The Critical Temperatures and Pressures of Binary Systems: Hydrocarbons of All Types and Hydrogen

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A method of the prediction of the critical temperatures and pressures of mixtures has been developed, primarily on the basis of data for binary hydrocarbon systems available in the literature. These mixtures may contain aliphatic (normal paraffinic, isoparaffinic, and olefinic), naphthenic, and aromatic hydrocarbons as well as hydrogen. The mixtures may be of varying complexity, and, although this method has been tested chiefly on binary systems, it has been applied to a limited number of mixtures containing more than two components.

This study introduces two dimensionless temperature parameters, γ and θ, which account for the composition of the mixture and for the nature of the components involved. These parameters are defined by the molar average boiling point, the boiling point, and the dew point, all at atmospheric pressure. For a given composition the ratios of the actual critical values to the pseudocritical values have been found to be functions of γ and θ. These relationships are presented graphically and permit the direct calculation of the critical temperature and pressure of the mixture.

The validity of this method has been checked not only on the binary systems used to obtain these correlations but also on binary and ternary systems which have not been included in this development. Critical values for eighteen systems, consisting primarily of two components, have been calculated for ninety-six compositions and have been compared with the experimental values presented in the literature. For temperature the average absolute deviation has been found to be 0.76% (based on degrees Rankine) and for pressure, 2.7%. The results for the majority of these systems have been compared with values calculated by the methods of Eilerts *et al.* (4), Organick and Brown (15), Kurata and Katz (11), Mayfield (12), and Smith and Watson (23).

The growing interest in critical properties necessitates the establishment of more exacting critical temperatures and pressures. These properties are receiving considerable attention, particularly since attempts are being made presently to use them directly instead of the corresponding pseudocritical values. The critical points of mixtures are of considerable interest in vapor-liquid equilibrium studies and represent a condition under which the equilibrium constants of all the components become unity.

A knowledge of the critical temperature and pressure of a multicomponent system defines the limiting condition under which the system can exist in coexisting vapor and liquid phases. In contrast to the case of a pure substance, for which the boiling point and dew point are the same for a fixed pressure, a mixture of a given composition normally has a boiling point and a dew point which are distinct and which become identical at the critical point. In view of this, the critical point of a mixture becomes that temperature and pressure at which the boiling- and dew-point lines meet. The critical point therefore becomes a function not only of the components involved but also of the composition of the mixture.

An application of the phase rule at the critical point limits the degrees of freedom to zero for a pure substance, to 1 deg. for a binary system, to 2 deg. for a ternary system, etc. Since two of the variants at the critical point must be the critical temperature and critical pressure for systems of more than three components, the composition of one or more components of the mixture becomes an additional variable in establishing the critical point. From this it is obvious that the degree of complication in establishing the critical point increases with the number of components present in the mixture; therefore when the effect of composition must be accounted for, it is desirable to use a method which can be applied to systems containing an unrestricted number of components.

Methods to predict the critical temperatures and pressures of mixtures are presented in the literature. In 1937 Smith and Watson (23) developed a correlation that permits the estimation of critical and pseudocritical temperatures and pressures of petroleum fractions. Their method requires a knowledge of the gravity of the stock, of the molecular weight, and of the molar average and weighted average boiling points. In the early 1940's Mayfield (12), using available critical-constant data, developed a correlation for binary paraffinic systems. He recommends the use of a weighted average for the critical temperature and bases his prediction for the critical pressures on the differences between the weighted average critical-pressure values and the experimental literature values. In 1942 Kurata and Katz (11), in attempting to extend the method of Smith and Watson to volatile mixtures consisting of pure hydrocarbons, developed a new correlation based on the molecular weight, the pseudocritical temperature, and a function to represent the boiling range of the mixture. In 1952 Organick and Brown (15), as an integral part of their vapor-liquid equilibrium studies, presented a means of estimating the critical temperatures and pressures for multicomponent systems. They also suggest the use of a weighted average for the calculated critical temperature. The application of their method for the critical pressure requires the use of the molar average boiling point and the weight average equivalent molecular weight. In 1957 Eilerts *et al.* (4) developed a series of correlations for binary and complex mixtures based upon the boiling points of the pure components involved, the molar average boiling point, the pseudocritical pressure, and a weighted combination of the critical temperatures and boiling points of the pure components.

Although these methods produce satisfactory results, it was deemed desirable to broaden the scope of this study to include all types of hydrocarbons and other components such as hydrogen.

