Technical Note 136——

PROCEDURE FOR USE OF ELECTRONIC DIGITAL COMPUTERS IN CALCULATING FLASH VAPORIZATION HYDROCARBON EQUILIBRIUM

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ABSTRACT

The effectiveness of digital computing machines in making technical calculations depends on how well the work is arranged to utilize the capability of the machines. This note presents a particularly useful way of calculating hydrocarbon vapor-liquid equilibrium in the flash vaporization (or condensation) system. The method is well suited to sequence-controlled computing equipment. It is not limited to equilibrium calculations and may be used for solution of most implicit equations in one variable.

INTRODUCTION

There is increasing interest in the use of electronic digital computers in research and engineering calculations. This is a fortunate and inevitable trend in view of both the increasingly extensive numerical work which is becoming a routine part of many daily production operations and growing demand for the overwhelming amounts of calculations required by newly developed numerical methods for solving heretofore unsolved problems.

Machines are in many ways ideally suited to the task but of necessity present certain difficulties, for a particular problem to be solved must often be formulated quite differently from the way it would be arranged for manual solution. This is done in order to take advantage of the inherent speed and precision of electronic computers and at the same time to limit the need for number storage to the capacity of the machine. Therefore, this note is submitted to present a general and quite powerful method of finding solutions of the frequently encountered implicit equation:

$$F(x, y_1, y_2, \dots y_n) = 0 \quad \dots \dots \dots \quad (1)$$

where the root, x_0, is to be found for a given set of $y_1 \dots y_n$. The procedure is well suited for use with computing machines, for it usually requires but little storage or programming beyond that necessary to evaluate F.

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HYDROCARBON EQUILIBRIUM

The method is described in terms of the problem it was designed to solve, *i.e.*, the calculation of hydrocarbon vapor-liquid equilibrium in flash vaporization. Given the composition of a hydrocarbon mixture and appropriate values of the equilibrium ratios K, to find the phase ratio and compositions in a closed system: let z_i be the mol fraction of the i-th component in the mixture. If K_i is the ratio y_i/x_i, where y_i and x_i

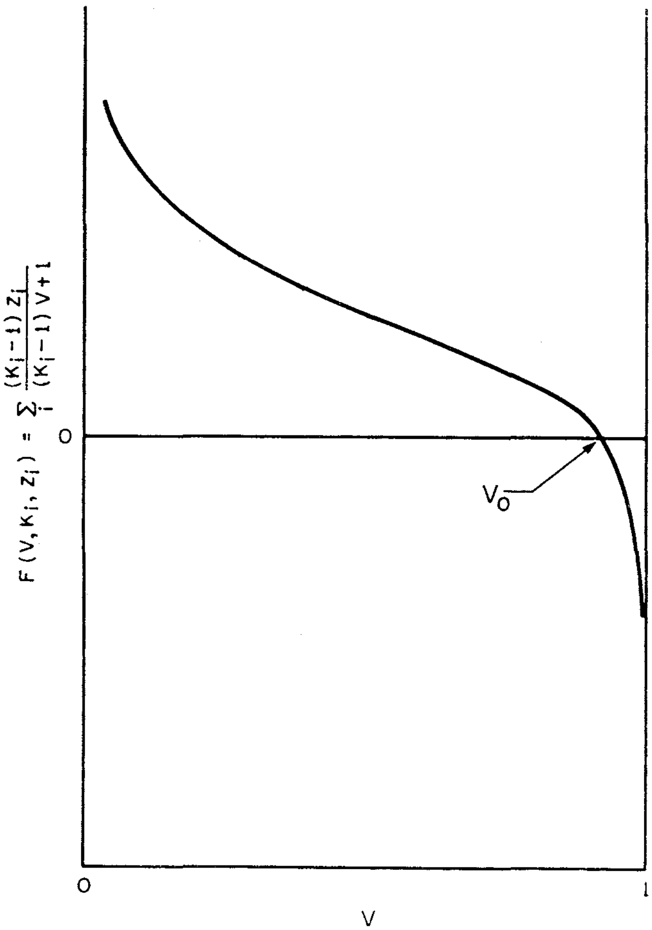

FIG. 1 — FUNCTION DEFINED BY EQUATION 6.

