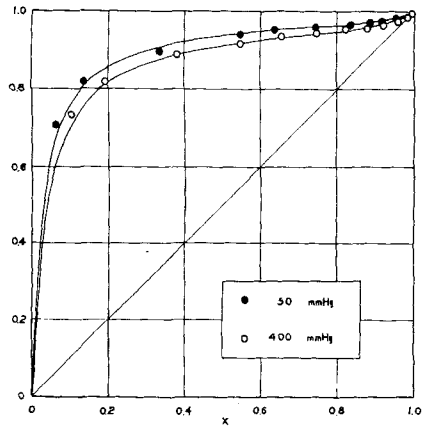

Fig. 2. Predicted and experimental vapor-liquid equilibrium for water-diacetone alcohol system (5): ——— predicted, o experimental.

A'_0, B'_0 = predicted values of A_0 and B_0
ΔE = internal energy of vaporization
k = constant
n = exponent
P = vapor pressure of pure component
R = gas constant
t = temperature, °C.
T = temperature, °K.
V = molar volume
x = mole fraction in liquid phase
y = mole fraction in vapor phase
Z = volume fraction
γ = activity coefficient
δ = solubility parameter of Hildebrand (8)

Subscripts

1, 2 = components 1 and 2

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Part II. Hydrocarbon Systems

This article proposes an empirical method for predicting the vapor-liquid equilibrium data on binary hydrocarbon systems without any experimental data on the mixtures. The method was tested for twenty-six systems under atmospheric pressure and three isothermal systems. The predicted results are in excellent agreement with experimental data.

The increasing importance of obtaining accurate and complete vapor-liquid equilibrium data on nonideal mixtures for the design of distillation equipments in chemical industries stimulates one to devote his efforts to accumulating new data and correlating them. However existing literature data are now sketchy, so that available methods are useful for extending a limited amount of boiling point data, azeotropic data, or solubility data into prediction of vapor-liquid equilibria over the entire concentration range with a sufficient degree of accuracy and also for extending vapor-liquid equilibrium data available at a given condition (temperature or pressure) to other conditions. Such methods need at least a minimum amount of data on the mixture under consideration.

The extent of deviations from ideal solution is expressed by the liquid phase activity coefficients different from unity. The values of the activity coefficients are strongly dependent upon the differences in intermolecular forces, polarity, chemical structure, and molecular size among the individual components in the mixtures. Recently Pierotti, Deal, and Derr (23) presented a very interesting attempt to express the terminal values of activity coefficients as a function of the molecular structure of the binary components quantitatively.

Prediction of vapor-liquid equilibria of binary hydrocarbon mixtures, which show positive deviation from ideality, with the usual two-constant Margules or Van Laar equations evaluated from such two terminal values cannot give satisfactory results, if they are applied for a system of a wide boiling range, because these equations are valid only at isothermal conditions and are not suitable for the isobaric systems (3, 21). In this case one must take into consideration the temperature dependence of activity coefficients and follow a lengthy process of calculations.

A simple approach to the same problem was suggested by Lu and Graydon (17). They proposed an empirical method in prediction of vapor-liquid behavior for binary hydrocarbon systems containing one aromatic component using only the physical properties of pure components. Their calculated results were in good agreement with experimental data on fourteen systems at atmospheric pressure with three notable exceptions: benzene-2,4-dimethyl pentane, benzene-2,2,3-trimethyl butane, and *n*-pentane-benzene systems. The present article presents a modification of Lu-Graydon's method to include paraffin-naphthene mixtures. Not only isobaric systems but also isothermal systems can be treated by this method as well.

PROPOSED METHOD

A_0 and B_0 in Equations (2) to (5) of Part I are empirically expressed in the same form as proposed by Lu and Graydon. Thus

$$A_0 = \frac{1}{E}\left|\delta_1 - (\delta_1\delta_2)^{1/2}\right|(C_1 + C_2) \quad \text{at } t_1 \qquad (1)$$

$$B_0 = \frac{1}{E}\left|\delta_2 - (\delta_1\delta_2)^{1/2}\right|(C_1 + C_2) \quad \text{at } t_2 \qquad (2)$$

where δ is the solubility parameter of Hildebrand (11). The quantities C_1 and C_2 are constants defined below, which differ from the definition by Lu and Graydon in its temperature factor.