BEHAVIOR OF MIXTURES

The pressure-temperature behavior of mixtures at saturated conditions can be represented best on a plot of log P as ordinate against the reciprocal of the absolute temperature as abscissa. When one uses this approach, the boiling- and dew-point lines of the mixture become nearly linear in the low-pressure region and curve at elevated pressures to meet at the critical point. In this low-pressure region boiling- and dew-point values can be calculated directly from vapor-pressure data when one assumes ideal-gas behavior in the vapor phase and ideal-solution behavior in the liquid phase. Based on these as-

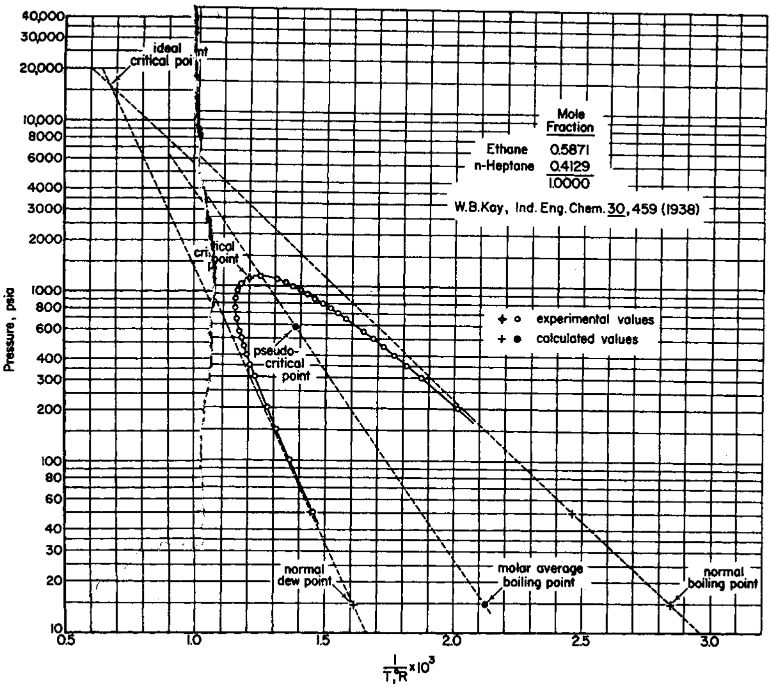

Fig. 1. Pressure-temperature relationship for a typical system.

sumptions the boiling- and dew-point lines are straight and nearly coincide with the experimental curves. The extensions of these lines intersect at a point located at a higher pressure than the critical pressure. This point of intersection may be considered to be an ideal critical point. The actual saturation envelope of the mixture is confined ordinarily within the area bounded by the two straight lines. Such a diagram can be constructed from available saturation data not only for binary systems but also for multicomponent systems. The shape and location of the boiling- and dew-point curves, as well as the critical point, change with the composition of a given mixture but retain the general pattern of behavior already presented. The consistencies observed from the regular behavior of such a relationship have led to the development of the two temperature parameters that constitute the essence of this study.

In order to show more explicitly the general behavior of a multicomponent system, a plot of log P vs. $1/T$ for the binary system containing 0.5871 mole fraction ethane and 0.4129 mole fraction *n*-heptane is presented in Figure 1, where the boiling- and dew-point lines meet at the critical point ($T_c =$ 833.6°R., $P_c = 1{,}106$ lb./sq. in. abs.). Ideal-gas and -solution boiling points and dew points have been calculated arbitrarily at 14.7 and 50 lb./sq. in. abs. The two straight lines joining the two calculated boiling points and dew points, respectively, have been constructed and extended. It may be observed that the experimental curves approach the calculated lines at low pressures. For this mixture the corresponding pseudocritical temperature and pressure ($T'_c = 724.5$°R., $P'_c =$ 581.5 lb./sq. in. abs.) as well as the molar average boiling point ($T'_b =$ 471.0°R.) have been calculated and are included in this figure. These two calculated points are directly obtainable from the composition and the properties of the pure components of the mixture and therefore should be related to the actual critical point of the mixture. A line connecting these two pseudopoints, when extended, falls in the neighborhood of the actual critical point and frequently passes through it for certain systems and compositions. It was observed that the actual critical point and this line varied in the same manner with the composition and components of the mixture as the difference between the normal boiling and dew points varied. From a consideration of this behavior, exhibited by a large number of systems and compositions, it appeared likely that an interrelationship should exist between the normal boiling point and normal dew point on the one hand and the molar average boiling point, the pseudocritical point, and the actual critical point on the other hand.