are the mol fractions of the i-th component in the vapor and liquid phases, respectively, then by material balance

$$z_i = Lx_i + VK_ix_i \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

where L and V are the mol fractions of the components in the liquid and vapor, respectively. Since $L = 1 - V$, the relations follow

$$y_i = \frac{K_i z_i}{(K_i - 1)V + 1} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$x_i = \frac{z_i}{(K_i - 1)V + 1} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

By a total material balance for an S-component system

$$\sum_{i=1}^{S} y_i = \sum_{i=1}^{S} x_i = 1 \quad . \; . \; . \; . \; . \quad (5)$$

or

$$\sum_i (y_i - x_i) = \sum_i \frac{(K_i - 1) z_i}{(K_i - 1)V + 1} = 0 \; . \; (6)$$

Equation (6) is of the form of (1)

$$F(\mathrm{V}, K_1, K_2, \ldots K_S, z_1, z_2, \ldots z_S) = 0 \quad . \; . \; . \quad (1')$$

and for any set of K_i and z_i must be solved for root V_o.

From physical considerations it is necessary to study only the region $0 < \mathrm{V} < 1$, and it is known that only one, if any, root exists within these limits. Further, differentiating (6) with respect to V yields

$$\sum_i \frac{-(K_i - 1)^2 z_i}{[(K_i - 1)V - 1]^2} = \frac{dF}{dV} \quad . \; . \; . \quad (7)$$

which shows $\frac{dF}{dV}$ to be everywhere negative. Therefore, if a root exists, F must lie above the axis to the left of the root, and below the axis to the right, as shown in the figure.

When the function F has a root near either zero or one, the derivatives of F with respect to V may be high near the root. This seriously interferes with customary interpolation and extrapolation procedures; thus, it is desirable to locate the root by a method which does not depend on derivatives of the function.

PROCEDURE

Consider the V-axis from zero to one to be divided into 2^n equal segments, $(k-1)2^{-n} \leqslant V < k \cdot 2^{-n}$, $k = 1,2, \ldots 2^n$. The single root must lie within one of these segments. The sign of $F(0.5, K_i, z_i)$ is negative if the root $V_o < 0.5$, positive if $V_o > 0.5$. There are then only 2^{n-1} segments on either side of 0.5 in which V_o may lie. If W_1 is the set of segments which contains V_o, and T_1 is the mid-point of W_1, and $F(T_1, K_i, z_i)$ is evaluated, the sign of F at T_1 determines which of the two sets of 2^{n-2} segments of W_1 contains V_o. This is defined as W_2. F is again evaluated and the sign examined as before. The process is continued for $n-1$ cycles. The value of T_{n-1} is within 2^{-n} of V_o.

This sequence of operations is easy to perform on any computer which has the capacity to evaluate the terms of Equation (6), and may conditionally alter its program as a result of a test for sign. The first trial $T_o = 0.5$ is used to evaluate the sum of Equation (6). The sign is sensed to control the operation which gives $T_1 = T_o \pm 2^{-2}$, the plus sign being used if F is positive. The function F is then computed from Equation (6) at T_1, from which $T_2 = T_1 \pm 2^{-3}, \ldots T_{n-1} = T_{n-2} \pm 2^{-n}$. The value T_{n-1} is then equal to V_o within 2^{-n}. This procedure has been used for computing V_o for several hundred systems with values for V_o ranging from 0.000001 to 0.999999 with good results. The work was done on an IBM 604 Electronic Calculator, which is a popular computer for accounting work and therefore, has widespread availability in the petroleum industry. The procedure is very readily programmed for this machine, and the solution is rapid. A 12-component flash may be computed to six significant figures and the results x_i, y_i, and V_o punched onto tabulating cards in 2.4 minutes. In general, for an S-component system calculated to m significant digits in V_o, the time, θ, in minutes for the punched answers, is given approximately by

$$\theta = mS/30$$

The method is quite powerful for other types of function F. The only requirements are that in the region studied the function have no discontinuities across the axis and have only one root, and that the sign of the derivative be known at the root sought. The wide latitude in permissible behavior of F, the ease of programming the iterative procedure, and the small storage requirement provide a good general-purpose method that has been found to be quite convenient in a number of practical computing applications. ★ ★ ★