# AN ELECTRICAL COMPUTER FOR SOLVING PHASE EQUILIBRIUM PROBLEMS 

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## INTRODUCTION

In both production and refining operations of the oil industry many processes are controlled by the gas-liquid phase relationships of the hydrocarbon mixtures of interest. The quantitative behavior of fractionating or distillation columns and stills depends on the changes in the equilibrium distributions of the hydrocarbon components between the gas and liquid phases as the pressure or temperature conditions may vary along the length of the column or as the gross operating parameters and compositions are varied. In oil producing operations the nature and amount of gas phase developed within an underground reservoir as it is being depleted and its pressure declines also involve the basic equilibrium gas-liquid phase interactions. The influence of surface conditions of temperature and pressure and various separation procedures on the nature and amount of stock tank oil and natural gas recovered from a given well stream is likewise determined by the same basic phase equilibrium characteristics of the hydrocarbon systems. Such equilibrium separation of the gas and liquid phases in a well stream is of importance both in establishing optimum separator conditions for obtaining maximum stock tank oil yields and in the general problem of crude stabilization.

The phenomena involved in these problems and their quantitative aspects can, of course, be established in each individual instance by appropriate laboratory experimentation. It has been found, however, that by associating with the individual hydrocarbon components functional characteristics de-

[^0]scribing their individual gas-liquid phase equilibrium behavior, the phase properties of the composite mixtures can be predicted by mathematical computation. These characteristics have been termed "equilibrium constants", or "equilibrium ratios",* and are defined by the general equation:
\[

$$
\begin{equation*}
\mathbf{K}_{j}=\frac{\mathbf{y}_{\mathrm{s}}}{\mathbf{x}_{\mathrm{j}}} \tag{1}
\end{equation*}
$$

\]

where $K_{f}$ is the equilibrium ratio for the $j$ th component, $y_{j}$ is the mol fraction of that component in the gas phase, and $\mathrm{x}_{\mathrm{j}}$ is the corresponding mol fraction in the coexisting liquid phase.

Considering the $\mathrm{K}_{\mathrm{j}}$ as representing available and measurable properties of the individual components of a mixture, and as defined by Eq. (1), it is readily shown that in a coexisting gas-liquid system the mol fraction concentrations of the individual components in the gas phase, $y_{j}$, and those in the liquid phase, $\mathrm{x}_{i}$, are given by the expressions:

[^1]\[

$$
\begin{align*}
& y_{j}=\frac{n_{j} K_{j}}{1+n_{j}\left(K_{j}-1\right)} ; \\
& x_{j}=\frac{n_{j}}{1+n_{g}\left(K_{j}-1\right)} \tag{2}
\end{align*}
$$
\]

where the $n_{j}$ are the corresponding mol fraction concentrations in the composite system, and $n_{g}$ is the mol fraction of the whole which is in the gas phase. The basic unknown in Eq. (2) is $n_{F}$, which gives the gross separation between the gas and liquid phases. This may be determined in principle by imposing the requirement that the sums of the mol fractions in both the gas and liquid phases are unity, i.e. by the equations:

$$
\begin{align*}
& \Sigma \frac{n_{j} K_{j}}{1+n_{s}\left(K_{j}-1\right)}=1 \\
& \Sigma \frac{n_{j}}{1+n_{g}\left(K_{j}-1\right)}=1 \tag{3}
\end{align*}
$$

The solution of the equivalent Eqs. (3) lying between 0 and 1 , when inserted into Eqs. (2), provides a complete description of the compositions of the coexisting gas and liquid phases. While the Eqs. (3) are essentially equivalent to polynomial equations, such transformations are of little value when dealing with multicomponent sys-


FIG. 1 - SIMPLIFIED SCHEMATIC DIAGRAM OF THE PHASE EQUILIBRIUM COMPUTER.
tems. It has therefore been common practice to resort to direct numerical trial and error methods of solution, often supplemented by graphical interpolation. Such procedures are especially laborious when 7 or more components are involved and when a single problem requires multiple sequences of phase determinations, as in tray-to-tray or stage separation studies. An apparatus has therefore been developed for the purpose of solving Eqs. (3) by a special electrical circuit analog. This will be described in the following sections.