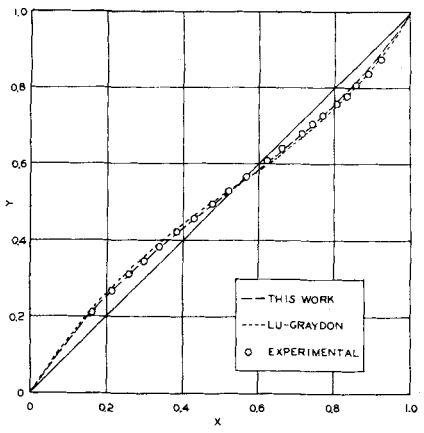

Fig. 1. Predicted and experimental vapor-liquid equilibrium for benzene-2,4 dimethyl pentane system (26).

	A	B	
1	Benzene	Methylcyclopentane	(9,20)
2	Cyclohexene	Benzene	(10)
3	Cyclohexane	*n*-heptane	(21)
4	Ethylbenzene	*n*-octane	(34)
5	*n*-heptane	Benzene	(19,30)
6	*n*-heptane	Ethylbenzene	(19)
7	*n*-hexane	Methylcyclohexane	(21)
8	*n*-hexane	Toluene	(19,29)
9	Toluene	Methylcyclohexane	(25)
10	2,2,5-trimethylhexane	Ethylbenzene	(32)

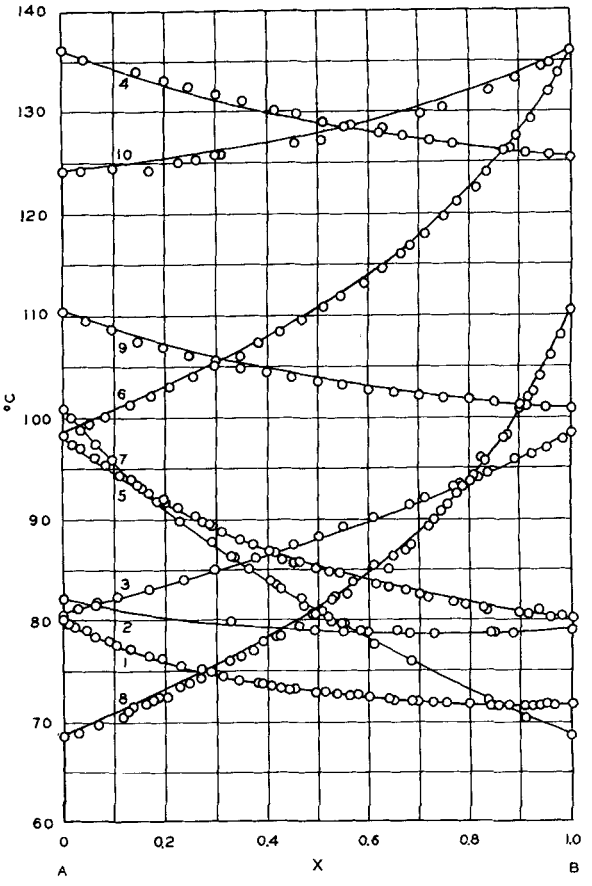

Fig. 2. Boiling point-liquid composition diagram: ——— predicted, ○ experimental.

Empirical Assignments for Quality C

Component	C
Type 1 Benzene	$(V_L/V_H)_i$
Type 2 Aromatic hydrocarbons except benzene. Naphthenes (cyclohexane etc.)	$\dfrac{(M_2/M_1)^2(V_L/V_H)_i}{(T^\circ_2 - T^\circ_1 + 1)^{1/5}\ (T^\circ_2/T^\circ_1)}$
Type 3 Other hydrocarbons (paraffins, cycloparaffins)	$\dfrac{(M_2/M_1)\ (V_L/V_H)_i^{2}}{(T^\circ_2 - T^\circ_1 + 1)^{1/5}\ (T^\circ_2/T^\circ_1)}$

