real, is what one would expect on the qualitative basis of the Hildebrand-Scatchard theory, since in benzene $\gamma_{2,3DMB}$ should be greater than γ_{nC_6}. β is given properly by Equation (3) rather than (4), so that one would expect β and ϵ to be greater in this case when the effects of nonideality in the hydrocarbon phase are greater. The extension of this to two-solvent extraction is obvious.

Since a "group contributions" method is successful in handling thermodynamic data for pure compounds and has been used for some simple mixtures (4), one might expect a similar method to be useful to correlate selectivity parameters. For the separation of 2,2-dimethylbutane from 2,3-dimethylbutane, the difference in structural groups is

$$\begin{aligned} 2{,}2\text{DMB} &= 4\text{CH}_3 + 1\text{CH}_2 + 0\text{CH} + 1\text{C} \\ \underline{2{,}3\text{DMB}} &\underline{= 4\text{CH}_3 + 0\text{CH}_2 + 2\text{CH} + 0\text{C}} \\ &= 0\text{CH}_3 + 1\text{CH}_2 - 2\text{CH} + 1\text{C} \qquad (11) \end{aligned}$$

which corresponds to $\epsilon_{2,3DMB}^{2,2DMB} = CH_2 - 2CH + C = 44$. By choosing appropriate pairs of hydrocarbons one can determine contributions to $\epsilon_j^{\,i}$ for each structural group. The values calculated by a group contributions method are also shown in Table 2. The pairs for which no values are shown were the basis set used to determine the values for each structural group. The agreement is fair. Since this method of calculation does not require a knowledge of any physical properties of the hydrocarbons, it would be useful for high molecular weight compounds for which reliable data are not available; but one would expect a somewhat lower accuracy for this correlation than the previous one, as well as slight differences depending on the choice of structural groups. With these choices, ϵ_{3MP}^{2MP} should be zero and the experimental value only 10.

It is sometimes more convenient to use volume fractions than mole fractions in discussing solutions and the Hildebrand-Scatchard treatment itself uses volume fractions (9). All these selectivity data may be calculated in terms of volume fractions instead of mole fractions by use of the equation,

$$T \ln \beta_2^{\,1} = \epsilon_2^{\,1}\, \Phi_s^{\,2}/T \qquad (12)$$

instead of Equation (7). The data can be satisfied equally well by (7) or (12) and the average deviations of the $\epsilon_j^{\,i}$ values are about the same. A similar correlation to that shown in Figure 1 holds for these data as well.

Table 3. Selectivity Parameters for other Fluorochemicals

	$(C_4F_9)_3N$	$C_6F_{11}CF_3$
$\epsilon_{nC_8}^{2,2,4TMP}$	234 ± 4	255 ± 15
$\epsilon_{nC_8}^{2,3,4TMP}$	163 ± 4	168 ± 13
$\epsilon_{2,3,4TMP}^{2,2,4TMP}$	71 ± 3	86 ± 3
$\epsilon_{nC_6}^{2,3,DMB}$	128 ± 9	115 ± 4
$\epsilon_{3MP}^{2,3DMB}$	51 ± 11	48 ± 1
$\epsilon_{2,3DMB}^{2,2DMB}$	47 ± 6	46 ± 3

In order to determine which is the more selective solvent, one should compare $\epsilon_j^{\,i}$ values for a given separation, or better, for several pairs. Table 3 shows this comparison for two other fluorochemicals. All three of these fluorochemicals have essentially the same selectivity. This similarity is to be expected, since the basic properties of the amine and heterocyclic oxygen are drastically reduced in the fully fluorinated compounds compared to their hydrogen analogs and all of these fluorochemicals should show essentially only a fluorocarbon-hydrocarbon interaction. The solubility parameters of these compounds are about the same and they each show the same "anomalous behavior" with regard to hydrocarbons that is characteristic of other fluorocarbons (*15*), so that one should not expect appreciable differences in selectivity parameters for these fluorochemicals.