## DEVELOPMENT OF THE ANALOGOUS CIRCUIT FOR THE ELECTRICAL COMPUTER

Electrical analogs of both algebraic and differential equations have been used for many years to facilitate their numerical solution. That which has been developed for the solution of Eqs. (3) is unique in that it is comprised of linear circuit elements, although the
basic unknown appears in an essentially non-linear manner.
The electrical circuit analog of Eqs. (3) can be formally expressed in a variety of ways, such as:

$$
\begin{align*}
& \Sigma \mathrm{I}_{\mathrm{j}} \mathrm{R}_{\mathrm{j}}=1 \\
& \Sigma \frac{\mathrm{E}_{j}}{\mathrm{I}_{j}}=1 \\
& \Sigma \frac{\mathrm{E}_{j}}{\mathrm{R}_{j}}=1 . \tag{4}
\end{align*}
$$

where $I_{j}, R_{j}, E_{j}$ denote appropriate current, resistance or potential drop analogs of the individual terms in Eqs. (3). It is the last which has been taken as the basis for the computer to be described here. The direct equivalent of the last of Eqs. (4) would comprise a set of parallel variable resistances in which voltages proportional to the $n_{j}$ are imposed on the individual elements and their resistances are made proportional to $1+n_{g}\left(K_{j}-1\right)$. By varying the $n_{g}$ so that the measured resultant current is unity, or an appropriate scale factor, the correct value of $\mathrm{n}_{\mathrm{g}}$ or the
solution to the equations will be obtained.
A transformation of Eqs. (3) to the form:

$$
\begin{equation*}
\Sigma \frac{c_{j} n_{j}}{n_{g}+c_{j}}=1 ; c_{j}=\frac{1}{K_{j}-1} . \tag{5}
\end{equation*}
$$

leads to simplified circuit adjustments, since the variable resistors in the various circuit elements would be the common term $\mathrm{n}_{6}$, which could be ganged together to insure identical values and variations. However, a still simpler equivalent of Eqs. (3) and (5), and the one which has been chosen for designing the Computer, ${ }^{*}$ is:

$$
\begin{equation*}
\Sigma \frac{n_{j}}{c_{j}+n_{g}}=0 \tag{6}
\end{equation*}
$$

In Eq. (6) the voltages applied to the separate component analogs are given directly by the total composition

[^2]

FIG. 2 - PHOTOGRAPH OF THE 12 COMPONENT PHASE EQUILIBRIUM COMPUTER.
mol fractions $n_{j}$. The physical characteristics of the individual components enter only as the fixed resistance elements $c_{j}$. And the basic unknown $n_{g}$ can again be simulated by a set of ganged identical variable resistors. Moreover, Eq. (6) permits the use of a null method - zero resultant current - for locating the desired solution $n_{8}$.

As is obvious from the form of Eq. (6), and as is to be expected physically, in any equilibrium mixture comprised of coexisting gas and liquid phases it is necessary that for some of the components $K_{j}>1$ while for others $K_{j}<1$. In terms of the $c_{j}$ this means that for some of the components $c_{j}>0$, while for the others $c_{j}<0$. This fact requires that the actual composite circuit be constructed of 2 basic groups,
in one of which the $c_{3}$ are positive, and in the other the $c_{j}$ are negative, as shown diagramatically in Fig. 1. Here only two circuit branches are shown to represent components of the mixture for which $c_{\jmath}>0$ and two circuit branches for $c_{j}<0$, but it is obvious that any number of components in a mixture could be handled simply by adding more parallel branches to the circuit.
In Fig. 1 the current in the first group of branches in which $c_{J}$ is positive ( $\mathrm{K}_{\mathrm{j}}>\mathbf{l}$ ) is obviously:

$$
\begin{equation*}
\frac{V_{j}}{c_{j}+n_{g}}=\frac{n_{j}}{c_{j}+n_{g}} \tag{7}
\end{equation*}
$$

The current in the second group of branches in which $c_{j}$ is negative $\left(K_{j}<1\right)$ can be written:
$\frac{V_{j}}{-c_{i}-1+\left(1-n_{g}\right)}=\frac{-n_{j}}{-c_{j}-n_{g}}=\frac{n_{j}}{c_{j}+n_{g}}$

Since $-\mathrm{n}_{\mathrm{j}}$ is a negative quantity in Eq. (8), it is simply represented as a neg. ative voltage. And since the $c_{\jmath}$ are neg. ative for the branches represented by Eq. (8), the sums of the resistances in the various branches are $\left|c_{s}\right|-n_{g}$. Therefore Eq. (8) gives the values of negative currents. The expression for the summation of the currents in the branches of Fig. 1 thus reduces to Eq. (6) when the current through the galvanometer, G, is zero.
In addition to using such a circuit to solve for $n_{g}$ it can be used either to determine the $\mathrm{x}_{\mathrm{j}}$ for $\mathrm{K}_{\mathrm{j}}>1$ by measuring the voltages across the resistors c , in the first group of branches, or to determine the $y_{j}$ for $K_{j}<1$ by measuring the absolute values of the voltages across the resistors $-\mathrm{c}_{\mathrm{j}}-1$ in the second

fig. 3 - CIRCUIT DIAGRAM OF THE PHASE EQUILIBRIUM COMPUTER.
group of branches. The remaining values of $x_{j}$ and $y_{j}$ can be calculated from Eq. (1) or Eqs. (2). However, Eqs. (2) will usually give more accurate results than Eq. (1), and for this reason Eqs. (2) have been used in all examples presented in this study.