In the calculation of the quantity C hydrocarbons are classified into three types. The first type is benzene only. Aromatic hydrocarbons except benzene and napthenes (cyclohexane, methylcyclohexane, etc.) belong to the second type. Paraffins and cycloparaffins (cyclopentane, methylcyclopentane) are included in the third type. In isothermal systems one should take care that the value of $(T^\circ_2 - T^\circ_1 + 1)^{1/6}$ (T°_2/T°_1) does not reduce to unity. The numerical value of E is assigned to be 2 for the mixtures containing one aromatic component and four for naphthene-paraffin mixtures. It is taken into consideration that in extensive experimental work by Myers (*19, 20, 21*) naphthene-paraffin mixtures show less positive deviations from ideality than aromatic-paraffin and aromatic-naphthene mixtures do: namely narrow-boiling naphthene-paraffin mixtures are essentially ideal. But for wide-boiling mixtures of this type terminal activity coefficients can exceed 1.1. The symbol | | denotes the absolute value of the argument. The molar volumes of the pure components were obtained from the compilation of Francis (*6, 7*). The vapor pressure data and heats of vaporization were taken from Lange (*15*).

RESULTS

The calculated results are shown in Table 1, where the average deviation of y is listed on Column 8 for twenty-six systems together with the values of constants used. The average deviation in the systems tested by Lu and Graydon is also listed for the sake of comparison. The symbol $|y_{\text{pred}} - y_{\text{exptl}}|_{\text{avg}}$ represents the absolute value of average deviation of the predicted values of y from the smoothed experimental values at nine points of the 0.1 mole fraction interval of x. When one compares the results of the present work with those by Lu and Graydon, it is generally found that the Lu and Graydon method gives lower values of y in the range of higher concentration of x and higher values of y in the range of lower concentration of x than the predicted y of the present method. As an example of this statement Figure 1 shows the calculated values by both methods and the experimental data by Richards and Hargreaves (*26*) for the benzene-2,4-dimethyl pentane systems.

The mean deviation from the smoothed experimental values for twenty-six systems is 0.003 by the present method and the maximum deviation is 0.007 for 2,2,5-trimethylhexane-ethylbenzene system. On the other hand in accordance with Lu and Graydon's method the mean deviation of seventeen systems is 0.006, and the benzene-2,4-dimethyl pentane system gives a maximum deviation of 0.015. This fact shows the superiority of the present method to Lu and Graydon's method.

Lu and Graydon stated that three systems of their calculated seventeen systems are examples of the poorest agreement with experimental data. Those are the systems benzene-2,4-di-

