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MULTIPHASE, MULTICOMPONENT COMPRESSIBILITY IN PETROLEUM RESERVOIR ENGINEERING

By

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ABSTRACT

Adiabatic and isothermal compressibility below the bubble point and production compressibility were computed with a thermodynamic model for single and multicomponent systems. The thermodynamic model consists of an energy balance including a rock component, and a mass balance, with appropriate thermodynamic relationships for enthalpy and equilibrium ratios utilizing the virial equation of state. Runs consisted of modeling a flash process, either adiabatically or isothermally and calculating fluid compressibilities below the bubble point for H_2O, $H_2O - CO_2$, $nC_4 - iC_4 - C_5 - C_{10}$, $C_1 - C_7$, and $C_1 - C_7 - H_2O$ systems. The production compressibility was computed for gas production, and for production according to relative permeability relationships for a one-component system. Results showed a two-phase compressibility higher than gas compressibility for similar conditions, and a production compressibility that could be larger than either the two-phase compressibility or the gas-phase compressibility, under the same conditions.

The two-phase compressibility results tend to corroborate an observation that a two-phase system has the effective density of the liquid phase, but the compressibility of a gas. Production compressibility is large because of a reduction in the amount of liquid in the system because of the effects of vaporization and production enhanced by the effect of heat, available from rock in the system.

Total system compressibility plays an important role in the interpretation of well test analysis, specifically for systems below the bubble point. Accurate

information on the total effective fluid compressibility is necessary for the possible isolation of formation compressibility from interference testing in subsiding systems.

Non-condensible gas content of discharged fluid for a steam-dominated geothermal system was studied with the thermodynamic model. An initial increase in the non-condensible gas concentration was observed, followed by a stabilization period, and finally a decline in the non-condensible gas concentration, behavior that resembles actual field results. Study of the behavior of non-condensible gases in produced geothermal fluids is important for planning turbine design.

Table of Contents

LIST OF FIGURES

1. INTRODUCTION

One of the most important methods for in situ measurement of geological parameters of reservoirs is pressure (and rate) transient analysis. This field of study has been termed the single most important. area of study in reservoir engineering, Dake (1978). All present methods of analysis depend upon solutions of the diffusivity equation.

In the solution of the diffusivity equation, the diffusivity is considered a constant, independent of pressure. Strictly speaking, all terms in the diffusivity (permeability, porosity, fluid viscosity, and cornpressi'bility) usually do depend on pressure and some may depend on space coordinates. If one assumes properties independent of space coordinates, the question of pressure dependency remains. In cases where pressure changes, or changes in pressure-related properties are small, the assumption of a constant diffusivity is reasonable. But, when, fluid and rock properties change considerably over the range of pressures considered, the assumption of constant diffusivity is not justified.

Total isothermal compressibility is defined as the fractional volume change of the Auid content of a porous medium per unit change in pressure, and it is a term that appears in the solution of all problems on isothermal transient flow of fluids in a porous medium. Recently, it has been reported (Grant, 1976) that the total system compressibility for systems where a change of phase and production are involved is usually higher than the compressibility of the gaseous phase at the same conditions. Evaluation of total system effective compressibility for multiphase systems for different production modes is the purpose of this study.

In order to perform this study, the change in volume in a reservoir with respect to pressure was computed with a therniodynamic model for a flash system. The model has the capability of considering different production modes: gas production, and production according to relative permeability-saturation relationships (multiphase production).

Runs were made to compute the two-phase compressibility for a single-component water system, and multicomponent systems: $H_2O - CO_2$, $C_1 - C_3$, $nC_4 - iC_4 - C_5 - C_{10}$, $C_1 - C_7$ and $C_1 - C_7 + H_2O$. Production runs were made for gas production, and production according to relative permeability- saturation relationships. Resulls can provide information on total system effective compressibility essential in the interpretation of well test analysis for many reservoir-fluid systems.

With the development of highly-precise quartz crystal pressure gauges, a sensitivity was obtained that permits interference testing in reservoirs subject to subsiding conditions. Interference testing can be used to measure porosity-total system effective compressibility product for such systems. Accurate knowledge of total effective fluid compressibility should allow the isolation of the formation compressibility. Thus unusually large values of formation compressibility could indicate potential subsidence at an early stage in the life of a reservoir, and indicate reservoir operational conditions under which environmental problems could be minimized.

In the design of turbines for geothermal field electric production, it is necessary to have an estimate of the noncondensible gas content of the produced geothermal steam. A thermodynamic compositional model can give information on the noncondensible gas behavior for a given system of interest. Runs were made with a system simulating a vapor-dominated geothermal field with two components: $H_2O - CO_2$. Results indicated an increase in the concentration of carbon dioxide in the produced fluid, followed by a stabilization period, and finally an eventual decline in the produced CO_2 concentration, behavior that resembles field results, Pruess et al. (1985). Theory and pertinent literature on total system compressibility will be considered in the next section.