## DESCRIPTION OF THE <br> ELECTRICAL COMPUTER

The Computer to be dowcribed here is a twelve component instrument. A photograph of this Computer is reproduced in Fig. 2. The controls for each circuit representing a single component are arranged in horizontal lines across each cabinet. Starting on the left side the first controls are switches for turning the voltage on in each circuit and simultaneously determining whether it is a positive or negative voltage. The second control from the left in each series adjusts the value of this voltage to represent the quantity $n_{j}$. The other
four controls for each component adjust the value of four resistors which can be put in series by means of patch cords, and the total resistance will represent $c_{j}$ (or ( $-c_{j}-1$ ) if $K<1$ ).

The vacuum-tube-voltmeter used for measuring all voltages can be seen at the lower left of Fig. 2. There are a number of switches at the bottom of the left-hand cabinet which permit this -voltmeter to be connected to any of the voltage points corresponding to the $n_{1}$ or the $x_{j}$ or $y_{j}$.
The value of $n_{z}$ is read directly, when the circuits are balanced, from the dial shown in Fig. 2 at the lower left of the right-liand cabinet. This dial adjusts simultaneously the value of the $\mathrm{n}_{\mathrm{g}}$ resistors in all of the component branches. The condition of balance is indicated on the microammeter just to the right of this dial.

The main power supply and a separate electronic voltage regulator for each voltage source is contained in the cabinets. A Sorensen voltage regulator is also used to regulate the 60 cycle line voltage. The detailed circuit diagram of these units is given in Fig. 3.
The overall accuracy of the Computer will depend primarily on the precision of the resistor elements and the control of the voltages. To provide for the former extremely accurate precision resistor units were selected to represent $c_{5}$ and $n_{8}$. To obtain stable voltages the high degree of regulation previously mentioned was provided. It has been found that in general the computer will give results accurate to within 0.5 per cent to 1 per cent depending somewhat upon the problem.

The time necessary for the solution of each flash vaporization will, of course, depend upon the number of


FIG. 5 - ISOBARIC CHART OF THE EQUILIERIUM RAIO FUNCTION FOR PROPANE, $c_{3}, V S$. THE TEMPERATURE. DASHED SEGMENTS GIVE ABSOLUTE VALUES WHERE $\mathrm{c}_{3}<0$.
components used, since most of the time is spent in setting the values of the resistors and voltages. It is usually necessary to reset the voltage dials two or three times as the voltages will vary slightly as the $\mathrm{n}_{\mathrm{g}}$ dial is adjusted to the position of circuit balance. However, an experienced operator can make a complete solution on the Computer in from ten to twenty minutes, as the number of components ranges from 6 to 12 , half of which time is generally consumed in adjusting the $n_{j}$ voltage settings.

## SAMPLE PROBLEMS AND USES OF THE ELECTRICAL COMPUTER

Tests of the general operational performance of the Computer readily demonstrated that it functioned in accordance with the planned circuit design, and as a true analog of the transformed phase equilibrium equations. To eval-
uate its practical value, however, it was necessary to check on the overall accuracy of the instrument, the ease of operation, and the time saving it would afford over direct numerical solution of the equilibrium equation. Accordingly, systematic comparative calculations have been made, numerically and with the Computer, both on purely theoretical problems and some of direct interest in oil production. Several of these will be discussed in the following sections.
As a preliminary to making actual calculations on the Computer it is convenient to convert the equilibrium ratios $\mathrm{K}_{\mathrm{j}}$, to the equivalent $\mathrm{c}_{\mathrm{j}}$. These may be prepared in graphical form to take the place of the charts usually used for the $K_{j}$. To show the nature of such $c_{j}$ charts those for methane, propane, $n$ pentane and $n$-lieptane, as calculated from the corresponding $\mathrm{K}_{\mathrm{j}}$ charts published by the NGAA, are reproduced
in Figs. 4-7. In the case of Fig. 4 for methane the $c_{j}$ are all positive, since the corresponding $\mathrm{K}_{\mathrm{j}}$ exceed 1 , and give smooth continuous curves. For propane, n-pentane, and n-heptane, however, the $c_{j}$ curves each have two segments, joining where the $\mathrm{K}_{\mathrm{j}}$ equal l . At these junction points the $c_{j}$ theoretically become infinite, and they change sign on passing the singularities, although for simplicity only the absolute values are ploted in Figs. 5-7. The overlapping of the curves on Figs. 5-7 thus do not imply any ambiguity in the $c_{j}$ values, and experience has shown that these charts can be used with the Computer quite as conveniently as the $\mathrm{K}_{\mathrm{j}}$ charts in the conventional numerical calculations.

