Prediction of Equilibrium Ratios from Nomograms of Improved Accuracy

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THE DESIGN of fractionating columns, and many other chemical engineering calculations, require vapor-liquid equilibrium data on the fluids to be separated. For hydrocarbon systems, these data are usually obtained from one of several generalized prediction procedures. Relatively small differences in the predicted values cause serious uncertainties in column computations for systems of low relative volatility. This indefiniteness creates a continual demand for ways to predict equilibrium data with the best possible accuracy. In 1957, Meyers and Lenoir (*34*) presented a nomogram for predicting hydrocarbon *K*'s, which was convenient to use and comparable in accuracy with other correlations (*3, 35, 50, 68*).

A revised nomogram and charts, the result of extensive recorrelation of published experimental data are presented here. Using selected data, the new nomogram has reduced the average prediction error by about 2%, as compared to the former nomogram. The new correlation predicts equilibrium ratios in certain regions, such as high concentrations of one component, with much better accuracy.

At first glance, a 2% reduction in prediction error appears to be of little practical importance. But, equilibrium ratios are mainly used in repetitive computations such as tray-to-tray calculations, and the error for any given system tends to be systematic, rather than random. As a result, the error can lead to astonishing discrepancies in many design computations.

DATA SELECTION

The intrinsic accuracy of the various sets of measurements was studied. Those measurements performed on the same system by different investigators are of particular help. For the methane-propane system, the measurements of two studies (*46, 55*) deviate by an arithmetic average of 5.37%. With ethylene-ethane (*19, 28*) the deviation averages 4.13%. With propylene-propane (*18, 45*) the deviation is 1.2%. Values of *K* for propane in pentane systems (*53, 63*) show a deviation of 2.6%. Miscellaneous duplicate measurements (*6, 7, 40, 41, 49, 57*) show deviations that average 5%, with a maximum deviation of 35%. The data of careful experimenters show deviations as low as 1% but the inherent uncertainty appears to be about 3%.

If the best data have an error of 5% or less, measurements where the precision is significantly poorer than 5% can be rejected. As a general rule, experimental results with multicomponent systems show relatively poor precision, because of the greater analytical difficulties. Lower precision also occurs when the concentration of a component becomes very small, and when measurements are obtained at the edges of the range of temperatures and pressures studied. The high precision, and presumably high accuracy, data are confined to binary systems with *K* values from 0.02 to 50.

A total of 58 measurement studies were considered, and are listed and identified by components in Table I. For this

Table I. Data Sources

System	References
Hydrogen-methane	(*32*)
Methane-ethylene	(*64*)
Methane-ethane	(*6, 32, 41, 49*)
Methane-propane	(*1, 41, 46, 55*)
Methane–2-methylpropane	(*38*)
Methane-butane	(*36, 52*)
Methane–2-methylbutane	(*2*)
Methane-pentane	(*7, 57*)
Methane-hexane	(*7*)
Methane-heptane	(*7, 40*)
Methane-decane	(*43*)
Ethylene-ethane	(*19, 28*)
Ethylene-heptane	(*27*)
Ethane-propylene	(*33*)
Ethane-propane	(*41*)
Ethane-butane	(*25*)
Ethane-heptane	(*24*)
Propylene-propane	(*18, 45*)
Propylene-1-butene	(*15*)
Propylene–2-methylpropane	(*14*)
Propane-butylene	(*58*)
Propane-butane	(*37*)
Propane–2-methylbutane	(*63*)
Propane-pentane	(*53, 63*)
Butylene-butane	(*54*)
Butane-heptane	(*26*)
Pentane-heptane	(*10*)
Methane-ethylene–2-methylpropane	(*4*)
Methane-ethane-pentane	(*5*)
Methane-propane-pentane	(*9, 11*)
Methane-butane-decane	(*42*)
Methane-ethane-propane-butane-pentane-hexane	(*17*)
Helium-nitrogen-methane-ethane-propane-butane plus	(*60*)
Natural gas–crude oil	(*8, 22, 23, 39, 44, 47, 56, 59, 62*)
Natural gas–condensate	(*20, 21*)
Natural gas–absorption oil	(*22, 29, 65*)
Natural gas–distillate	(*48, 51*)
Naphtha-furnace oil	(*66*)

correlation, 1936 measured values from 25 binary and ternary studies were selected. Although some experimental work of high accuracy probably was omitted, the extensive range of studies chosen precludes serious deficiency because of data selection. As far as could be determined, the results not utilized showed no difference in the pattern of equilibrium-ratio behavior, only in the random fluctuations. The particular systems selected are methane-ethane (*6, 41*), methane-propane (*1, 41, 46*), methane-2-methylpropane (*38*), methane-butane (*52*), methane-pentane (*57*), ethane-propylene (*33*), ethane-propane (*41*), ethane-butane (*25*), ethane-heptane (*24*), propane-butane (*37*) propane-2-methylbutane (*63*), propane-pentane (*53*), butane-heptane (*26*), pentane-heptane (*10*), ethane-ethylene (*19, 28*), ethylene-heptane (*27*), propane-propylene (*18, 45*), propylene-2-methylpropane (*14*), butylene-butane (*54*), methane-ethane-pentane (*5*), methane-ethylene-2-methylpropane (*4*), and methane-propane-pentane (*9, 11*). These studies present both convergence pressures and equilibrium ratios, except for the methane-ethylene-2-methylpropane system, where convergence pressures were computed (*31*).