Several combinations of these variables were attempted. Of these the most promising parameters were found to be two that have been designated arbitrarily as γ and θ, where $\gamma = T_d/T_b$ and $\theta = (T'_b - T_b)/(T_d - T_b)$. Both these parameters are dimensionless and independent of the number of components present in any given mixture.

In order to determine the actual critical temperatures and pressures of mixtures, the ratios of the actual critical values to the pseudocritical values have been introduced and found to be functions of γ and θ. Thus for a given mixture and composition, upon calculation of γ and θ, $\tau = T_c/T'_c$ and $\pi = P_c/P'_c$ may be determined from the correlation, and so the critical values may be predicted. The pseudocritical temperature and pressure are the molar average of the critical values of the pure components contained in the mixture.

CORRELATIONS OF CRITICAL TEMPERATURES AND PRESSURES

Initially plots were made to relate the ratios $\tau = T_c/T'_c$ and $\pi = P_c/P'_c$ to the temperature variable θ with the particular system under consideration as the parameter. Figures 2 and 3 include the resulting relationships for the systems: *n*-butane—*n*-heptane (*7*), ethane—*n*-butane (*6*), ethane—benzene (*11*), ethane—cyclohexane (*9*), ethane—*n*-heptane (*5*), ethylene—*n*-heptane (*8*), and methane—*n*-butane (*19*). The values of γ corresponding to each experimental point and thus to each composition of the given system are designated in these figures. These graphs indicate that, as the pure component state is approached, γ approaches unity and θ becomes either 0 or 1. It will be observed that the maximum values of τ and π increase as γ increases and that the maxima of the curves shift to the left of $\theta = 0.5$ as γ increases. Also it may be observed that the curves of Figures 2 and 3 are of a parabolic shape, reaching a maximum value in the range of θ between 0.2 and 0.5 and decreasing to unity at $\theta = 0$ and $\theta = 1$.

In addition to the systems used in Figures 2 and 3, the following systems have been treated in a similar manner: methane—*n*-pentane (*22*), methane—*n*-decane (*16*), hydrogen—*n*-hexane (*13*), hydrogen—methane (*1*), hydrogen—propane (*2*), methane-butane-decane (*17*), and methane-propane-butane (*18*).

The information presented in Figure 2 together with that derived for systems not included in it has been cross-plotted to produce the final correlation for critical temperature which is presented in Figures 4 and 5. These figures may be applied for values of γ ranging from 1.0 to 15. It should be noted that the range $\gamma > 5$ in Figure 5 is generally applicable to hydrogen-containing systems. Following a similar procedure, the final critical-pressure correlation, presented in Figures 6, 7, and 8, was developed and covers a similar range of γ values. It may be observed that these curves are also of a