## Theoretical Problem

A theoretical problem was chosen which involved the determination of the phase equilibrium in a mixture of me-

fig. 6-ISOBARIC CHART OF THE EQUILIBRIUM RATIO FUNCTION FOR N-PENTANE, $c_{5}$, VS. THE TEMPERATURE. DASHED SEGMENTS GIVE ABSOLUTE VALUES WHERE $\mathrm{c}_{\mathrm{s}}<0$.


FIG. 7 - ISOBARIC CHART OF THE EQUILIBRIUM RATIO FUNCTION FOR N.HEPTANE, $c_{7}$, VS. THE TEMPERATURE. DASHED SEGMENTS GIVE ABSOLUTE VALUES WHERE $c_{5}<0$.
thane, ethane, pentanes, and heptanes at a temperature of $245^{\circ} \mathrm{F}$, and a pressure of 500 psia . The relative amounts of methane and heptanes present in the mixture were changed keeping a constant percentage, 10 per cent, of both ethane and pentanes. The value of $\mathrm{n}_{\mathrm{F}}$ and the $x_{1}$ 's were calculated numerically using Eqs. (2) and (3), and the results were compared with those obtained by using the Computer. These results and comparisons are presented in Table I. The errors in $\mathrm{n}_{5}$ and $\Sigma_{\mathbf{X}}$ are tabulated for each case. The largest error in $\mathrm{n}_{\mathrm{g}}$ is 0.0015 . Although this error amounts to 3.2 per cent of the value of $\mathrm{n}_{\mathrm{g}}$ in one case, the resulting error in $\Sigma_{X_{j}}$ for this case is only 0.0004 or 0.04 per cent. The largest error in $\Sigma \mathrm{x}_{\mathrm{j}}$ is 0.6 per cent. It thus appears that an error of $\pm 0.002$ may result in the value of $n_{g}$. However; with care, better accuracy can be obtained, especially if the resistor settings are made by the use of a resistance measuring bridge to obtain more accurate values.
A Sample Problem for Determining Optimum Separator Pressures
As an example of an application of the Computer to a study of crude oil separation in field operations, Computer calculations were made on the effect of separator conditions on the gas-oil ratio, stock tank gravity and yield for the oil produced from the Witcher pool in Oklahoma. Equivalent complete numerical calculations had been previously made on this problem,* thus providing a basis for comparison of the two methods. For purposes of brevity only a typical set of results will be shown here.

Fig. 8 gives a series of curves for the case of single stage separation only, and thus shows the comparison of the results of Wilkins with the Computer calculations in graphical form. The differences between the smooth curves and the plotted points indicating the laboratory results are quite small, except for two points on the per cent increase in oil recovery curve. While the latter discrepancies seem quite large because of the scales used, the differences in absolute yields are only 0.13 per cent and 0.24 per cent. The Computer results would indicate that a maximum

[^3]TABLE I - Accuracy of the Electrical Computer as Indicated By an Equilibrium Problem Involving a Mixture of Four Hydrocarbons