THE K_{10} CONCEPT

Convergence pressure methods assert that equilibrium ratios are defined by four parameters—identity, temperature, pressure, and convergence pressure.

$$K = f_1(i, T, P, Pg) \tag{1}$$

But the graphical representation of a four-variable function is awkward. The presentation problem is simplified by using an intermediate variable to replace two of the primary variables. In the method described here, the intermediate variable is the low pressure equilibrium ratio, arbitrarily taken at 10 p.s.i.a., and at 5000 p.s.i.a. convergence pressure.

$$K_{10} = f_2(i, T) \tag{2}$$

Then the equilibrium ratio at any pressure is defined by K_{10}, pressure, and convergence pressure.

$$K = f_3(K_{10}, P, Pg) \tag{3}$$

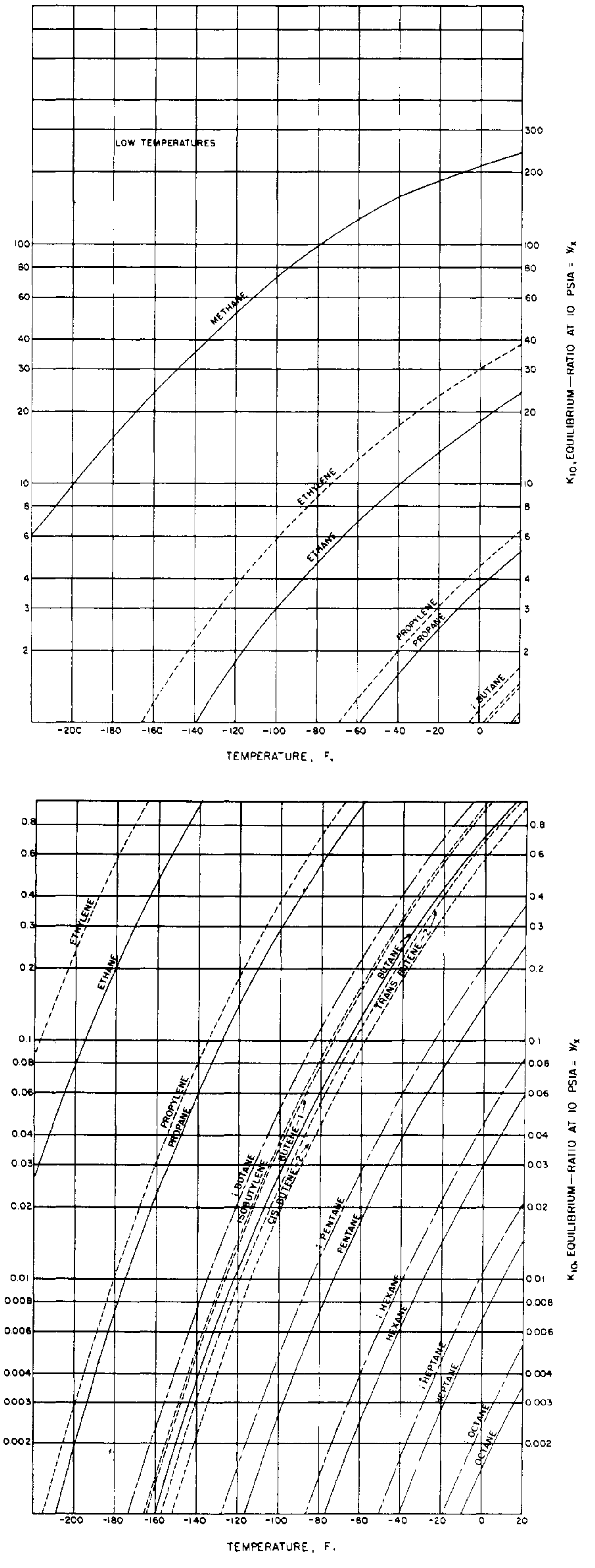
Physically this substitution states that the isothermal curves for different hydrocarbons at different temperatures are the same if their K_{10} values and convergence pressures are the same. Components will follow the same K *vs.* P plot if their terminal values are identical. Terminal values are the value of K at 10 p.s.i.a., and the value of pressure at $K = 1.0$.

The simplification accomplished by this substitution is considerable. The equilibrium ratio charts present the K_{10}'s for 58 hydrocarbon components and 10 hydrocarbon fractions from −200° to 900° F. These 12 charts plus the nomogram are a presentation of equilibrium ratios that would require 680 charts if shown as K *vs.* P for lines of constant temperature and pages of constant convergence pressure for 10 increments of convergence pressure. The present development not only reduces this number to 14 charts, but also eliminates interpolation between charts.

The K_{10} concept has another advantage. Hydrocarbon equilibrium ratios for which no experimental data are available may be predicted from vapor pressure information. For K_{10} less than 2.5,