2. THEORY AND LITERATURE REVIEW

This section considers both the theory and presents a brief review of pertinent literature concerning total system compressibility.

2.1. Theory

The most common kinds of compressibilities are: (1) isothermal compressibility. (2) adiabatic compressibility, and (3) total system apparent compressibility. A brief description of each follows.

Isothermal Compressibility -- An equation of state is a relation connecting pressure, temperature, volume for any pure homogeneous fluid or mixture of fluids. An equation of state can be solved for any of the two variables in terms of the other, for example (Smith et al., 1975):

$$V = V(T, p) \tag{2.1}$$

then:

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp \tag{2.2}$$

The partial derivatives in this equation represent measurable physical properties of the fluid :

Volume expansivity:

$$\kappa = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{2.3}$$

The isothermal compressibility:

$$c = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \qquad 2.4$$

The isothermal compressibility or the volume expansivity can be obtained from graphs of pressure-volume-temperature (pVT) data (Muskat, 1949). The isothermal Compressibility is a point function, and can be calculated from the slope of an isotherm of a pressure versus specific volume curve for each value of pressure.

The partial of volume with respect to pressure is usually a negative number (Amyx et al., 1960), reflecting that an increment in pressure gives a decreased volume. The magnitude of the isothermal compressibility increases with increasing temperature, and diminishes with increasing pressure. Therefore the pressure effects are larger at high temperatures and low pressures.

A p-V diagram for a pure material is illustrated in Fig. 2.1. This figure shows that an isotherm on the left part of the diagram corresponds to the liquid phase. Liquid isotherms are steep and closely spaced. This shows that both $\left(\frac{\partial V}{\partial p}\right)_T$ and $\left(\frac{\partial V}{\partial T}\right)_p$, and therefore the isothermal compressibility and the volume expansivity, are small. This is a liquid characteristic, as long as the region near the critical point is not considered. It is from this fact that the common idealization in fluid mechanics known as the incompressible Auid arises. For an incompressible fluid, the values of the isothermal compressibility and volume expansivity are considered to be zero.

For real gases, the isothermal compressibility can be expressed as:

$$c = \frac{1}{p} - \frac{1}{Z}\left(\frac{\partial Z}{\partial p}\right)_T \qquad 2.5$$

