$\mathcal{N}_x$ = number of liquid phase transfer units
$\mathcal{N}_y$ = number of vapor phase transfer units
$[\mathcal{N}_x]$ = liquid phase transfer unit matrix
$[\mathcal{N}_y]$ = vapor phase transfer unit matrix
$\mathcal{N}$ = number of overall vapor transfer units
$[\mathcal{N}]$ = overall vapor transfer unit matrix
$\mathcal{N}_i$ = characteristic roots of $[\mathcal{N}]$
$p$ = constant
$x_i$ = mole fraction of species $i$ in liquid
$(x)$ = column vector whose elements are $x_i$
$y_i$ = mole fraction of species $i$ in vapor
$(y)$ = column vector whose elements are $y_i$
$(y(o))$ = column vector whose elements are the mole fractions in the vapor entering the stage
$(y(e))$ = column vector whose elements are the mole fractions in the vapor leaving the stage
$y_i^*$ = mole fraction in equilibrium with $\bar{x}_i$
$(y^*)$ = column vector whose elements are $y_i^*$
$(y^*(e))$ = column vector whose elements are the mole fractions in vapor in equilibrium with liquid leaving the stage
$[Z_o]$ = matrix defined by Equation (13*a*)
( ) = column vector of order $n$
[ ] = square matrix of order $n$

**Superscripts**

$-$ = bulk average value

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# Application of Benedict-Webb-Rubin Equation of State to Hydrogen Sulfide-Hydrocarbon Mixtures

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The BWR equation of state relates pressure, volume, temperature, and composition of gaseous systems. Used in conjunction with a computer the equation is an important tool for making engineering calculations. The equation is intended for use in a region up to twice the critical density. As an example for a typical natural gas twice the critical density corresponds to about 6,000 lb./sq. in. abs. at 200°F.

The simplest form of the BWR equation is

$$P = RTd + \left( B_oRT - A_o - \frac{C_o}{T^2} \right) d^2 + (bRT - a)d^3 + a\,\alpha\, d^6 + \frac{cd^3}{T^2}\,(1 + \gamma\, d^2)\,\exp\,(-\gamma\, d^2) \tag{1}$$

Equation (1) can be used for pure compounds when the constants are known. In order to apply the equation to mixtures it is necessary to calculate the constants for the mixtures from the constants for the pure compounds contained in the mixtures. The rules for combining constants can be found in the literature (*4*). The Lorentz form of the combination rule for $B_o$ was used in this work.

The constants for light hydrocarbons, nitrogen, carbon dioxide, and miscellaneous other compounds have been developed previously (*1, 2, 3, 4, 8*).* However a satisfactory set of constants for hydrogen sulfide in hydrogen sulfide-hydrocarbon systems has not been published. Because of the need to predict performance of sour gas reservoirs and to calculate the behavior of sour gases in absorption plants, pipe lines, compressors, etc., the authors have developed a set of hydrogen sulfide constants. These constants were developed by a mathematical analysis of experimental data and the results are presented in the following sections.

## PROCEDURE

The procedure which was used to develop the BWR constants for hydrogen sulfide consisted of three principal steps:

1. Select experimental data from hydrogen sulfide-methane system.
2. Calculate the constants to fit these data.
3. Evaluate the constants for use in multicomponent systems.

1. The hydrogen sulfide-methane system was chosen as the basis for the constants because studies by the authors showed that the available experimental data for this system (*5*) were more accurate than the data available for other binary or multicomponent systems. Also the use of the constants for engineering calculations will generally be for gases with a high concentration of methane.

The data were chosen to cover the range of pressures from 600 to 5,000 lb./sq.in.abs. and temperatures from 160° to 280°F. Two different hydrogen sulfide-methane compositions were used with seven different pressures and three different temperatures to give a combination of forty-two data points.