$$K_{10} = Pv/10 \tag{4}$$

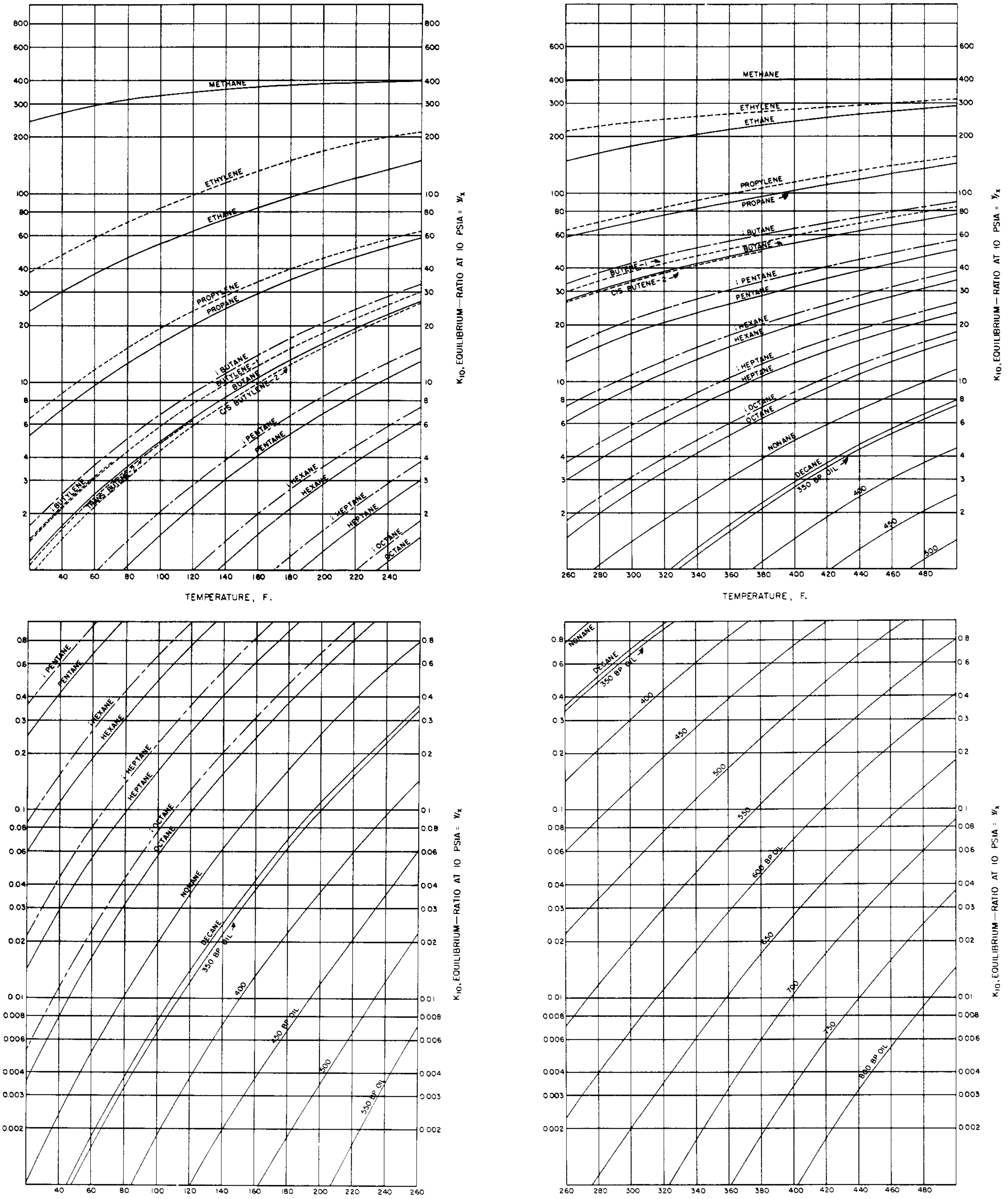
Equilibrium ratios of aliphatic hydrocarbons at 10 p.s.i.a.



The K_{10} curve from Equation 4 is drawn on the appropriate K_{10} chart, and extrapolated parallel to the existing curves. For K_{10} greater than 2.5, Equation 4 gives high results, roughly 50% high at the critical temperature.

If the vapor-pressure curve is unknown, a rough K_{10} can

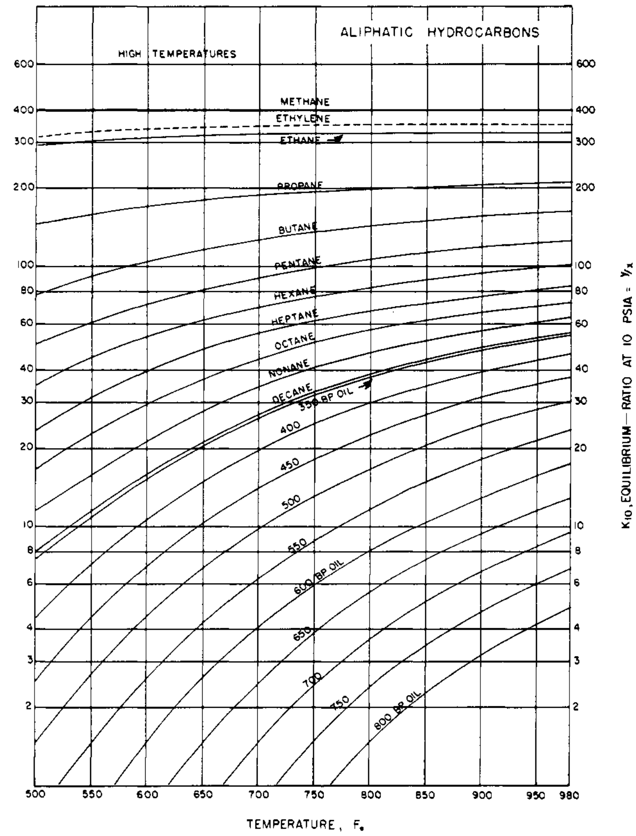
Equilibrium ratios of aliphatic hydrocarbons at 10 p.s.i.a.