| \% Methane | \% Heptanes | ng Calculated | $\mathrm{ng}_{\mathrm{g}}$ from Computer | Error in ng | $\Sigma \mathrm{xj}_{j}$ using $\mathrm{ng}_{\mathrm{g}}$ | Error in $\mathrm{\Sigma xj}^{\text {j }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 10 | 70 | 0.0465 | 0.0450 | 0.0015 | 0.9996 | -0.0004 |
| 20 | 60 | 0.1902 | 0.1900 | 0.0002 | 1.0000 | 0.0000 |
| 30 | 50 | 0.3270 | 0.3255 | 0.0015 | 0.9987 | $-0.0013$ |
| 35 | 45 | 0.3942 | 0.3935 | 0.0007 | 0.9991 | -0.0009 |
| 40 | 40 | 0.4613 | 0.4600 | 0.0013 | 0.9983 | -0.0017 |
| 45 | 35 | 0.5285 | 0.5270 | 0.0015 | 0.9978 | $-0.0022$ |
| 50 | 30 | 0.5959 | 0.5960 | 0.0001 | 1.0002 | +0.0002 |
| 55 | 25 | 0.6638 | 0.6626 | 0.0012 | 0.9977 | -0.0023 |
| 60 | 20 | 0.7325 | 0.7320 | 0.0005 | 0.9989 | $-0.0011$ |
| 65 | 15 | 0.8026 | 0.8032 | 0.0006 | 1.0020 | $+0.0020$ |
| 70 | 10 | 0.8747 | 0.8750 | 0.0003 | 1.0013 | $+0.0013$ |
| 75 | 5 | 0.9501 | 0.9508 | 0.0007 | 1.0060 | $+0.0060$ |

No ts : For this theoretical problem a four component mixture was used having $10 \%$ Ethane, $10 \%$ Pentanes, in addition to hydrocarbons above.
Temperature was $245 \circ$ F., pressure $500_{2}$ psia, $\mathrm{K}_{1}=9.7, \mathrm{~K}_{2}=2.7, \mathrm{~K}_{5}=0.38$, and $\mathrm{K}_{7}=0.03$.
TABLE II — Indication of Accuracy of Two Sample Calculations of Two Successive Flash Vaporizations Using the Electrical Computer

| Component | $\mathrm{n}_{1}$ | Pres. $=300$ psia., Temp. $=95^{\circ} \mathrm{F}$. |  |  | Pres. $=14$ psia., Temp. $=65^{\circ} \mathrm{F}$. |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $\mathrm{x}_{5}=\mathrm{n}_{5}$ | $\bar{x}_{j}=\bar{n}_{j}$ | Error in $\mathrm{x}_{5}$ | $\mathrm{x}_{1}{ }^{\prime}$ | $\bar{x}_{j}$ | Error in $\mathrm{x}_{\mathrm{j}}$, |
| $\mathrm{C}_{1}$ | 0.4548 | 0.0633 | 0.0629 | +0.0004 | 0.0009 | 0.0010 | -0.0001 |
| $\mathrm{C}_{2}$ | 0.0987 | 0.0625 | 0.0617 | $+0.0008$ | 0.0068 | 0.0068 | 0.0000 |
| $\mathrm{C}_{3}$ | 0.0699 | 0.0864 | 0.0864 | 0.0000 | 0.0310 | 0.0304 | $+0.0006$ |
| $\mathrm{C}_{4}$ | 0.0475 | 0.0812 | 0.0814 | -0.0002 | 0.0575 | 0.0575 | 0.0000 |
| $\mathrm{C}_{5}$ | 0.0289 | 0.0580 | 0.0582 | $-0.0002$ | 0.0599 | 0.0601 | -0.0002 |
| $\mathrm{C}_{6+}$ | 0.3002 | 0.6476 | 0.6494 | -0.0018 | 0.8452 | 0.0842 | +0.0010 |
|  | 1.0000 | 0.9990 | 1.0000 | -0.0010 | 1.0013 | 1.0000 | $+0.0013$ |

$$
\begin{array}{cc}
\mathrm{n}_{\mathrm{g}}=0.545, \overline{\mathrm{n}}_{\mathrm{g}}=0.5464 & \mathrm{n}_{\mathrm{g}^{\prime}}=0.263, \overline{\mathrm{n}}_{\mathrm{g}},=0.2596 \\
\text { Error }=0.0014 & \text { Error }=0.0034
\end{array}
$$