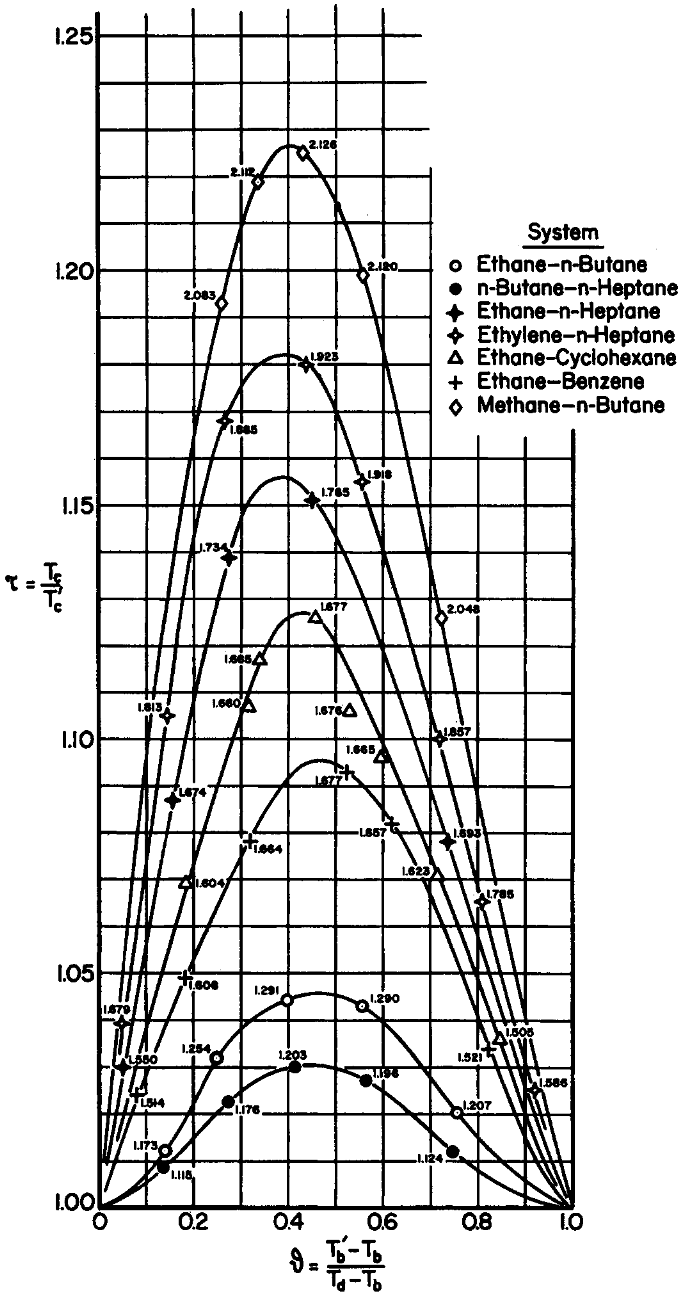

Fig. 2. Relationships of τ and θ for a number of binary systems.

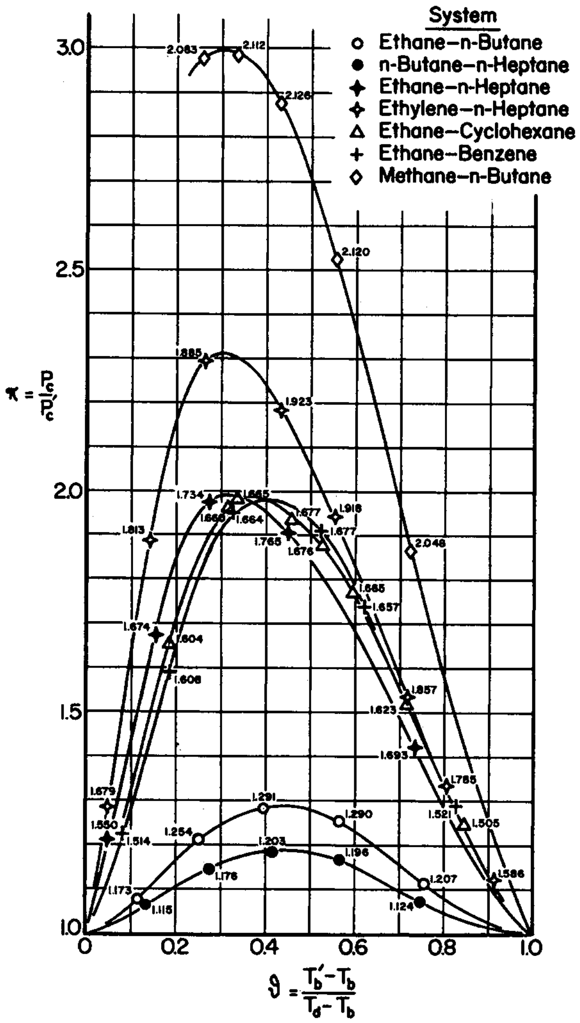

Fig. 3. Relationship of π vs. θ for a number of binary systems.

parabolic shape. The values of γ from 5 to 15 are useful for hydrogen systems and for other systems having unusually large dew-point–boiling-point differences.

Example Calculation 1

Determine the critical temperature and pressure for a system consisting of 0.5871 mole fraction of ethane and 0.4129 mole fraction of *n*-heptane.

	T_b, °R.	T_c, °R.	P_c, lb./sq. in. abs.
Ethane	331.7	549.8	712
n-Heptane	669.0	973.0	396

The boiling point at atmospheric pressure is calculated from the relationship

$$P_2x_2 + P_7x_7 = 14.7$$

A trial-and-error procedure gave a value of $T_b = 351.0$°R.

The dew point at atmospheric pressure is calculated from the relationship

$$\frac{1}{14.7} = \frac{y_2}{P_2} + \frac{y_7}{P_7}$$

A trial-and-error procedure was used to obtain a normal dew-point value of $T_d = 619.7$°R.

$$T'_c = 549.8\ (0.5871) + 973.0\ (0.4129) = 724.5°\text{R}$$

$$P'_c = 712\ (0.5871) + 396.0\ (0.4129) = 581.5 \text{ lb./sq. in. abs.}$$

$$T'_b = 331.7\ (0.5871) + 669.0\ (0.4129) = 471.0°\text{R}$$

From these values γ and θ are calculated to be

$$\gamma = \frac{T_d}{T_b} = \frac{619.7}{351.0} = 1.765$$

$$\theta = \frac{T'_b - T_b}{T_d - T_b} = \frac{471.0 - 351.0}{619.7 - 351.0} = 0.447$$

From Figures 4 and 5 $\tau = 1.153$ and $\pi = 1.908$.

$$T_c = 1.153 \times 724.5 = 835°\text{R}.$$

$$P_c = 1.908 \times 581.5 = 1{,}110 \text{ lb./sq.in.abs.}$$

Kay (5) reports for this composition $T_c = 835$°R. and $P_c = 1{,}106$ lb./sq. in. abs.