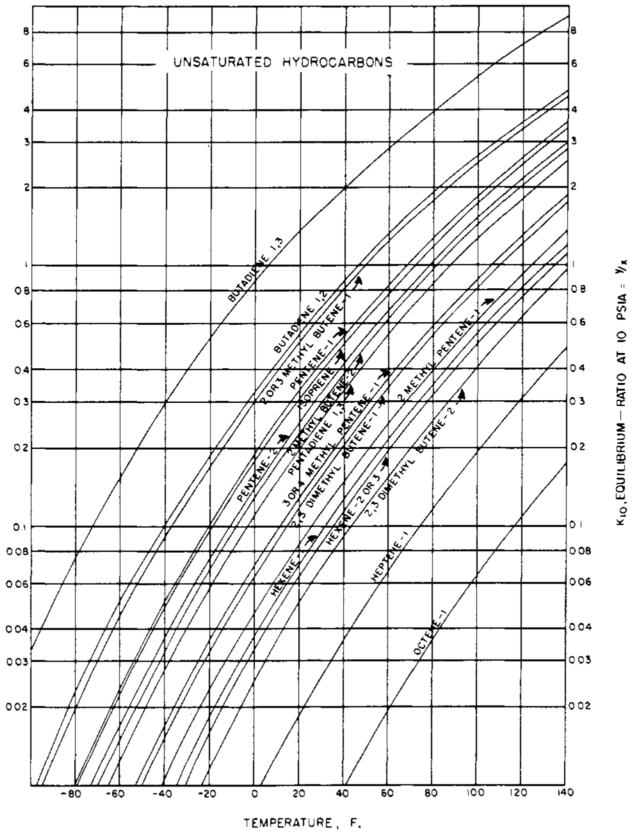


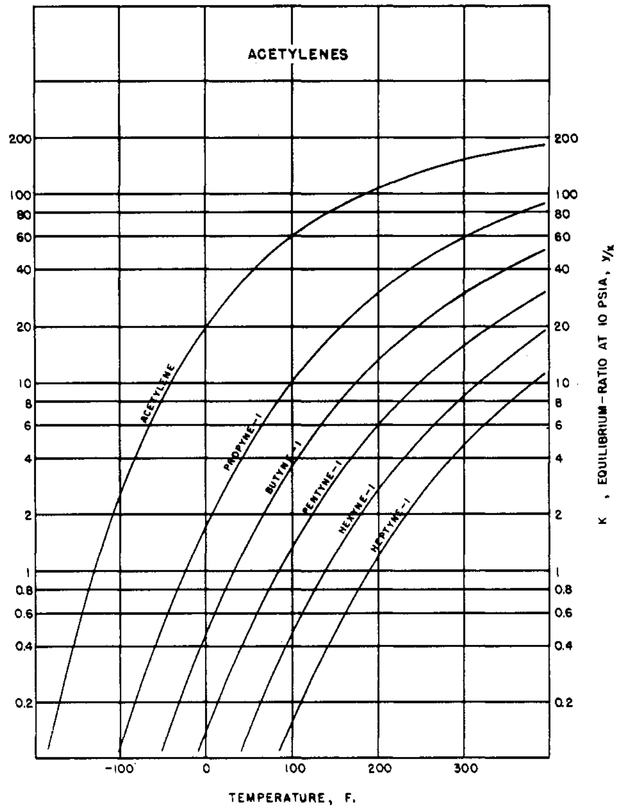
be developed from the normal boiling point. On the appropriate K_{10} chart, plot $K_{10} = 14.7/10 = 1.47$ at the atmospheric boiling point. From this point, the whole K_{10} curve can be sketched in by similitude to the known K_{10} curves for homologous hydrocarbons.

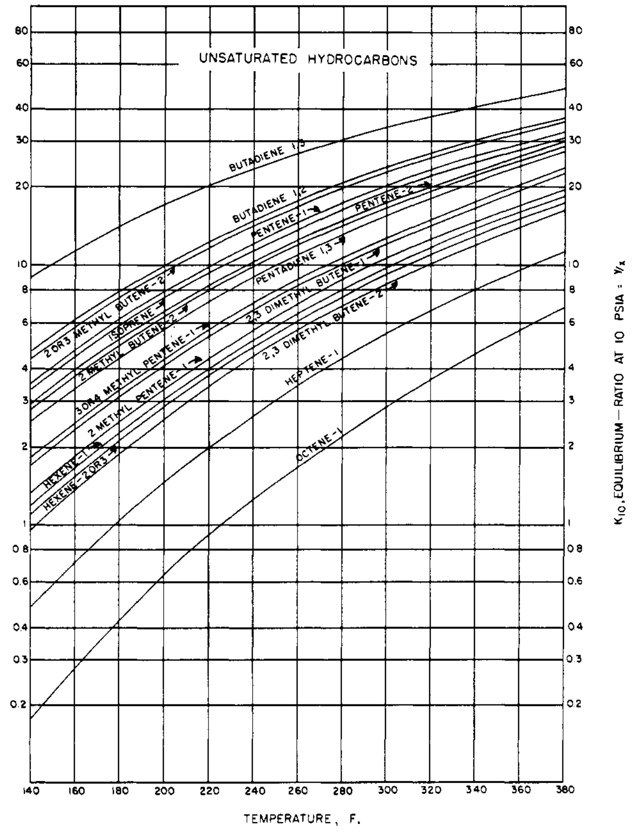
The curves for K_{10} greater than 2.5 that are presented in the equilibrium ratio charts are based on experimental values of equilibrium ratios, combined with the established relation between K, Pg, and P, as given by Equation 3. The value of K_{10} presented is the true equilibrium ratio at 10 p.s.i.a. For K_{10} less than 70, K_{10} is independent of convergence pressure. At K_{10} values greater than 70, K_{10}

Equilibrium ratios of aliphatic hydrocarbons at 10 p.s.i.a.