2. By using the hydrogen sulfide-methane data described above with the BWR constants for methane (*2*) and the mixture rules the authors calculated a set of hydrogen sulfide constants which gave the best results. By best results is meant a minimum value of the sum of the squares of the difference between observed and computed pressures divided by the observed pressures. This function will be referred to as the *object function* and can be written as

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* Incorrect values of $A_o$ for n-hexane and isopentane have been published. The correct values are n-hexane: $A_o$ = 54,443.4, isopentane: $A_o$ = 48,253.6

Table 1. BWR Equation of State Constants for Hydrogen Sulfide

| | $H_2S$ |
|---|---|
| $B_o$ | 1.07286 |
| $A_o$ | 10,498.9 |
| $C_o$ | $2.70231 \times 10^9$ |
| $b$ | 1.76919 |
| $a$ | 46791.8 |
| $c$ | $6.07236 \times 10^9$ |
| $\alpha$ | 2.21446 |
| $\gamma$ | 4.89531 |

$$f = \sum_{i=1}^{K} \left( \frac{P_{\text{obs}} - P_{\text{calc}}}{P_{\text{obs}}} \right)_i^2 \tag{2}$$

$f$ is a function of the eight constants in the BWR equation. Thus

$$f = f(A_o, B_o, C_o, a, b, c, \alpha, \gamma) = f(x_1, x_2, \ldots x_8) \tag{3}$$

In order to minimize $f$ the method of steepest descents was used. This method involves the following steps:

1. First trial values are chosen for the eight hydrogen sulfide constants.
2. The object function is calculated.
3. The derivative of the object function with respect to each parameter is calculated.
4. From the sizes and signs of the derivatives the direction of greatest change (steepest descent) of the object function is found.
5. The constants are adjusted in the direction found in the previous step until a minimum in this direction is found.
6. If not terminated the process starts over at step 1 with the chosen values being those found in step 5.
7. The procedure is terminated when the object function decreases to some specified value or the allowable number of iterations is reached.

A detailed discussion of the mathematical principles involved in the method of steepest descents is given in the Appendix. Because of the complexity of the object function the necessary calculations were done on a digital computer.

3. The hydrogen sulfide constants calculated by the above method were evaluated by comparing experimental data with calculated values. Comparisons were made for seventy-one multicomponent data points (7) and also for the hydrogen sulfide-propane (6) and hydrogen sulfide-n-pentane (5) binary systems.

## RESULTS

The set of hydrogen sulfide constants which gave the best results for the hydrogen sulfide-methane system is shown on Table 1. The comparisons which were made to evaluate these constants showed the following.

For the hydrogen sulfide-methane system the average absolute deviation was 0.4% for forty-two hydrogen sulfide-methane points with a maximum deviation of 2.1% at the worst point. The average absolute deviation for eighteen hydrogen sulfide-propane points was 1.8% in the range of 200 to 600 lb./sq.in.abs. and 100 to 280°F. Deviations near the critical point of this system were in the order of 40%. For the hydrogen sulfide-pentane system the average absolute deviation for eight points in the range of 200 to 400 lb./sq.in.abs. and 280 to 340°F. was 0.88%.

A comparison was also made for seventy-one multicomponent points (7). The average absolute deviation was 2.8%, and the maximum deviation was 7.0%.

The details of the above comparisons are on file.[*]

## CONCLUSION

The hydrogen sulfide constants presented in Table 1 can be used with the BWR equation to predict the behavior of gaseous hydrogen sulfide-hydrocarbon mixtures with an accuracy in the order of 5%. This accuracy applies to mixtures whose hydrogen sulfide concentrations do not exceed 20 mole %.

## NOTATION

$B$ = scale factor
$d$ = density, lb. moles/cu. ft.
$f$ = function being minimized
$\vec{i}_j$ = unit vector in direction of axis $j$
$P$ = pressure, lb./sq.in.abs.
$R$ = gas constant, 10.7335 lb./sq.in.-cu. ft./lb. mole-°R.
$T$ = temperature, °R.
$x_i$ = variable

$$\left.\begin{array}{l} B_o \\ A_o \\ C_o \\ b \\ a \\ c \\ \alpha \\ \gamma \end{array}\right\} = \text{BWR equation constants}$$

$\vec{\theta}$ = gradient vector

$$\text{average absolute deviation} = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{P_{\text{OBS}} - P_{\text{calc}}}{P_{\text{OBS}}} \right|_i$$

$P_{\text{calc}}$ was determined with Equation (1) and the constants in Table 1.