| Component | $\mathrm{n}_{\mathrm{j}}$ | Pres $=150$ psia., Temp. $=75^{\circ} \mathrm{F}$. |  |  | Pres. $=14$ psia., Temp. $=65^{\circ} \mathrm{F}$. |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $\mathrm{x}_{\mathrm{j}}=\mathrm{n}_{\mathrm{j}}$, | $\bar{x}_{j}=\bar{n}_{j}$, | Error in $\mathrm{x}_{\mathrm{j}}$ | $x_{j}$, | $\bar{x}_{\mathrm{j}},$ | Error in $\mathrm{x}_{\mathrm{j}}$, |
| $\mathrm{C}_{1}$ | 0.4548 | 0.0318 | 0.0320 | -0.0002 | 0.0008 | 0.0008 | 0.0000 |
| $\mathrm{C}_{2}$ | 0.0987 | 0.0415 | 0.0419 | -0.0004 | 0.0069 | 0.0069 | 0.0000 |
| $\mathrm{C}_{3}$ | 0.0699 | 0.0729 | 0.0729 | 0.0000 | 0.0342 | 0.0338 | +0.0004 |
| $\mathrm{C}_{4}$ | 0.0475 | 0.0796 | 0.0795 | +0.0001 | 0.0640 | 0.0631 | +0.0009 |
| $\mathrm{C}_{5}$ | 0.0289 | 0.0619 | 0.0618 | +0.0001 | 0.0631 | 0.0630 | +0.0001 |
| $\mathrm{C}_{6+}$ | 0.3002 | 0.7135 | 0.7119 | +0.0016 | 0.8344 | 0.8324 | +0.0020 |
|  | 1.0000 | 1.0012 | 1.0000 | +0.0012 | 1.0034 | 1.0000 | +0.0034 |

$$
\begin{aligned}
& n_{\mathrm{g}}=0.589, \overline{\mathrm{n}}_{\mathrm{g}}=0.5880 \\
& \text { Error }=0.001
\end{aligned}
$$

$$
\begin{gathered}
n_{z^{\prime}}=0.163, \bar{n}_{g^{\prime}}=0.1628 \\
\text { Error }=0.0002
\end{gathered}
$$

Note: $\bar{x}_{j}$ and $\bar{n}_{\dot{b}}$ represent accurate calculated results. The primed symbols, such as $\mathrm{x}_{\mathrm{j}}$, or $\overline{\mathrm{x}}_{\mathrm{j}}$, rep , resent values of the quantities for the second flash vaporization in each of the two examples.

## TABLE III - Comparison of Electrical Computer Results with Calculated Results of Buckley for a Flash Vaporization at $130^{\circ} F$ and 0 PSIG

| Component | Weight in $\%$ | Molecular Weight | $\underset{\text { Fraction } n_{j}}{\mathrm{Mol}}$ | $\begin{gathered} \text { Equi. } \\ \text { Ratio } \\ \mathrm{K}=\mathrm{y} / \mathrm{x} \end{gathered}$ | $\begin{gathered} \mathrm{x}_{\mathrm{j}} \\ \text { Buckley } \end{gathered}$ | $\begin{gathered} x_{3} \\ \text { Elec. Comp. } \end{gathered}$ | $\underset{\text { Buckley }}{\mathbf{y}_{\boldsymbol{f}}}$ | $\underset{\text { Elec. Comp }}{\mathbf{y}_{\mathrm{f}}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Methane | 7.45 | 16.03 | 0.4380 | 256.0 | 0.0031 | 0.0032 | 0.7925 | 0.7924 |
| Ethane. | 1.22 | 30.05 | 0.0382 | 28.0 | 0.0024 | 0.0024 | 0.0673 | 0.0674 |
| Propane... | 1.06 | 44.06 | 0.0227 | 13.0 | 0.0030 | 0.0029 | 0.0387 | 0.0388 |
| Iso-butane.. | 0.91 | 58.08 | 0.0148 | 6.7 | 0.0036 | 0.0037 | 0.0239 | 0.0240 |
| N-butane... | 0.73 | 58.08 | 0.0119 | 4.9 | 0.0038 | 0.0038 | 0.0185 | 0.0185 |
| Iso-pentane. | 0.50 | 72.09 | 0.0065 | 2.1 | 0.0041 | 0.0042 | 0.0085 | 0.0085 |
| N-pentane. | 0.79 | 72.09 | 0.0104 | 1.66 | 0.0076 | 0.0078 | 0.0126 | 0.0127 |
| Hexanes. | 2.11 | 86.11 | 0.0231 | 0.63 | 0.0290 | 0.0290 | 0.0183 | 0.0178 |
| Heptanes. | 3.27 | 100 | 0.0307 | 0.245 | 0.0525 | 0.0526 | 0.0129 | 0.0132 |
| Octanes. | 3.21 | 114 | 0.0265 | 0.087 | 0.0333 | 0.0533 | 0.0047 | 0.0046 |
| Nonanes | 4.21 | 128 | 0.0309 | 0.032 | 0.0661 | 0.0662 | 0.0021 | 0.0020 |
| Heavier | 74.54 | 203 | 0.3463 | 0.000 | 0.7715 | 0.7713 |  |  |
|  | 100.00 |  | 1.0000 |  | 1.0000 | 1.0004 | 1.0000 | 0.9999 |
| Buckley's Elec. Comp <br> $\mathrm{ng}=0.551$ $\mathrm{ng}=0.55$ |  |  |  |  |  |  |  |  |

value (or minimum) of each curve would be reached at a separator pressure of about 150 psia instead of 110 psia. However, the difference in oil recovery, oil gravity or gas-oil ratio would be almost negligible at these two pressures, and the use of the optimum conditions indicated by the Computer would lead to results which would not be sig. nificantly less satisfactory from a practical standpoint. The agreement between the calculated and Computer results on the whole were within 0.5 per cent.