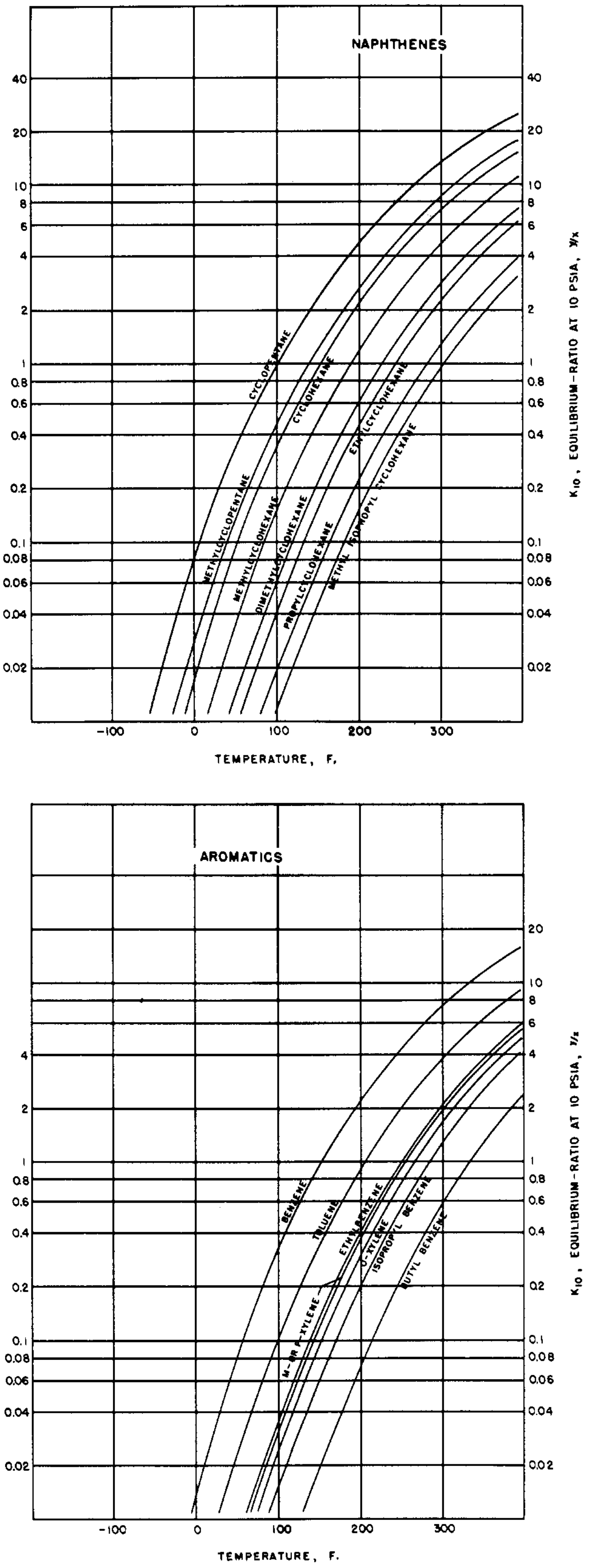




depends upon convergence pressure. The values of K_{10} presented in the equilibrium ratio charts for K_{10} greater than 70 are for a convergence pressure of 5000 p.s.i.a.

NOMOGRAM

The development of the nomogram followed procedures previously presented (*30, 34*). Briefly, the measured equilibrium ratios were plotted as isotherms. By extensive and careful cross-plotting, approximately 3000 smoothed equilibrium ratios were obtained from the isotherms. These were at 10° F. intervals and arbitrarily selected pressure and convergence-pressure levels. At constant pressure and convergence pressure,



Equilibrium ratios of ring hydrocarbons at 10 p.s.i.a.

$$\log K = \alpha \log K_{10} + \log \beta \quad (5)$$

where α and β are constants dependent only on pressure and convergence pressure (*30*). Equation 5 is the mathematical rule utilized for constructing the nomogram, and appears valid for all ranges of K and K_{10}. In the present development, selecting more accurate data before correlation permitted the establishment of straight-line plots of log K against log K_{10} with more certainty than when the lines were established using all data.

Figure 1 shows the developed nomogram for the pressure range from 10 to 500 p.s.i.a. Figure 2 shows the nomogram from 150 to 1000 p.s.i.a. The convergence-pressure range extends to the very low level of 300 p.s.i.a. The geometry of the nomogram is not suitable for high accuracy prediction in the pressure ranges above 1000 p.s.i.a.

To use the nomogram, the point of intersection of pressure is connected by a straight line with the value of K_{10}, intersecting the value of K. Convergence-pressure values may be obtained from charts previously presented (*31*). For conditions where K_{10} exceeds 70, the insert on the nomogram shows K_{10} at any particular convergence pressure dependent on K_{10} at Pg = 5000 p.s.i.a., as obtained from the equilibrium ratio charts. It is important to use the true value of K_{10} for accurate prediction when the values of K_{10} exceed 70.

Those who prefer charts to nomograms can plot the same data as log of equilibrium ratio *vs.* log pressure, for lines of constant K_{10} and pages of constant convergence pressure. Ten charts should cover the range of convergence pressures adequately. Such a method of plotting requires interpolation between charts for convergence pressure and interpolation between lines for K_{10}. The reading accuracy of these charts is probably less than the reading accuracy of the large-scale nomogram.