CONCLUSIONS

This equation for the separation factor, (7), may be used generally for interpolating and extrapolating extraction data, since most liquid-liquid extraction solvents for hydrocarbon separations involve only relatively weak complexes. The actual representation of the data for a particular system cannot be assumed without experiment, however, because the conditions of applicability are not well defined. As illustrations of the applicability of (7) to other systems, two sets of data were taken. The isothermal data on the separation of styrene from ethylbenzene with diethylene glycol (3) give a selectivity parameter which is constant within 6%. The limiting ratios of activity coefficients of benzene and hexane, which are reasonable approximations to selectivity parameters, in several solvents at 25, 60, and 100°C., give selectivity parameters which are constant within 10% or better (6). The correlation of selectivity parameters with differences in heats of vaporization, which is sufficient to represent the data for the noncomplexing fluorochemical-hydrocarbon systems, would probably not hold for systems in which there is strong hydrogen bonding.

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NOTATION

a_{ij} =activity of component i in phase j

$k\binom{m}{n}$ =distribution coefficient for component i between phases m and n, $= x_{im}/x_{in}$
R =molar gas constant
T =temperature in °K.
V_i =molar volume of component i

x_{HC}, Φ_{HC} = total mole fraction or volume fraction of hydrocarbon in the predominantly solvent phase, *a*
x_{ij} =mole fraction of component *i* in phase *j*
x_s, Φ_s =mole fraction or volume fraction of the solvent in the predominantly solvent phase, *a*

Greek Letters

$\beta_j{}^i$ =separation factor for components *i* and *j* with solvent
γ_{ij} =activity coefficient of component *i* in phase *j*
$\Delta H_{v,i}$ =molar heat of vaporization of component *i*
δ_i, δ_s =solubility parameter of component *i* or solvent $= [(\Delta H_v - RT)/V]^{1/2}$
$\epsilon_j{}^i$ =selectivity parameter for the separation of components *i* and *j* with a solvent
ρ $= (V_j/V_i) - 1$

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Isothermal Activity Coefficients for the System Cyclohexane—*n*-Heptane—Toluene at 25°C.

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Isothermal vapor-liquid equilibrium data at 25°C. are presented for the ternary and binary systems containing cyclohexane, *n*-heptane, and toluene. These data were obtained by static equilibration in the presence of diluent nitrogen by chromatographic analysis of the saturated vapor. The data obtained were of at least comparable accuracy to those available at the normal boiling point, and the procedure appears to offer several substantial advantages. Neither a priori prediction of activity coefficients from regular solution theory nor extrapolation of data taken at the normal boiling point is a satisfactory substitute for the isothermal data.

Isothermal vapor-liquid equilibrium data are presented for the system cyclohexane–*n*-heptane–toluene at 25°C. These data were obtained by analysis of vapors in equilibrium with a liquid of known composition, and were correlated by the Redlich-Kister equations. The liquid and vapor were equilibrated by a static method and the vapor was analyzed by gas chromatography. Success in the chromatographic analysis permitted use of the simple and reliable static equilibration method as opposed to the more common dynamic methods.

Dynamic, or circulating, stills have been used widely, primarily because they provide large amounts of condensed vapor for analysis. However, these stills are difficult to construct, require highly skilled operators, and are subject to several systematic errors resulting from: (1) imperfect mixing of the boiling liquid; (2) entrainment (this is particularly serious at low gas density where entrainment has a greater effect and where bumping is likely); and (3) undue enrichment of the condensing vapor. In addition it is more difficult to obtain isothermal data than isobaric in this type of equipment.

The vapor chromatograph operated successfully with relatively small uncondensed gas samples (25 ml.) and thus permitted use of the static technique even at the low vapor pressures encountered in this work. In addition, use of nitrogen as an insoluble diluent permitted operation at

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