TABLE 1. PREDICTED RESULTS FOR SYSTEMS AT ATMOSPHERIC PRESSURE AND USED CONSTANTS

System	t_1, °C.	t_2, °C.	a_{12}	a_0	a_{21}	$\left(\frac{P_1}{P_2}\right)_{t_1}$	$\left(\frac{P_1}{P_2}\right)_{t_2}$	$\lvert y_{pred}-y_{expt}\rvert_{avg}$ This work	Lu-Graydon	t_{calc}, °C.	$t_{calc}-t_{expt}$
1. Benzene-cyclohexane* (*26, 29*)	80.1	80.7	0.711	1.047	0.722	1.019	1.019	0.003	0.011	77.7	0.1
2. -cyclohexene* (*10*)	79.2	82.1	0.870	1.125	0.833	1.087	1.087	0.002	0.006	79.0	0.1
3. -2, 4-dimethylpentane* (*1, 18, 26*)	80.1	80.5	0.613	1.217	0.779	1.012	1.012	0.006	0.015	76.7	0.1
4. -*n*-heptane (*4, 19, 29*)	80.1	98.4	1.255	2.216	0.958	1.771	1.701	0.003	0.005	85.4	−0.3
5. -2, 2, 3-trimethylbutane* (*10, 29*)	79.1	79.9	0.592	1.216	0.738	1.022	1.024	0.003	0.013	75.6	0
6. 1, 3-butadiene-styrene (*33*)	−4.4	145.0	593.36	31.137	0.189	828.50	3.483	0.001	0.001	8.8	−1.2
7. Cyclohexane-*n*-heptane (*21*)	80.7	98.4	1.590	1.881	1.050	1.736	1.652	0.004		87.8	−0.4
8. Cyclopentane-benzene (*20*)	49.3	80.1	1.990	2.416	0.650	2.881	2.493	0.003		58.2	−0.2
9. *n*-heptane-ethylbenzene (*19*)	98.4	136.2	2.439	2.499	0.729	3.12	2.62	0.002	0.003	110.6	0.3
10. -toluene (*2, 12, 27, 29, 30*)	98.4	110.6	1.145	1.261	0.699	1.434	1.412	0.004	0.004	102.1	0.6
11. *n*-hexane-benzene (*19, 29, 31*)	68.7	80.1	0.970	1.189	0.535	1.440	1.410	0.002	0.009	79.9	0.4
12. -cyclohexane (*21*)	68.7	80.7	1.328	1.309	0.825	1.458	1.434	0.001		73.5	−0.2
13. -methylcyclohexane (*21*)	68.7	100.9	2.513	2.163	0.789	2.742	2.484	0.004		80.8	0.1
14. -methylcyclopentane (*21*)	68.7	71.8	1.020	1.027	0.876	1.100	1.078	0.002		69.7	−0.3
15. -toluene (*19, 29*)	68.7	110.6	2.997	2.885	0.671	3.914	3.157	0.003	0.003	81.2	0.4
16. Methylcyclohexane-toluene (*25*)	100.9	110.6	1.101	1.244	0.783	1.330	1.303	0.002	0.003	104.0	0.4
17. Methylcyclopentane-benzene* (*9, 20*)	71.8	80.1	0.930	1.192	0.651	1.301	1.282	0.003	0.007	71.7	0
18. -toluene (*20*)	71.8	110.6	2.761	2.800	0.753	3.490	2.876	0.002		84.5	0.5
19. *n*-octane-ethylbenzene (*34*)	125.6	136.2	1.126	0.984	0.598	1.338	1.328	0.003	0.004	129.0	−0.3
20. *n*-pentane-benzene (*19*)	36.1	80.1	2.906	3.571	0.548	4.89	3.60	0.003	0.005	47.2	0.1
21. -cyclohexane (*21*)	36.1	80.7	4.225	3.291	0.762	4.829	3.687	0.003		50.5	0.2
22. -methylcyclohexane (*21*)	36.1	100.9	9.134	3.890	0.549	10.157	5.960	0.006		53.7	−0.3
23. -methylcyclopentane (*21*)	36.1	71.8	3.143	2.575	0.782	3.491	2.932	0.005		48.7	−0.2
24. Toluene-*n*-octane (*2, 16*)	110.6	125.6	1.171	1.766	0.914	1.550	1.502	0.003	0.005	115.3	1.4
25. 2, 2, 5-trimethylhexane-ethylbenzene (32)	124.1	136.2	1.163	1.296	0.772	1.400	1.375	0.007	0.006	127.9	0.6
26. 2, 2, 4-trimethylpentane-toluene (*5, 8, 29*)	99.2	110.6	1.158	1.118	0.656	1.400	1.364	0.003	0.002	102.8	1.1

* Azeotrope. The calculated boiling point in Column 9 indicates the azeotropic temperature.

methylpentane and benzene-2,2,3-trimethyl butane.*

It is to be noted that the present method can predict these systems with sufficient accuracy.

As the present empirical method predicts the *x-y* correlation satisfactorily, the second step is to calculate the boiling points of the mixtures. The following thermodynamic formula correlating constant pressure vapor-liquid equilibrium data with the latent heat of vaporization of the solution has been developed by Othmer et al. (*22*) and Ibl and Dodge (*13*):

$$\left[\frac{y}{x}-\frac{(1-y)}{(1-x)}\right]\left(\frac{dy}{dx}\right)_p = \frac{\Delta H}{RT^2}\left(\frac{dT}{dx}\right)_p \qquad (3)$$

ΔH may be evaluated from the heat of mixing and the ideal heats of vaporization of the pure components. In most cases the heat of vaporization is large in comparison with the heat of mixing, so that the latter may be neglected. Here ΔH is approximately estimated by

$$\Delta H = H_1 x + H_2(1-x) \qquad (4)$$

Substituting Prahl's equation and Equation (4) into Equation (3) one can perform the integration of Equation (3). The analytic integration however is formidably complex. Step-by-step integration with respect to the small increments of Δx and Δy is simple. Of course the precision of calculations depends upon the magnitude of the increment of Δx. The calculated boiling points at the equimolar composition or azeotropic point are listed on Column 10 of Table 1. The graphical representation is given in Figure 2.