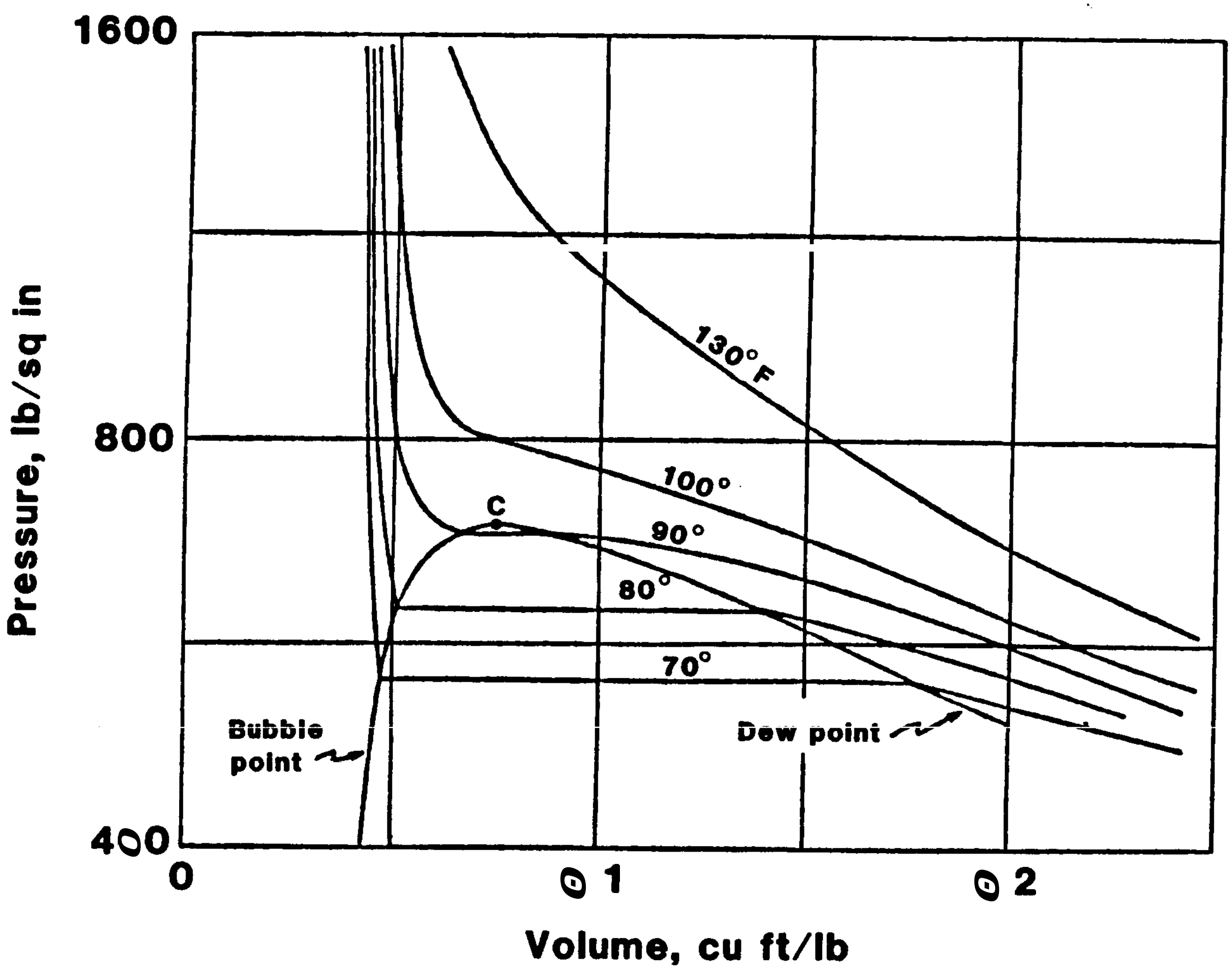


Fig. 2.1 Pressure versus Specific Volume for a Pure Material

Muskat (1949), showed that as $\left(\frac{\partial Z}{\partial p}\right)_T < 0$ at low pressures, the isothermal compressibility of a gas phase will be greater than the compressibility for an ideal gas. This will continue for temperatures beyond the critical point to the Boyle point, the pressure at which Z is a minimum. Above the Boyle point, $\left(\frac{\partial Z}{\partial p}\right)_T$ will be positive. Therefore the compressibility will fall below that of an ideal gas.

For the coexisting two-phase compressibility (gas and liquid), it can be shown from a p-V diagram, Fig. 2.1 and **2.2.** for either a pure component, or a two-component system, that the inverse of the slope of an isotherm for the two-phase region, $\left(\frac{\partial p}{\partial V}\right)_T$ will be greater than the corresponding slopes of either the gas or liquid region. We now turn to consideration of adiabatic compressibility.

Adiabatic Compressibility - - Measuring the change in temperature and specific volume for a given small pressure change in a reversible adiabatic process provides enough information to calculate the adiabatic compressibility:

$$c_s = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_H \qquad 2.6$$

Keiffer(1977) in a study of the velocity of sound in liquid-gas mixtures, calculated sonic velocities for water-air and water-steam mixtures that were lower than the sonic velocity of the gas phase. The existence: **of** gas or vapor bubbles in **a** liquid reduces the speed of sound in the liquid. This phenomenon was explained by suggesting that a two-phase system has the effective density of the liquid, **but** the compressibility of a gas. Sonic velocity can be related to adiabatic compressibility by the expression:

$$v_s = \left(c_s \rho\right)^{-1/2} \qquad 2.7$$

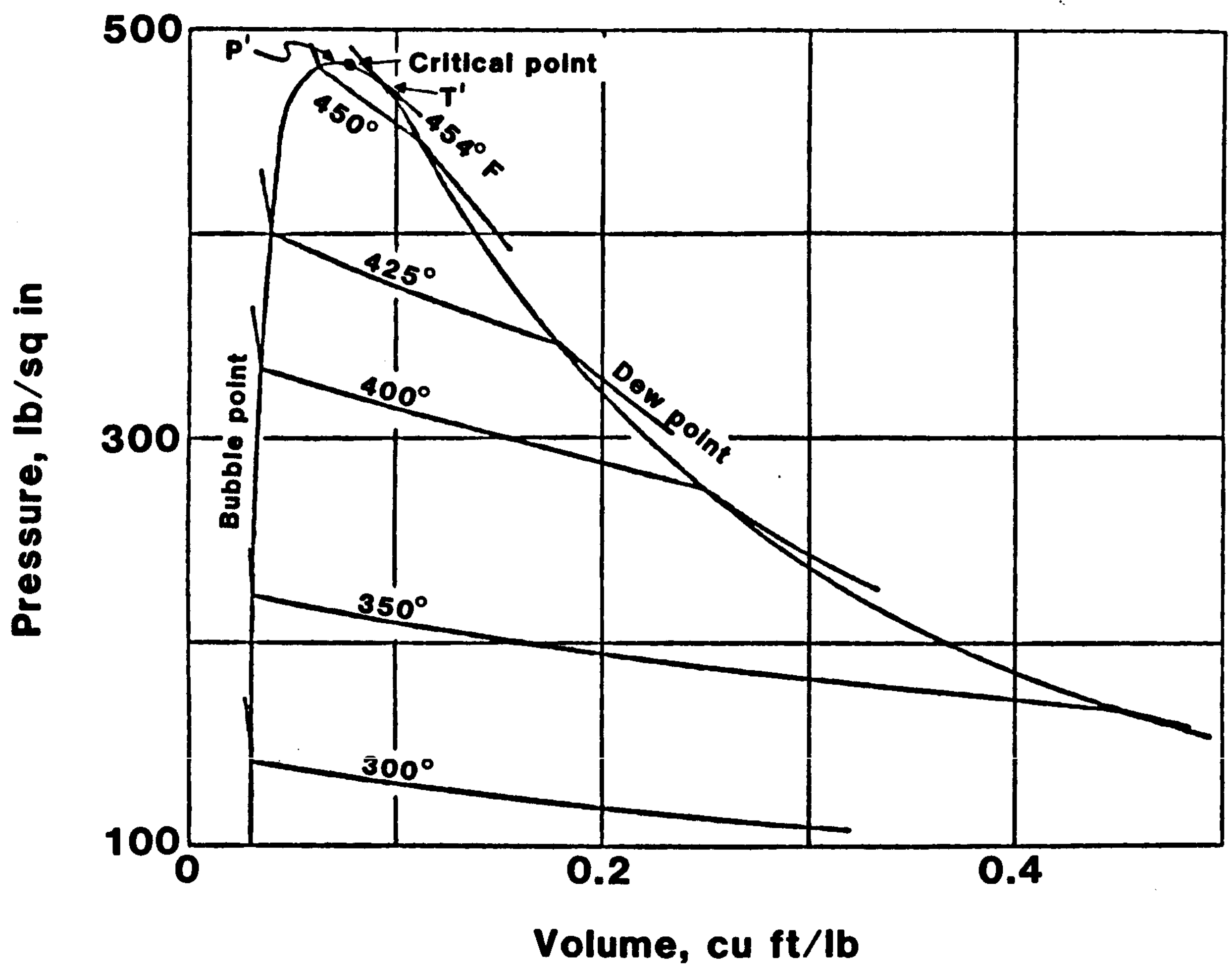


Fig. 2.2 Pressure versus Specific Volume, Two-component System

From this, it is apparent that a low sonic velocity v_s corresponds to high compressibility.

Apparent Compressibility -- For an oil system below the bubble point, for which the liquid volume increases with an increase in pressure as a consequence of gas dissolving in the liquid, Earlougher (1972) presents the following definition of "Apparent Compressibility":

$$c_{oa} = \left[-\frac{1}{B_o} \frac{\partial B_o}{\partial p} + \frac{B_g}{B_o} \frac{\partial R_s}{\partial p} \right]_T \qquad 2.0$$

This concept is related to the older concept of total system isothermal compressibility. Literature on this subject is presented in the next section.

2.2. Total System Isothermal Compressibility

Perrine (1956) presented an empirical extension of single-phase pressure buildup methods to multiphase situations. He showed that improper use of single- phase buildup analysis in certain multiphase flow conditions could lead to errors in the estimation of static formation pressure, permeability and well condition.

A theoretical foundation for Perrine's suggestion was established by Martin (1959). It was found that under certain conditions of small saturation and pressure gradients, the equations for multiphase Auid flow .may be combined into an equation for effective single-phase flow.

Cook (1959), concluded that calculations of static reservoir pressure from buildup curves in reservoirs producing at, or below the original bubble point, required the use of two-phase fluid compressibility, otherwise the calculated static pressure would be in error. This error could grow in proportion to the buildup curve slope, and could also increase for low values of crude oil gravity, reservoir pressure, and dimensionless shut-in time. It was also shown that in the equation for the two-phase compressibility, there exists the inherent assumption that the solution gas oil ratio (GOR) curve, and the oil formation volume factor curve are completely reversible. This implies that a sufficient surface contact area exists between the free gas and the oil that the same volume of gas will redissolve per unit of pressure increase as had been liberated per unit of pressure decrease. Otherwise, conditions of supersaturation or undersaturation would be generated. Based on a work by Higgins (1954), Cook (1959) concluded that negligible supersaturation or undersaturation should occur for uniform distribution of phases, even under rates of pressure change encountered in pressure build up tests. Higgins (1954), measured saturation rates in porous media. His results showed that because of the rapid diffusion of gas in the small dimensions of pore space no supersaturation exists during the flow of oil to wells, or undersaturation during repressuring in reservoirs sands having some effective permeability to gas.