In addition to the above discussed comparison of the gross results, a com-
parison between the Computer and accurate numerical calculations of the complete compositions for several flash vaporizations was made. The results are given in Table II for, (1) a flash vaporization at 300 psia and $95^{\circ} \mathrm{F}$, and the resulting liquid flashed again at atmospheric pressure and $65^{\circ} \mathrm{F}$, and (2) a flash vaporization at 150 psia and $75^{\circ} \mathrm{F}$ and the resulting liquid flashed at atmospheric pressure and $65^{\circ} \mathrm{F}$. It will be noted that the error in the Computer values for $\Sigma \mathrm{x}_{\mathrm{j}}$ ranges up to 0.0034 . However, this represents an accumulated error of two successive computations, since no attempt was made to


FIG. 8-COMPARISCN OF CALCULATED (CURVES) AND PHASE EQUILIBRIUM COMPUTER RESULTS (FOINTS) FOR SINGLE STAGE SEPARATION AS A FUNCTION OF THE SEPARATOR PRESSURE.

fig. 9 - the variation of the mol fraction of hydrocarbon mixtures in the gas PHASE WITH THE CONCENTRATION OF THE HEAVIEST COMPONENT, WHILE KEEPING THE SUM OF THE LATTER AND OF METHANE FIXED.
--: 6 COMPONENT MIXTURE AT 14 PSIA, $65^{\circ} \mathrm{F}$, WITH $\mathrm{n}_{1}+\mathrm{n}_{\mathbf{n}^{+}}=0.744$;
--- --; 6 COMPONENT MIXTURE AT 300 PSIA, $95^{\circ} \mathrm{F}$, WITH $n_{1}+n_{\mathrm{c}^{+}}=0.755$;
-- --: 4 COMPONENT MIXTURE AT 500 PSIA, $245^{\circ} \mathrm{F}$, WITH $n_{1}+n_{3}=0.80$.
correct the mol fractions of each component in the liquid phase after the first flash vaporization so that their sums would equal one. It can be seen that the errors in the values of $x_{j}$ vary somewhat as the magnitude of the $\mathrm{x}_{\mathrm{j}}$ 's. The error in $n_{g}$ ranges up to 0.0034 , but this also represents an accumulated error. These results should serve to indicate the accuracy of the various quantities involved in using the Phase Equilibrium Computer.

## Sample Problems Showing Variation of $n_{g}$ with the Composition

In Fig. 9 are shown the variations in the mol fractions in the gas phase, $n_{8}$. with the composition of various hydrocarbon mixtures. The basic data for the solid and dot-dash curves were obtained from Table II, the methane and hexane + components being varied so that their total would remain the same. The data for the dashed curve were obtained from Table I. In all cases the curves are nearly straight lines, and the corresponding curves for each problem are nearly parallel. The position of the curves will of course depend on the other components in the mixture and the pressure and temperature. However, all the graphs have slight curvatures, which tend to increase in some cases as the percentage of methane (or the heavier component) approaches either zero or its maximum value.

This type of calculation serves to show the sensitivity of the phase equil. ibrium separation to the exact composition of the mixture, and the effect of errors in the latter on the quantitative features of the phase separation. By using the Computer, studies of this kind can be made perhaps a hundred times as fast as by direct numerical solution of the equilibrium equations.

## The Sensitivity of the Phase <br> Equilibrium Separation to the Accuracy of the Equilibrium Ratios

An especially interesting and valuable application of the Computer is the investigation of the effect of the sensitivity of the phase calculations to the accuracy of the equilibrium data. While such a study would require laborious repeat calculations, if done numerically, it is solved with extreme simplicity on the Computer by merely observing the change in the null setting of the $n_{k}$
dial as the corresponding $c_{j}$ dial is changed. Figs. 10 and 11 show typical results of such an application. While the curves of these figures show rather systematic variations of the values of $\mathrm{n}_{\mathrm{g}}$ with changes in the values of the $K_{j}$, they are to be considered only as illustrative of a type of application of the Computer. The absolute magnitudes given in these figures and the relative values for the different components are undoubtedly rather complex functions of the values of the individual components and the compositions of the composit mixtures. It is undoubtedly for this reason that the characteristics of the curves for Fig. 10, which roughly simulates a reservoir crude oil-natural gas mixture, is radically different from those of Fig. 11, which refers to a low pressure gas depleted crude oil. In any case, however, it does appear from these preliminary and illustrative results that the absolute value of $n_{g}$ is not very sensitive to the accuracy with which the equilibrium ratios are determined. This, in itself, is of considerable practical interest.