For convenience in predicting the critical temperatures of systems having values of γ that range up to 2.0 and for values of θ ranging from 0.2 to 0.8, the following expression may be applied as an approximation:

$$\tau = 0.985\gamma^{2/9} \qquad (1)$$

where the values of γ and τ are the same as those already indicated.

A similar calculation may be applied to aliphatic- and hydrogen-containing systems but not to systems containing naphthenic or aromatic components.

ADJUSTMENTS FOR NAPHTHENIC AND AROMATIC COMPONENTS

For the critical temperature of naphthenes no correction is necessary. However for aromatics the value of γ to be used with Figures 4 and 5 should be 0.9 times the value calculated from the boiling- and dew-point values ($\gamma_{corr} = 0.9\gamma$).

For the critical pressure, both γ and θ must be adjusted before the proper value of π is read from Figures 6, 7, and 8. This is necessary for both naphthenes and aromatics. A preliminary value for π is first obtained by use of uncorrected values of γ and θ. Then, with the aid of Figure 9, $\Delta\theta$ may be obtained for the respective stock corresponding to the preliminary value of π; $\Delta\theta$ is then subtracted from θ to give θ_{corr}. The value of γ is adjusted by multiplying the uncorrected value by 1.045 for both naphthenes and aromatics. Then using both γ_{corr} and θ_{corr} and Figures 6, 7, and 8, one may determine the final value of π.

Example Calculation 2

Determine the critical temperature and pressure for a system consisting of 0.5023 mole fraction ethane and 0.4977 mole fraction benzene.

	T_b, °R.	T_c, °R.	P_c, lb./sq. in. abs.
Ethane	331.7	549.8	712.0
Benzene	635.9	1,011.4	709.2

As shown in example 1, the boiling and dew points at atmospheric pressure were found to be 356.8° and 598.4°R. respectively. Also the following pseudovalues were calculated: T'_c = 779.4°R., P'_c = 708.2 lb./sq. in. abs., and T'_b = 483.1°R.

$$\gamma = \frac{598.4}{356.8} = 1.677$$

$$\theta = \frac{483.1 - 356.8}{498.4 - 356.8} = 0.523$$

Critical Temperature

At $\gamma_{corr} = 0.90\ (1.677) = 1.509$ and $\theta = 0.523$, $\tau = 1.089$ from Figure 4. Therefore

$$T_c = 1.089\ (779.4) = 848°\text{R.}$$

Critical Pressure

From Figure 6 the preliminary value of $\pi = 1.705$ for $\gamma = 1.677$ and $\theta = 0.523$. A correction for the aromatic mixture of $\Delta\theta = 0.102$ results from Figure 9 for $\pi_{prel} = 1.705$. $\theta_{corr} = 0.523 - 0.102 = 0.421$ and also $\gamma_{corr} = 1.045\ (1.677) = 1.752$.
For these adjusted parameters the final value of $\pi = 1.925$ is obtained from Figure 6. Thus

$$P_c = 1.925\ (708.2) = 1{,}362 \text{ lb./sq. in. abs.}$$

For this composition Kay and Nevens (10) report the values of T_c = 851.6°R. and P_c = 1,356 lb./sq. in. abs.

RESULTS AND CONCLUSIONS

The method presented for the prediction of the critical temperature and pressure has been tested both on the systems used in this development and on other systems available in the literature, some of which have been used by previous investigators involved with similar studies. Based on eighteen systems of two and three components each, and including systems with hydrogen as a component, and ninety-six compositions the critical temperature was estimated within 0.76% (in degrees Rankine) and the critical pressure within 2.72%.

A comparison of the results for nine binary paraffinic systems, calculated by the methods of Eilerts *et al.* (*4*), Organick and Brown (*15*), Kurata and Katz (*11*), Mayfield (*12*), Smith and Watson (*23*), and this investigation, is shown in Table 1, which presents the percentage errors resulting from a comparison between the calculated and experimental values.