Dodson, Goodwill and Mayer (1953) found that there is not enough information to prove that thermodynamic equilibrium is attained by the fluids in a reservoir under normal production practices. They mentioned that agitation is the most important factor to achieve thermodynamic equilibrium. They also suggested that in cases of slow flow towards a wellbore, caused either by low permeability or a small pressure differential, there is probably insufficient agitation or turbulence to attain thermodynamic equilibrium, thus producing supersaturation conditions. Unfortunately, the existence of this condition can not be measured by routine laboratory pVT analyses. When gas is injected in a reservoir, it is known that only a small portion of the gas dissolves in the reservoir oil, probably because there is not sufficient contact between gas and oil. Differences in composition between the volatile injected gas and the remaining heavier oil will possibly not produce a complete thermodynamic equilibrium, causing phase composition computations in gas injection projects to be in error if the assumption of thermodynamic equilibrium is made.

Perrine (1956), Martin (1959), and later Ramey (1964), pointed out that for single-phase and multiphase buildup analyses, the parameter corresponding to isothermal compressibility in the dimensionless time group should refer to the total system compressibility, with terms corresponding to the compressibility of oil, gas, water, reservoir rock, and also changes of solubility of gas in liquid phases. Ramey observed that there is an increase in the effective gas compressibility as a consequence of the solution of gas in water, specially when the magnitude of the water compressibility is important. He divided his work into four categories; rock compressibility, aquifers, gas reservoirs, and oil reservoirs.

Under rock compressibility, it was presented that. the effective rock pore space compressibility is a positive quantity, therefore it is added to the value of the fluid compressibilities. Rock compressibility was obtained from the correlation of rock compressibility as a function of porosity published by Hall (1953), and covered a range in magnitude from the compressibility of oil to the Compressibility of water. Rock compressibility is usually less than the compressibility of gas. However, rock compressibility can be a major component in the total compressibility expression, specially in systems with low gas saturation, small porosity, or small liquid compressibilities. Subsidence or compaction was later found to cause even larger effective compressibilities.

With respect to aquifers, Ramey concluded that data on the compressibility of the aquifer water is not usually available. Therefore, water compressibility must be obtained from existing correlations.

Gas compressibilities in gas reservoirs containing gas and water are usually computed from Trube's (1957) reduced compressibilities for natural gas. Ramey (ibid), reported that, **rock** and water compressibilities are small compared to gas compressibilities, although, it was recommended that the magnitude of each term in the total system compressibility be checked before neglecting them.

Oil reservoirs were considered to contain two **or** more fluids: oil, water, and in some cases, gas. When **gas** is present, it is often necessary to consider the contribution **of** each Auid **phase** and the **rock** to the total system isothermal compressibility:

$$c_t = S_o \left[-\frac{1}{B_o} \frac{\partial B_o}{\partial p} + \frac{B_g}{B_o} \frac{\partial R_s}{\partial p} \right] + S_w \left[-\frac{1}{B_w} \frac{\partial B_w}{\partial p} + \frac{B_g}{B_w} \frac{\partial R_{sw}}{\partial p} \right] + S_g \left[-\frac{1}{B_g} \frac{\partial B_g}{\partial p} \right] + \frac{1}{V_{pv}} \frac{\partial V_r}{\partial p} \qquad 2.9$$

Derivation of **Eq. 2.9,** (Ramey, 1975), is presented in Appendix A.

The contribution of water to compressibility consisted of two terms. The first term, $\left(\frac{\partial B_w}{\partial p}\right)_T$, was obtained from the correlations of Dodson and Standing (1944), or Culberson and McKetta (1951). To compute the pressure differential of the gas in solution, $\left(\frac{\partial R_{sw}}{\partial p}\right)_T$, the magnitude of which **is** usually greater than the compressibility of water, the data of Culberson and McKetta, **or** Dodson and Standing were differentiated and graphed.

With respect to the oil and gas contributions to the total system compressibility, and in the event of not having experimental data available, the change in formation volume factor and gas in solution with pressure were obtained and graphed from Standing's (1952) correlations **for** California black oils. All this information combined gave a method to compute total isothermal compressibility **for any** system containing a gas phase.

With data taken from one of Ramey's (1964) examples, Fig. **2.3** show the effect of gas in solution in oil.

When there is pressure drop caused by production in a two-phase fluid reservoir, the fluids may respond by boiling. Therefore, the withdrawn fluid may be replaced by steam. This causes an apparent compressibility for a two-phase system which may **be** 100-1000 times larger than the compressibility of liquid water, and 10 - 100 times larger than the compressibility of superheated steam, according to a study made **by** Grant(1978).

Moench (1980) presented results of a numerical study showing that the process of vaporization causes a delay in the pressure response. Moench and Atkinson (1978). Grant(1978), and Garg(1980) explained the phenomena combining energy and **flow** equations in a diffusion-type equation. This equation contained an apparent steam compressibility in the two-phase region that was many times larger than that of superheated steam.