## Problem Checking the Use

 of All Twelve ComponentsA final problem was solved to check the operation of the Computer when all twelve components are used. This problem is the same as one treated numerically by Buckley. ${ }^{1}$ Table III gives the necessary data and the results of the flash vaporizations at $130^{\circ} \mathrm{F}$. and 0 psi gauge. The agreement here is extremely close. To check if this agreement was entirely accidental, the problem was solved twice, but the results were almost identical. The $x_{j}$ 's were measured with the voltmeter through $n$-pentane, and calculated for the hexanes and heavier components using Eq. (2). The $\mathrm{y}_{\mathrm{j}}$ 's were calculated using Eq. (2) for methane through n-petane, and measured with the voltmeter for the hexanes and heavier components.

## CONCLUSIONS

The Phase Equilibrium Computer described in this paper should be of value in the solution of problems involving the phase equilibrium between gas and liquid in any hydrocarbon mixture, especially if such determinations must be made a large number of times. Depending on the number of components, each flash vaporization can be calculated in 10 to 20 minutes


FIG. 10 - THE EFFECT OF ERRORS IN THE EQUILIBRIUM RATIO ON THE COMPUTED VALUES OF THE MOL FRACTION IN THE GAS PHASE OF A HYDROCARBON MIXTURE WITH A COMPOSITION: $n_{1}, n_{2}, n_{3}, n_{1}, n_{5}, n_{0^{+}}=0.4548,0.0987,0.0699,0.0475,0.0289,0.3002$.
INDIVIDUAL CURVES REFER TO INDIVIDUAL K VALUES IN WHICH ERRORS WERE INTRODUCED. ASSUMED CORRECT K VALIJES ARE: $K_{1}, K_{2}, K_{3}, K_{4}, K_{5}, K_{6}{ }^{+},=12.4,2.1,0.65,0.238,0.079,0.0157$.


PerCent Error Assumed in Equilibrium Ratio
fig. 11 - the effect of errors in the equllibrium ratio on the computed values of THE MOL FRACTION IN THE GAS PHASE OF A HYDROCARBON MIXTURE WITH A COMPOSITION: $n_{1}, n_{2}, n_{3}, n_{4}, n_{5}, n_{6}+\ldots=. .0 .0320,0.0419,0.0729,0.0795,0.0618,0.7119$.
INDIVIDUAL CURVES REFER TO INDIVIDUAL K VALUES IN WHICH ERRORS WERE INTRODUCED. ASSUMED CORRECT $K$ VALUES ARE: $K_{1}, K_{2}, K_{3}, K_{4}, K_{5}, K_{6}+250,32.0,8.1,2.6,0.88,0.111$.
using the Computer. These time requirements can be substantialy reduced by providing more stable voltage supplies to eliminate the readjustment in initial voltage settings required as the result of interactions between the parallel circuits representing the individual components in the first model of the Computer. The error in the final results will be no greater than $0.5 \%$ for most problems, and may be reduced if the
resistors representing the $c_{j}$ are set according to their calibrated values.

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## REFERENCES

1. S. E. Buckley, Trans. AIME, 127, 178 (1938).

[^0]:    Manuscript received at office of Petroleum Branch August 3, 1949. Paper presented at San Antonio meeting of the Petroleum
    Branch, October $5-7,1949$.

[^1]:    * The latter term has been introduced to get away from the implication that the ratios $y_{j} / x_{j}$ are really constant, as was apparently hoped when these ratios were originally proposed for phase equilibrium analysis.

[^2]:    * It may be noted here that Eq. (6) is substantially reducing the time required for direct numerical solution of the equilibrium equations, as generally used in the form of Eqs. (3), provided the $\mathrm{K}_{\mathrm{J}}$ are converted into the corresponding $c j$ by preliminary calculations.

[^3]:    *This study has been made by R. B. Wilkins, and is being published in the oil and Gas Journal. The authors are indebted to him and the management of the Gulf Oil Corpora-
    tion at Tulsa for making this work available tion at Tulsa for making this work available
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