For seven additional systems, consisting of two and three components and containing hydrogen, olefins, naphthenes, and aromatics, in addition to normal paraffins (*1, 2, 8, 9, 10, 13, 17, 18*), the results calculated by this method produce a deviation from the experimental values of the critical temperature of 1.22% and a deviation of 3.13% for the critical pressure.

From these results this method is more exact than the methods of Or-

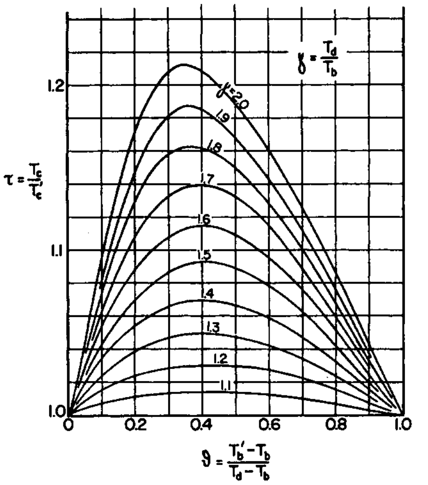

Fig. 4. Relationships of τ vs. θ for estimation of critical temperatures ($1.0 \leq \gamma \leq 2.0$).

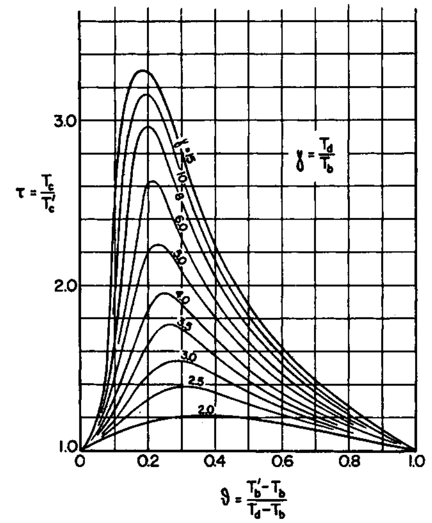

Fig. 5. Relationships of τ vs. θ for estimation of critical temperatures ($2.0 \leq \gamma \leq 15$).

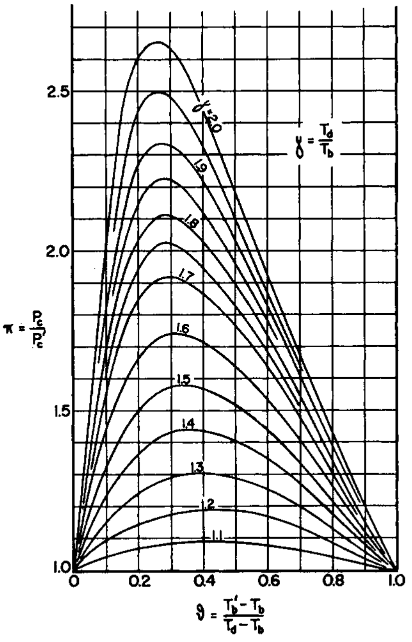

Fig. 6. Relationships of π vs. θ for estimation of critical pressures ($1.0 \leq \gamma \leq 2.0$).

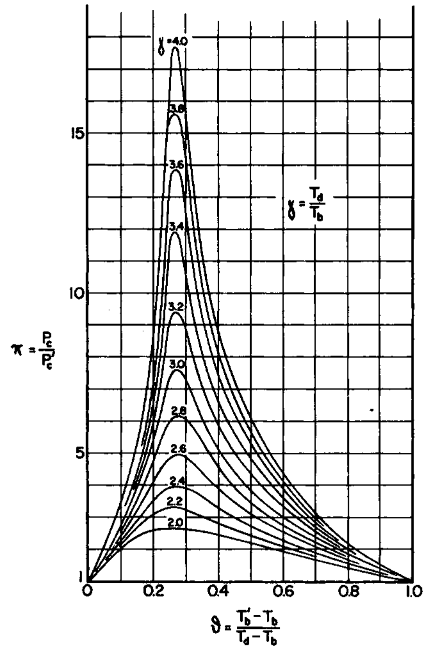

Fig. 7. Relationships of π vs. θ for estimation of critical pressures ($2.0 \leq \gamma \leq 4.0$).