Grant and Sorey (1979) combined the volume change and heat evolved in a phase change process to give an approximation of 'the two-phase apparent compressibility, ignoring the compressibility of each phase and the compressibility of the mixture. An example given by the authors shows a two-phase compressibility that is 30 times **larger** than the steam compressibility at the **same** conditions. Their equations are:

Increase in volume ΔV after Δp :

$$\Delta V = \Delta m \left(\frac{1}{\rho_s} - \frac{1}{\rho_w} \right) \qquad \textbf{2.10}$$

Thus:

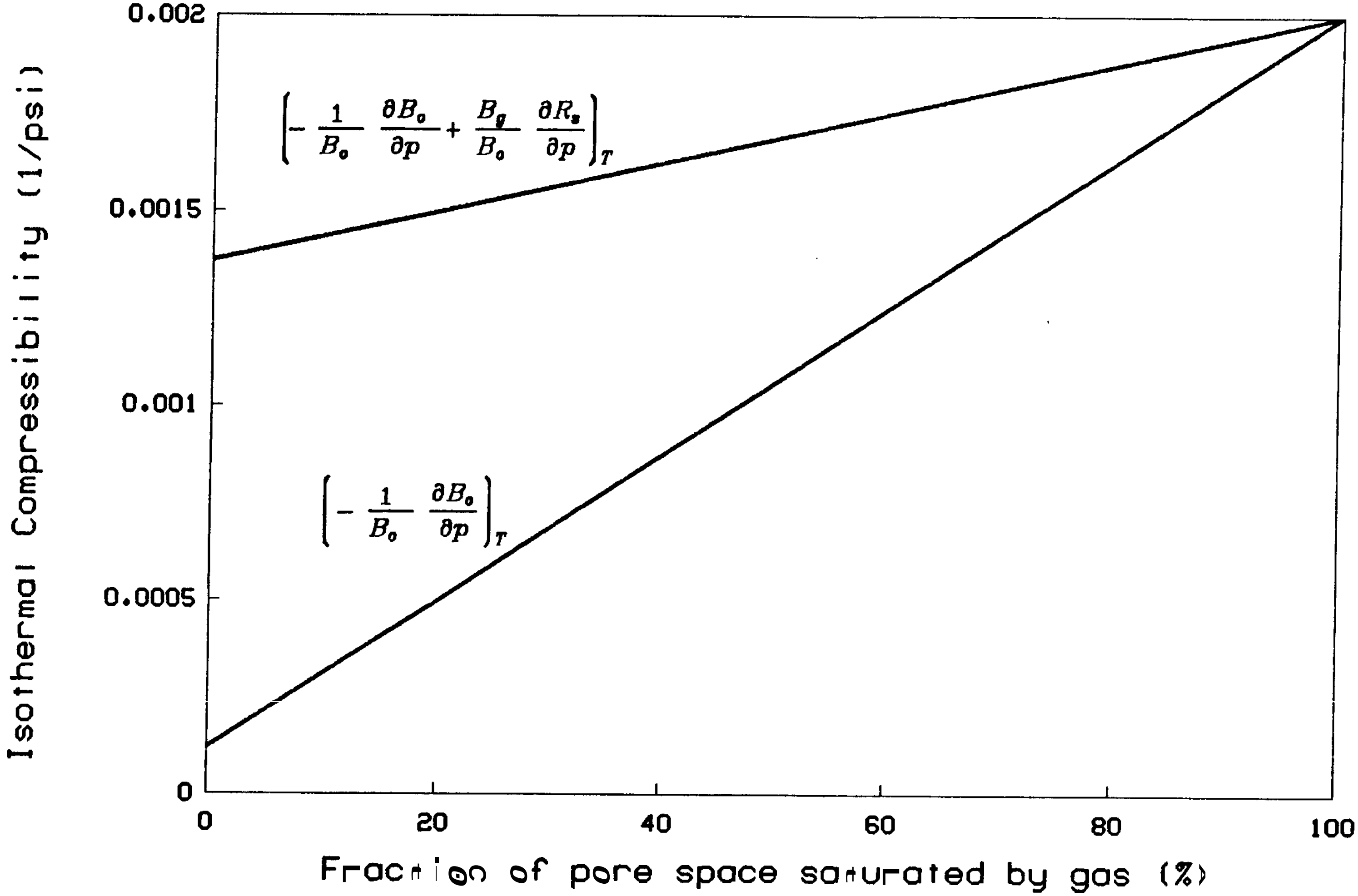


Fig. 2.3 Compressibility of live and dead oil versus pressure. Effect of Gas in Solution

$$\beta_t = \frac{(1-\Phi)(\rho_f c_p + \Phi S \rho_w c_w)(\rho_w - \rho_s)}{\Phi \lambda \frac{dp_s}{dT} \rho_w \rho_s} \quad 2.11$$

Avasthi and Kennedy (1968) developed equations for the prediction of molar volumes of gaseous hydrocarbons and liquid hydrocarbon mixtures. These equations were differentiated independently to give isothermal compressibility and isobaric thermal expansion for each phase independently. Their equations were developed using the residual volume method of Sage and Lacey. They computed the reference molar volumes from equations of state for gases and liquids respectively. and the molal volumes were obtained from correlations of molar volumes of gaseous hydrocarbon mixtures and liquid hydrocarbon mixtures. Water was not included in their calculations. The authors concluded that their equations expressed molal volumes with greater accuracy than the methods available at that time, and also that their equations were easily programmed on a digital computer.