QUASI-CONVERGENCE PRESSURES

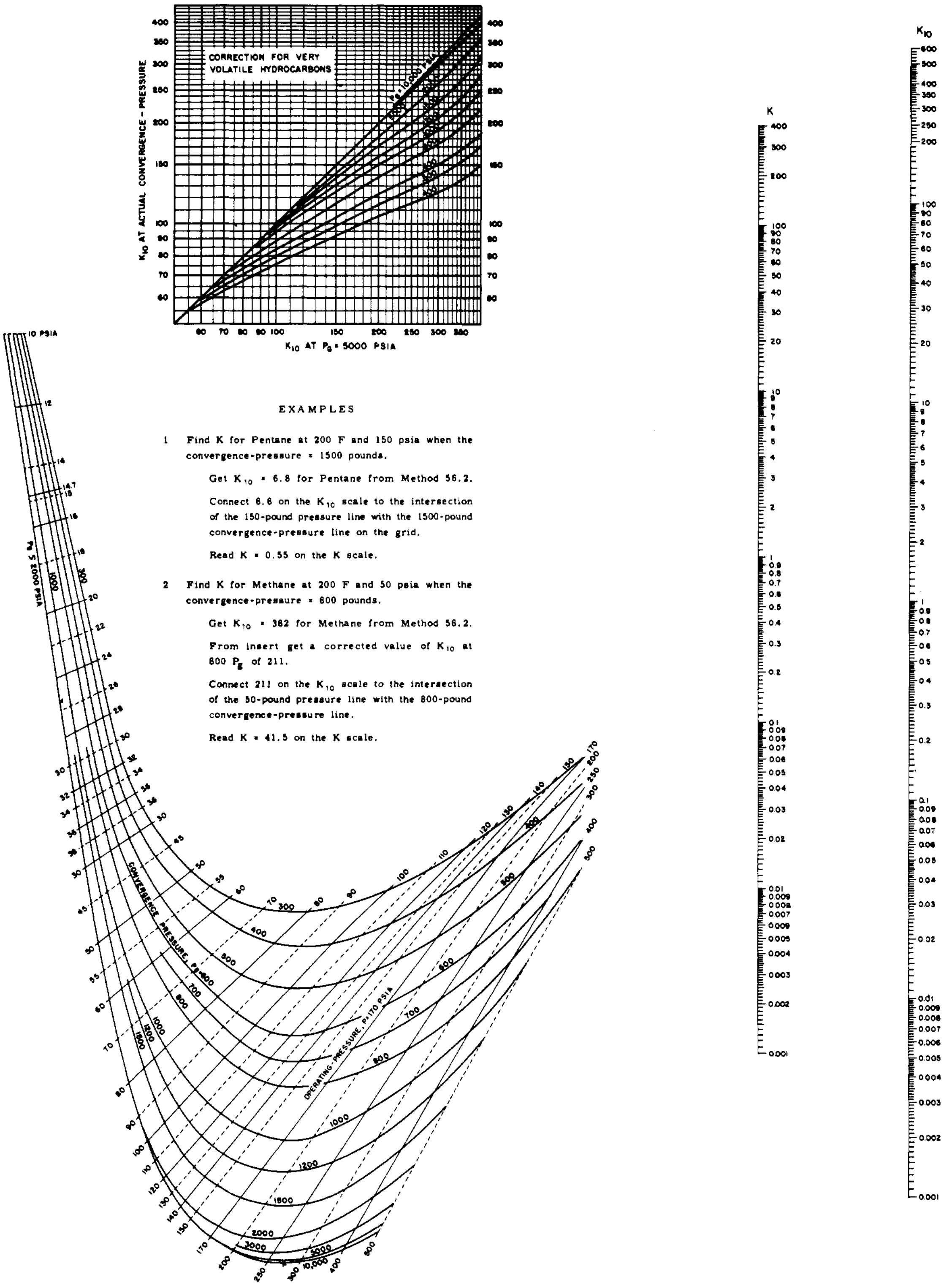
Below the critical temperatures of the lighter component of a binary mixture, no real convergence pressure exists. In this region the equilibrium ratios depend upon an imaginary value termed the quasi-convergence pressure (*16*). Previous studies indicated that the quasi-convergence pressure depended upon the temperature and the identity of the lighter component, independent of the identity of the heavier component (*31*). To get quasi-convergence pressure, the value of Pg is established that will result in the measured equilibrium ratio. This is an extrapolation procedure and magnifies the experimental error, causing the estimated quasi-convergence pressure to be uncertain.

If the rule that quasi-convergence pressure depends only on temperature and the identity of the lighter component has validity, vapor pressures can also be used to establish quasi-convergence pressures. The quasi-convergence pressure becomes the value that produces an equilibrium ratio of unity for a given value of K_{10} and pressure equal to the corresponding vapor pressure. Utilizing the nomogram for this purpose, Figure 3 was drawn, showing curves of quasi-convergence pressure established from highly accurate vapor pressures. Because Figure 3 is intended for use in predicting equilibrium ratios, it is presented in terms of the boiling point of the lighter component of a binary mixture, or the EBL_L for a multicomponent mixture (*31*). Figure 3 is valid where the lighter component is a paraffin or olefin, or mixture of the two.

ACCURACY

The equilibrium ratios predicted by the nomogram were compared with 1936 accurately measured experimental values, and showed an average arithmetical deviation of 4.60%, negative trend of 0.65%, and statistical deviation of 6.15%. Table II gives the results of the survey. Part I shows that there is no significant variation in prediction accuracy as the pressure changes and that the prediction accuracy is the same for the low-pressure nomogram and the high-pressure nomogram. The survey also showed no significant trend of accuracy behavior with convergence pressure.

Part II shows the effect of temperature level. In the



EXAMPLES

1 Find K for Pentane at 200 F and 150 psia when the convergence-pressure = 1500 pounds.

Get K_{10} = 6.8 for Pentane from Method 56.2.

Connect 6.6 on the K_{10} scale to the intersection of the 150-pound pressure line with the 1500-pound convergence-pressure line on the grid.

Read K = 0.55 on the K scale.

2 Find K for Methane at 200 F and 50 psia when the convergence-pressure = 800 pounds.

Get K_{10} = 382 for Methane from Method 56.2.

From insert get a corrected value of K_{10} at 800 P_g of 211.

Connect 211 on the K_{10} scale to the intersection of the 50-pound pressure line with the 800-pound convergence-pressure line.

Read K = 41.5 on the K scale.

Figure 1. Nomogram for predicting equilibrium ratios of hydrocarbons in the low pressure range

range from 0° to 100° F., the prediction accuracy is very high, approaching the maximum considered possible for a system based on experimental measurements. As the temperature level extends to higher, or lower, ranges, the prediction accuracy progressively becomes poorer. At temperatures below −100° F. an average deviaion of 8.86% exists. The authors believe that this lower prediction accuracy stems largely from the increased experimental difficulties of laboratory work at low temperatures.

Part III shows the prediction results compared for individual components. No particular pattern of deviation appears. Normally, the prediction accuracy is poorest for methane. With the nomogram, the average deviation for methane is only 3.88%, less than the average for all components.

Part IV of Table I shows how Figure 3 and the nomogram predict equilibrium ratios where the quasi-convergence pressure is pertinent. The average deviation is 5.5%, roughly 1% more than for equilibrium ratios where real convergence pressures occur. This agreement verifies the assumption that quasi-convergence pressures are independent of the identity of the heavier component.