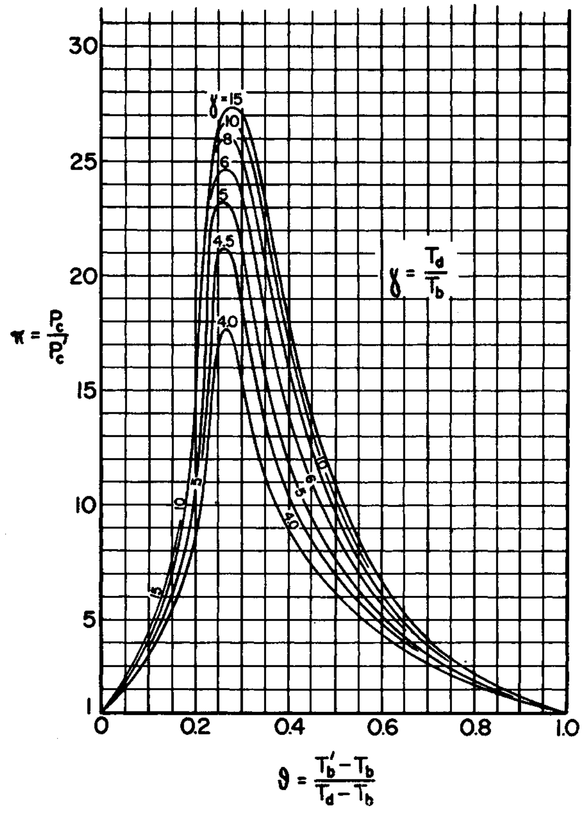

Fig. 8. Relationships of π vs. θ for estimation of critical pressures ($4.0 \leq \gamma \leq 15$).

ganick and Brown (*15*), Kurata and Katz (*11*), and Smith and Watson (*23*) for both critical temperatures and critical pressures. The methods of Eilerts *et al.* (*4*) and Mayfield (*12*) are comparable. However Mayfield is limited to paraffinic mixtures, and Eilerts *et al.* restrict their studies to mixtures with the boiling range no higher than that of methane–*n*-pentane. From a comparison based upon three systems containing an olefinic, a naphthenic, and an aromatic component Eilerts *et al.* (*4*) predict the critical temperatures with an error of 1.30% and the critical pressures with an error of 4.20%. The comparable values predicted by this correlation are 0.69 and 1.59%. Except for Organick and Brown (*15*) and this investigation, none of the investigators are able to treat mixtures containing hydrogen.

It should be noted that a decrease in accuracy results as the difference between the boiling points of the pure components increases, particularly for systems containing methane or hydrogen. The least deviation can be expected for closely boiling constituents. This method has not been applied extensively to mixtures of more than two components; however it is felt from a consideration of these three-component systems treated that this method may be applied with reservation.

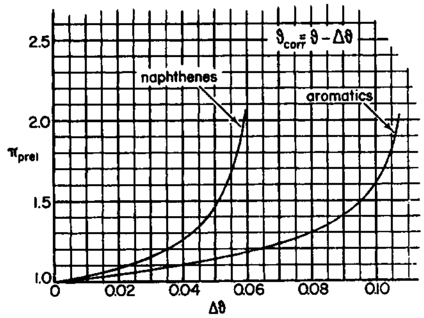

Fig. 9. $\Delta\theta$ corrections for naphthenic and aromatic compositions.

NOTATION

P_c = critical pressure, lb./sq. in. abs.
P'_c = pseudocritical pressure, lb./sq. in. abs.
P_i = vapor pressure of *i*th component, lb./sq. in. abs.
T_b = normal boiling point, °R.
T'_b = molar average boiling point, °R.
T_c = critical temperature, °R.
T'_c = pseudocritical temperature, °R.
T_d = normal dew point, °R.
x_i = mole fraction of *i*th component in liquid phase
y_i = mole fraction of *i*th component in vapor phase

Greek Symbols

γ = ratio of normal dew point to normal boiling point, dimensionless, T_d/T_b
γ_{corr} = corrected temperature parameter
θ = ratio of difference between molar average boiling point and normal boiling point to

TABLE 1. COMPARISON OF PERCENTAGE OF ERROR RESULTING FROM THIS STUDY AND OTHER AVAILABLE METHODS

$$\% \text{ error} = \frac{1}{n} \Sigma \frac{|\text{calculated-experimental}|}{\text{experimental}} \times 100$$