Atkinson et al.,(1980) presented a lumped-parameter model of a vapor-dominated geothermal reservoir having a high amount of carbon dioxide. Their model is an extension of the models by Brigham and Morrow (1974), and Grant (1978) combined. The authors used a modified form of Henry's law for carbon dioxide/liquid mole fractions, and the gas phase was assumed to behave ideally for a mixture of two components. The model was used to study the short and long term behavior of carbon dioxide with fluid production for the Bagnore field in Italy. One of their conclusions was that the use of lumped parameter models has proven to be very useful for studying the behavior of geothermal fields.

Esieh and Ramey (1983) studied vapor-pressure lowering phenomena in porous media. For steam, experimental results showed that the amount of water adsorbed on the surface of a consolidated rock can be much higher than the amount of steam in the pores, and this was believed to be caused by micropores in the porous media. Methane and Ethane adsorption on a Berea sandstone was also studied. It was observed that the amount of gas adsorbed was not high in comparison with the gas in the pore space. Due to experimental difficulties, more precise pressure measurements were needed in order to draw further conclusions. The cores studied had low surface areas compared to usual low-permeability gas reservoir rocks. Adsorption of water and hydrocarbon gases may also affect thermodynamic equilibrium in a reservoir, by affecting the form of the amount of gas-liquid contact available.

Figure *2.5,* presented by Standing (1979), depicts the approximate isothermal compressibility of reservoir fluids and rock. It can be seen that the compressibility of the rock can make an important contribution to the total system compressibility, specially in cases where rock subsidence is important.

Newman (1973), made laboratory measurements of pore volume compressibility for several consolidated and unconsolidated rock samples, and compared his results with published pore volume compressibility-porosity correlations of Hall (1953) and Van der Knaap (1959). Newman's laboratory measurements were not in agreement with published correlations. He recommended laboratory compressibility **measurements** to obtain **rock** compressibility for **a** specific reservoir. It was concluded that pore volume compressiibility varies widely with rock type, and that the data is too scattered to permit reliable correlations. Additional investigation of other stress-sensitive parameters was recommended, because pore volume compressibility is not only porosity dependent.

In the sequential solution method for rnultiphase flow in one dimension, **Aziz** and Settari (1979) observed that the total compressibility for a block in question is affected by production terms, and these terms can even make the compressibility negative.