Part V shows how well the nomograms predict vapor pressure. With the exception of methane, the deviation approximates 1%. With methane, the deviation rises to an average of 4.3%, comparable to the deviation for equi-

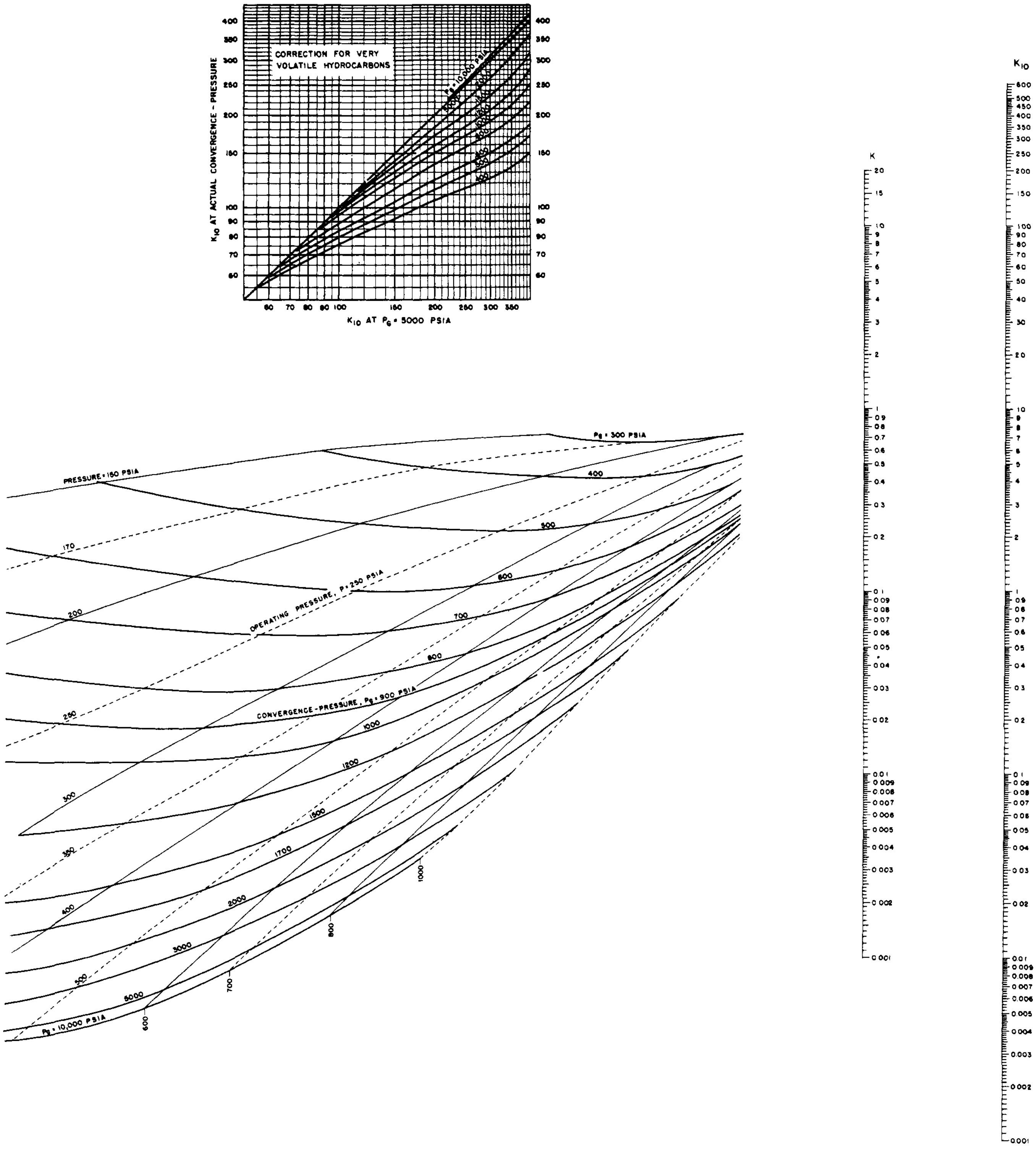


Figure 2. Nomogram for predicting equilibrium ratios of hydrocarbons in the high pressure range

librium ratios. Although the nomograms can be used to predict vapor pressures, direct graphs and tables of vapor pressure are more precise and simpler.

The nomogram predicts the 1936 selected experimental data with an average deviation of 4.6%. The previous nomogram (*34*) predicts the same data with an average deviation of 6.5%. This improvement is substantiated by a comparison based on data from all sources. The previous nomogram (*34*) has an over-all average deviation of 7.3%. A limited but random sampling of the data from all sources shows that the new nomogram has an average prediction error of 5.8%.

An accuracy study of four prediction methods, the NGAA charts (*35*), the tables of Rzasa, Glass, and Opfell (*50*), the nomogram of Winn (*68*), and the nomogram of Myers and Lenoir, was previously presented (*34*). Compared with all data, the four prediction methods gave an average deviation between predicted and experimental equilibrium ratios of 7.5%, with no significant differences in the accuracy of the individual methods. Similarly, the Kellogg charts (*3*) showed a prediction error of 6.7%.

Table III presents the change in column design caused by a 2% change in *K*'s for three relative volatilities. The example is a synthetic one, and makes these assumptions: The feed is an equimolar binary mixture at its bubble point. Contaminations are 1% in both distillate and bottoms.