System	*n*, number of compositions	Eilerts *et al.* (*4*)		Organick and Brown (*15*)		Kurata and Katz (*11*)		Mayfield (*12*)		Smith and Watson (*23*)		This investigation	
		T_c	P_c	T_c	P_c	T_c	P_c	T_c	P_c	T_c	P_c	T_c	P_c
Methane-propane (*20*)	4	0.43	2.70	0.79	6.23	0.26	2.90	0.79	1.25	2.02	11.00	0.48	7.85
Propane-*n*-butane (*14*)	5	0.24	0.41	0.17	3.36	0.86	3.90	0.17	0.09	0.83	2.90	0.26	1.11
Propane-*n*-pentane (*21*)	4	0.26	2.20	0.67	4.77	0.96	1.90	0.67	0.78	0.33	3.90	0.20	0.97
n-Pentane-*n*-heptane (*3*)	3	0.15	1.82	0.07	6.20	0.41	1.80	0.07	1.20	0.17	5.32	0.07	1.41
Methane-*n*-butane (*19*)	5	1.75	3.20	2.95	4.45	2.99	4.40	2.95	2.86	1.82	14.11	0.72	8.93
Ethane-*n*-heptane (*5*)	5	0.91	2.90	2.22	6.11	0.25	3.00	2.22	1.98	0.63	20.31	0.21	0.82
Ethane-*n*-butane (*6*)	5	0.18	1.31	0.69	2.35	1.09	1.90	0.69	0.26	0.62	3.60	0.19	0.75
n-Butane-*n*-heptane (*7*)	5	0.26	1.00	0.19	5.97	0.58	2.50	0.19	1.20	0.25	16.72	0.14	0.43
Methane-*n*-pentane (*22*)	5	0.56	4.90	2.15	11.06*	7.49*	6.00	2.15	8.16	3.84	7.51	0.77	3.82
Average % error		0.53	2.27	1.10	4.93	0.93	3.14	1.10	1.98	1.17	9.49	0.34	2.90

* This particular value not considered in computing the average percentage of error.

difference between normal dew point and normal boiling point, dimensionless, $T'_b - T_b / T_d - T_b$

θ_{corr} = corrected temperature parameter, $\theta - \Delta\theta$

π = pressure ratio dimensionless, P_c/P'_c

τ = temperature ratio, dimensionless, T_c/T'_c

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Filter Cake Washing Performance

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Differential equations for a filter cake wash cycle are derived on the assumption that the wash liquor executes plug flow in the pores of the cake, with continuous mass transfer between the liquor and a boundary film of filtrate. These equations are solved and the solutions presented as performance charts. The solutions are compared with certain experimental results.

There is considerable literature on filter cake washing (*6, 7, 8, 9*) based on filtration equations such as Kozeny's (*10, 11*). These filtration equations are essentially hydrodynamic equations, based in general on Hagen-Poiseuille flow, requiring the use of some (generally semiempirical) connection between pressure drop and flow rate in order to predict the behavior of a wash cycle.

There is however a different approach to wash analyses which assumes a known flow pattern in the filter cake and writes differential material balances involving empirical mass transfer coefficients. Rhodes (*5*) presented a performance equation of this general type and correlated it with certain data for sodium chloride washing, assuming that the wash liquor was perfectly mixed with the filtrate so that the mass transfer coefficients did not appear explicitly. His performance equation was accordingly a simple exponential decay in wash liquor solute concentration with time.

The present paper presents transport equations of a more realistic sort, assuming plug flow in the pores of the filter cake, with continuous mass exchange between the wash liquor and a boundary film of filtrate. The appropriate differential equations turn out to be a simple form of those studied by Goldstein (*2*) in another connection and have an explicit mathematical solution.

The physical model assumed for the washing is presented below, as are the differential equations. The mathematical solutions of these differential equations are given and compared with some of Rhodes' data. Figures 1 and 2 present these mathematical solutions in a concise graphical form, and so serve as design charts for a wash cycle. Certain extreme cases are discussed.

Figures 1 and 2 are plots of the solute concentration in the wash liquor and the filter cake respectively. In making a design to meet certain requirements on the filter cake concentration one would use Figure 2, either at the position corresponding to the highest concentration or at some average position. To make a design in this way requires of course a knowledge of such parameters as mass transfer coefficients which can only be obtained by experiment. In interpreting data, where only exit wash liquor concentrations would generally be available, one would use Figure 1 to determine those values of the parameters which made the theory agree best with the observations.

THE DIFFERENTIAL EQUATIONS

It is assumed that before the start of a wash cycle most of the filtrate has been forced out of the filter cake pore spaces by the pressure difference across the filter cloth. A channel for the flow of wash liquor is thus formed, with a stagnant film of filtrate remaining on its surface. The washing serves to extract the remaining solute from this film.

Whether the pore spaces have been created by the pressure difference across the filter cloth, or whether the excess liquid in the filter cake is pushed out by the first passage of wash liquor, is really of no consequence in what follows. The differential equations below are written only where the wash liquor contacts the pore surface, and the mathematical solutions apply at a given point only after the wash liquor has arrived there.

The flow channel and the filtrate film are taken to be of uniform cross section,