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## APPENDIX

### Method of Steepest Descents

It is possible to think of the $n$-dimensional space in which the problem is defined (nine dimensions in this case) as being made up of a family of $n - 1$ dimensional hypersurfaces of constant functional value. This is analogous to a map of the earth on which contour lines are drawn to indicate constant values of height above a datum. The minimization problem

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[*] Tabular material has been deposited as document 7974 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or for 35-mm. microfilm.

consists of moving from a given contour to the one having the smallest value in the region of definition. One obvious way to do this systematically is to always move along a path which is perpendicular to the surfaces of constant value. This procedure will guarantee that at any point movement is in the direction of greatest local change (or steepest descent). It should be noted however that there is no rigorous practical method for finding the absolute minimum of all the minima in the surface in a nonlinear problem such as this. In this work an exhaustive search of the surface was used.

In textbooks of vector calculus (*9*) it is proven that the vector perpendicular to a surface at a given point is given by

$$\vec{\theta} = \text{grad}\, f = \left(\frac{\partial}{\partial x_i}\vec{i_1} + \frac{\partial}{\partial x_2}\vec{i_2} + \ldots + \frac{\partial}{\partial x_n}\vec{i_n}\right) f \tag{A-1}$$

where the $\vec{i_j}$ are unit vectors along the coordinate axes.

Movement along the vector $\vec{\theta}$ can be accomplished by merely multiplying all of its components by a scale factor, call it $B$. Thus the components of a vector coincident with $\vec{\theta}$ but having a magnitude $B$ times as large as $\vec{\theta}$ will be

$$dx_i = B\left(\frac{\partial f}{\partial x_i}\right) \tag{A-2}$$

Since $\vec{\theta}$ points in the direction of maximum increase of $f$ (*10*), it is necessary to insert a negative sign into Equation (A-2) in order to insure movement in the direction of decrease of $f$. Thus Equation (A-2*a*) is the proper form to use in order to take steps along the gradient vector:

$$dx_i = -B\left(\frac{\partial f}{\partial x_i}\right) \tag{A-2a}$$

To obtain an estimate of $B$ the function $f$ is expanded in a Taylor series about a given point $a$:

$$f = f_a + \sum_{i=1}^{N} \left.\frac{\partial f}{\partial x_i}\right|_a dx_i + \text{higher order terms} \tag{A-3}$$

Neglecting the higher-order terms in Equation (A-3) and substituting Equation (A-2*a*) for $dx_i$ one gets

$$f = f_a - B\sum_{i=1}^{N}\left(\frac{\partial f}{\partial x_i}\right)_a^2 \tag{A-4}$$

or

$$B = \frac{(f_a - f)}{\sum_{i=1}^{N}\left(\frac{\partial f}{\partial x_i}\right)_a^2} \tag{A-5}$$

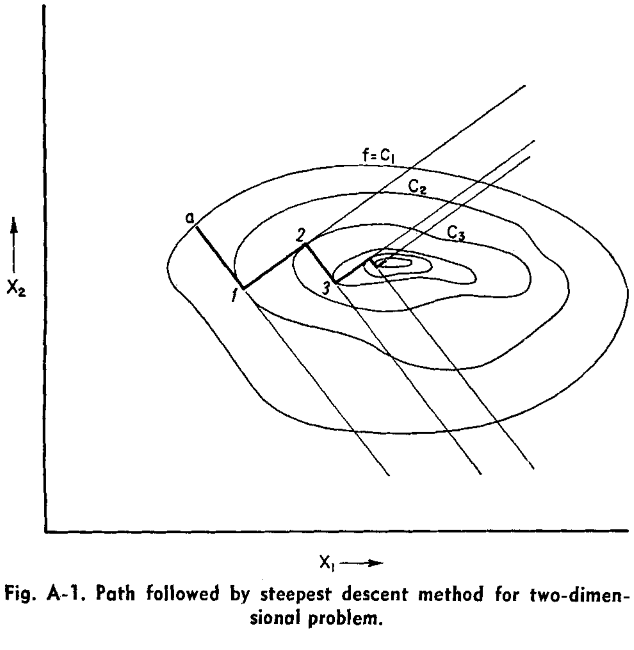

Fig. A-1. Path followed by steepest descent method for two-dimensional problem.