The present method was also tested for three isothermal systems, that is benzene-cyclohexane, *n*-pentane-cyclohexane, and 2,2,4-trimethyl pentane-toluene. The calculated results are shown in Table 2.

* They have counted *n*-pentane-benzene system as another example of low accuracy, but in accordance with the authors' recalculation by their method the predicted results for this system show a precise agreement with the experimental results. This seems to come from the difference in the source of the vapor-pressure data between Lu and Graydon and the authors' calculation. The vapor pressure of *n*-pentane at 80.1°C. was taken from (*14*), and the other vapor pressures of *n*-pentane and benzene were obtained from (*15*).

TABLE 2. PREDICTED RESULTS FOR ISOTHERMAL SYSTEMS

System	t, °C.	a_{12}	a_0	a_{21}	$\lvert y_{pred}-y_{expt}\rvert_{avg}$
Benzene-cyclohexane (*28*)	40	0.661	1.046	0.721	0.000
n-pentane-cyclohexane (*21*)	40	4.101	4.169	0.766	0.002
2, 2, 4-trimethyl pentane-toluene (*24*)	100	1.153	1.151	0.662	0.008

NOTATION

A_0 B_0 = constants
C = constant
E = constant
H = heat of vaporization of mixture
ΔH = heat of vaporization of pure component
M = molecular weight
R = gas constant
t = temperature, °C.
$T°$ = normal boiling point, °K.
V = molar volume, ml./mole
x = mole fraction in liquid phase
y = mole fraction in vapor phase
δ = solubility parameter of Hildebrand (*11*)

Subscripts

1, 2 = components
H = higher value
L = lower value
p = pressure
t = temperature

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Manuscript received April 25, 1961; revision received August 14, 1961; paper accepted August 16, 1961.

The Effect of Column Length on Separation in Thermogravitational Thermal Diffusion Columns

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A series of experiments was designed to test the phenomenological theory of thermogravitational thermal diffusion columns by obtaining data on the steady state separation and approach to equilibrium in a batch column as a function of column length. Data were obtained on the separation of an equimolar n-heptane-benzene solution at five different values of column length varying from 14.5 in. to 6 ft. All measurements were made in one concentric cylinder column in which the effective length was varied by controlling the liquid level in the annulus. Helium gas was used to displace the air in the annulus above the liquid in order to provide even temperature distribution throughout the column. The data were found to substantiate the effect of length predicted by application of the phenomenological theory and to be in very good agreement with other aspects of the theory.

If a temperature gradient is applied to a homogeneous, binary solution, a concentration gradient will usually be established. The name applied to this phenomenon is *thermal diffusion*. Although this effect was reported as early as 1856 (*11*), it remained primarily a laboratory curiosity until Clusius and Dickel introduced the thermogravitational thermal diffusion column in 1938 (*1*). This device makes use of convection currents to achieve a multistaging effect in one piece of equipment.

Several phenomenological theories describing thermogravitational thermal diffusion columns have been presented in the literature (*2, 3, 6, 9*). The treatment of Furry, Jones, and Onsager (*6*) has been widely applied. This treatment is based on the reduction of a complicated differential equation in two space dimensions to an equation involving only one space dimension corresponding to the length of the column. The reduced equation resulting from their analysis is called the *transport equation.*

The transport equation has been applied to predict the effect on separation of column dimensions, operating variables, and various physical properties of the solution being separated for both batch and continuous-flow columns operating under steady state and transient conditions. Many investigations have been reported which demonstrate the qualitative agreement between theory and experiment. Several investigators have considered the effect of column length as one of several column parameters being studied, but no one investigation has covered a large enough range of column length to substantiate or repudiate the theory.

As part of an extensive investigation of the effect of pressure on the steady state separation of gas mixtures in batch columns, Drickamer and coworkers (*5*) used columns which differed in length by a factor of two. Drickamer, Mellow, and Tung (*4*) used these results in preparing an empirical correlation which predicts a