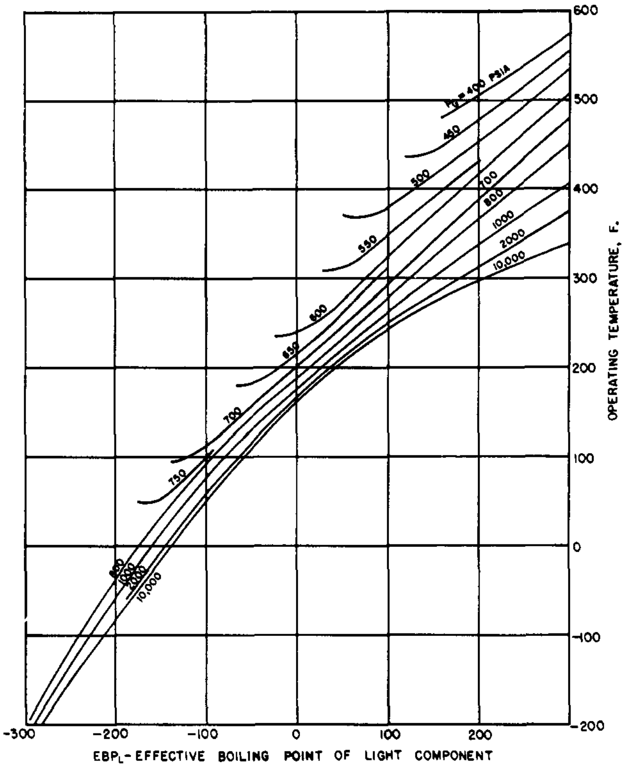


Figure 3. Quasi-convergence pressures established from vapor pressures

Table II. Prediction Accuracy Survey

	Number of Comparisons	Av. % Dev.	Trend, %	Statistical Dev.
Over-all	1936	4.60	-0.65	6.15
Part I. Effect of Pressure				
Low-pressure side of nomogram				
At 40 p.s.i.a.	33	4.7	-1.9	
60	51	3.8	-0.4	
80	65	4.6	-1.2	
100	117	5.6	-3.5	
200	202	5.3	-1.9	
300	170	5.0	0.6	
400	230	6.0	-1.4	
500	61	4.8	-0.5	
All pressures	844	4.56	-0.83	6.18
High-pressure side of nomogram				
At 300 p.s.i.a.	124	4.4	0.3	
400	309	5.8	-2.3	
500	163	4.0	0.4	
600	193	5.2	-0.4	
700	74	4.0	1.9	
800	153	5.8	-3.2	
1000	139	6.1	-2.9	
All pressures	1092	4.64	-0.6	6.14
Part II. Effect of Temperature, ° F.				
0° to 300°	1235	3.53	0.0	4.75
0° to 100°	392	3.13	0.8	4.20
100° to 300°	843	3.72	-0.2	5.00
300° and higher	353	5.76	-3.4	7.75
-100° to 0°	248	4.90	1.5	6.60
Below -100°	87	8.86	-3.4	12.0
Part III. Study by Component				
Methane	470	3.88	-0.6	5.25
Ethylene	131	4.83	-2.5	6.50
Ethane	341	4.12	0.1	5.55
Propylene	71	4.37	3.4	5.90
Propane	290	4.43	0.0	5.96
Butylene	24	2.30	1.5	3.10
Isobutane	67	5.10	-0.5	6.90
Butane	186	3.94	-0.3	5.30
Isopentane	23	2.46	-0.7	3.32
Pentane	104	6.71	-2.8	9.05
Heptane	196	5.35	-3.5	7.20
Part IV. Quasi-Convergence Pressure Region				
Lighter component	180	5.27	-1.4	7.10
Heavier component	143	5.68	2.2	7.65
Both components	323	5.50	-0.21	7.40
Part V. Prediction of Vapor Pressure				
Methane		4.34		
Ethane		1.40		
Propane		0.75		
Butane		1.00		
Pentane		0.50		
Hexane		1.14		
Heptane		0.80		
Ethylene		1.50		
Propylene		1.11		
Isobutane		0.65		
Average for vapor pressure		1.28		
Average omitting methane		1.04		

Table III. Effect of a 4% Uncertainty in Relative Volatility on a Column Design

Alpha	Minimum Trays	Minimum Reflux, $(L/D)_m$	Trays at $1.2(L/D)_m$
1.100	96.4	19.3	186
1.144	68.3	13.6	133
1.300	35.0	6.5	70.0
1.352	30.5	5.5	61.5
1.500	22.7	3.90	46.5
1.560	20.7	3.50	42.5

Internal flow rates are constant through each section of the column. And the relative volatility is constant throughout the column.

Because it is assumed that the error in each K can be 2%, the error in relative volatility can be 4%. And because the difference in final design is a function of the magnitude of the relative volatility, the computation has been repeated for nominal relative volatilities of 1.1, 1.3, and 1.5, and for each nominal value increased by 4%.

For each of the six relative volatilities,minimum theoretical trays were calculated by Fenske's method (*12*), minimum reflux by Underwood (*61*), and theoretical trays by 20% above minimum reflux by the Gilliland empirical correlation (*13*). The Fenske and Underwood techniques are rigorous for the conditions of this example.

Increasing the relative volatility by 4% at $\alpha = 1.1$, reduces the number of theoretical trays in the final design by 30%. At $\alpha = 1.3$, the 4% increase reduces theoretical trays by 13%. And at $\alpha = 1.5$, the 4% increase in α reduces the number of trays by 9%. The decrease in operating reflux for the three cases is 30, 15, and 9%.

These figures show that comparatively small errors in equilibrium ratios can have disproportionately large effects on calculations made with those equilibrium ratios. In fact, the best available K's are barely good enough for column design at low relative volatilities.

LIQUID-PHASE NONIDEALITY

The procedure outlines in this article applies to mixtures that behave ideally at low pressures. It cannot allow for activity-coefficient deviations which are caused by mixing different molecular types.

In general, the procedure is sound for mixtures of one molecular type. And it is good for mixtures of paraffins and olefins. For naphthenes mixed with olefins and paraffins, the accuracy is slightly poorer. For mixtures of aromatic with paraffins, olefins, or naphthenes, large errors can be expected. In this case, the predicted K's need to be multiplied by a generalized activity coefficient, or by some aromacity correction.

Full-size copies of nomograms and charts are available from the authors on request.

NOMENCLATURE

A, B = constants dependent upon P and Pg alone
EBP_L = effective boiling point for the lighter component of a binary mixture, or equivalent lighter component of a multicomponent mixture
f = function symbol
i = component identity
K = equilibrium ratio
K_{10} = equilibrium ratio at 10 p.s.i.a.
P = pressure, p.s.i.a.
Pg = convergence pressure, p.s.i.a.
Pv = vapor pressure, p.s.i.a.
T = temperature, ° F.

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