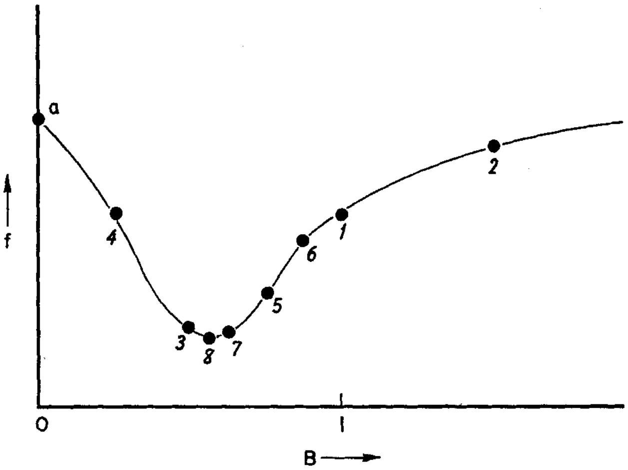

Fig. A-2. Typical series of trials to find minimum along path.

Therefore

$$\Delta x_i = dx_i = \frac{-(f_a - f)\left.\frac{\partial f}{\partial x_i}\right|_a}{\sum_{i=1}^{N}\left(\frac{\partial f}{\partial x_i}\right)_a^2} \tag{A-6}$$

Since $0 \leqq f_a - f \leqq f_a$, Equation (A-6) may be rewritten as

$$\Delta x_i = -Z\left[\frac{f\left(\frac{\partial f}{\partial x_i}\right)}{\sum_{i=1}^{N}\left(\frac{\partial f}{\partial x_i}\right)^2}\right]_a \tag{A-7}$$

where $0 < Z \leqq 1$.

By dropping the higher-order terms of Equation (A-3) movement is restricted to straight-line segments, whereas in general the path of steepest descent will be curved. The ideal solution to this problem would be to take a very small step along the line, then re-evaluate the $\partial f/\partial x_i$, and step out in this new direction and repeat this over and over. However since the computation of derivatives is the most time-consuming part of the process, it is not practical to do this. What is done is to follow the straight line until a minimum in that direction is found and then evaluate the derivatives and start anew. Figure A-1 is a sketch of the procedure for a function of two variables. Various methods of finding the minimum in a given direction have been proposed (*11*, *12*), and the computer program used in this study was written to use either of two procedures. The first and most successful method is to take a specified number of steps (both forward and backward) and bracket the minimum by interval halving. Figure A-2 shows a typical set of steps in a given direction. The steps start from the base point $a$ and proceed in the order shown on the figure. A test at each trial point indicates whether the direction of advance should be reversed. Successive steps in one direction are accompanied by halving of the step size. The second procedure is one suggested by Booth (*11*), whereby two points in addition to the base point are found and the minimum of the parabola through these points is taken as the minimum of $f$ in that direction. For this method the equation for $\Delta x_i$ is

$$\Delta x_i = \frac{-[f(1) - 4f(1/2) + 3f(0)]f(o)\left.\frac{\partial f}{\partial x_i}\right|_o}{4[f(1) - 2f(1/2) + f(o)]\left[\sum_{i=1}^{N}\left(\frac{\partial f}{\partial x_i}\right)^2\right]_o} \tag{A-8}$$

where $f(1)$ is the value of $f$ at the point given by applying the corrections from Equation (A-7) with $Z = 1$ and $f(1/2)$ the value with half these corrections.

In this problem no difficulties were encountered with saddle points although they may exist. Booth (*12*) gives a test which can be used to detect saddle points.