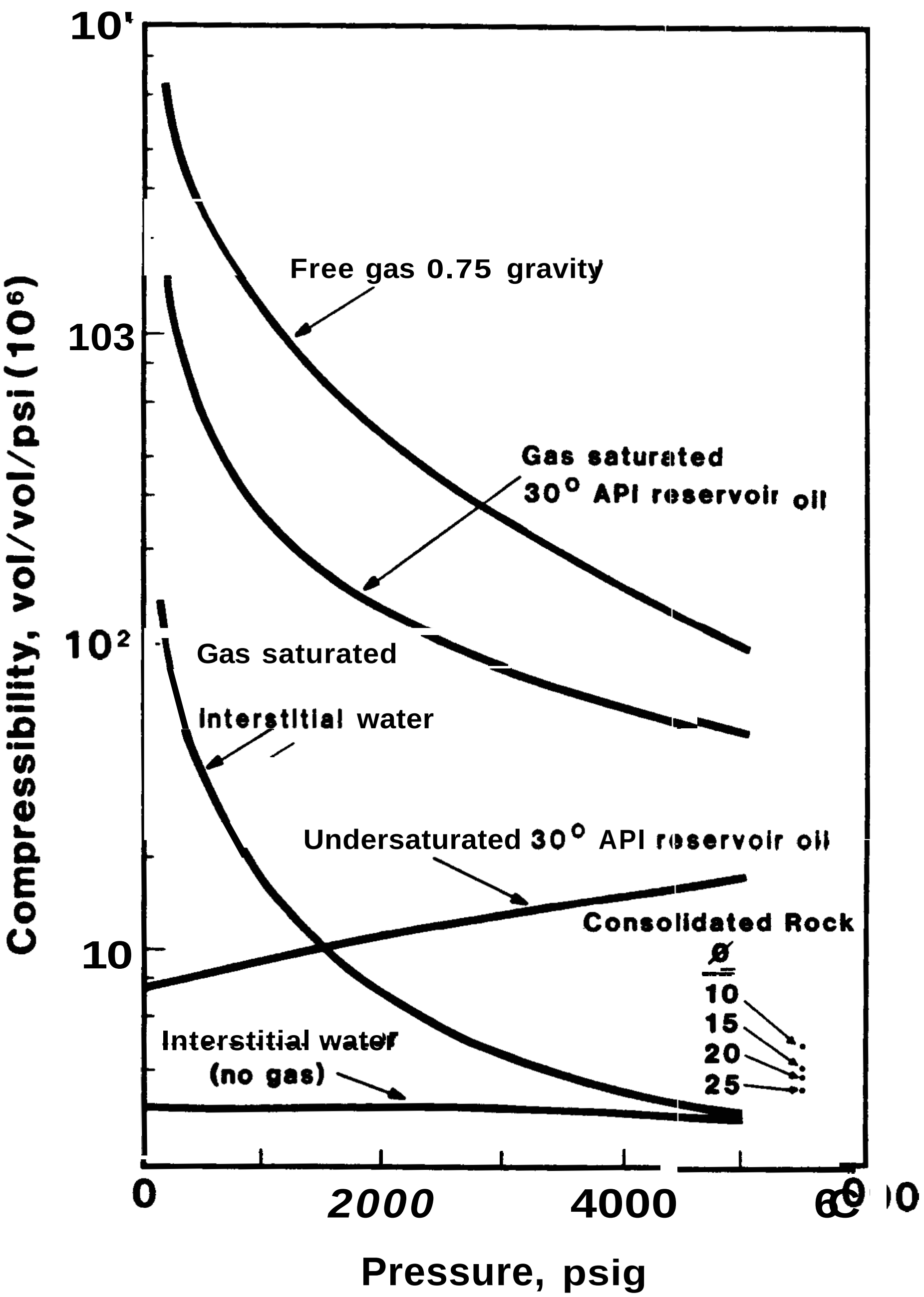


Fig. 2.4 **Approximate Isothermal Compressibility versus Pressure (Standing, 1979)**

From the preceding, it appears that many fluid thermodynamic factors affect multiphase system compressibility. Furthermore no thorough, modern study of the total system compressibility is available. In view of the importance of this factor to pressure transient analysis, the main objective of this study was to develop methods for a thorough investigation of total system effective compressibility. We now consider the method of solution.

3. METHOD OF SOLUTION

The change in volume of fluids in a reservoir caused by production can be expressed as a volume change due to a pressure change, plus the effective volume of the net fluid entering or leaving the reservoir. This can be expressed as suggested by Watts (1983) as:

$$V_{T_2} - V_{T_i} = \left(\frac{\partial V_{T_i}}{\partial p}\right)_N (p_2 - p_i) + \sum_m \left(\frac{\partial V_{T_i}}{\partial N_m}\right)_p (N_{m_2} - N_{m_i}) \qquad 3.1$$

or:

$$V_{T_2} - V_{T_i} = \left(\frac{\partial V_{T_i}}{\partial p}\right)_N (p_2 - p_i) + \sum_m \left[\bar{v}_{T_i} (N_{m_2} - N_{m_i})\right] \qquad 3.2$$

The first partial multiplying the pressure difference reflects the fluid compressibility (change in volume with respect to pressure at a constant composition, isothermal or adiabatic). Eq. 3.2 is divided b,y by $(p_2 - p_i)$, we obtain the change in volume corresponding to a pressure change. This relates to the compressibility of the reservoir fluid. considering the contribution from the fluid compressibility and the contribution due to a change in mass because of production, and can be expressed as follows:

$$\frac{V_{T_2} - V_{T_i}}{p_2 - p_i} = V_{T_i}\left[\frac{1}{v_{T_i}}\left(\frac{\partial v_{T_i}}{\partial p}\right)_z\right] + \frac{1}{p_2 - p_i}\sum_m \bar{v}_{T_i} \, (N_{m_2} - N_{m_i}) \qquad 3.3$$

For one component, this reduces to:

$$\frac{V_{T_2} - V_{T_1}}{p_2 - p_1} = V_{T_1} \left[\frac{1}{v_{T_1}} \left(\frac{\partial v_{T_1}}{\partial p} \right)_z \right] + \frac{1}{p_2 - p_1} v_i \quad (N_2 - N_1) \qquad 3.4$$

The first term on the right hand side of Eq. 3.4 corresponds to the isothermal or adiabatic compressibility at constant composition, and the second term represents the compressibility effect caused by net fluid leaving the reservoir. The second term on the right in Eq. 3.4 is analogous to the compressibility term used by Grant and Sorey (1979).

In the computation of total system fluid compressibility. two terms should be considered: the fluid compressibility (thermodynamic), and the compressibility caused by differences in volumes due to vaporization or a change of phase (condensation may cause negative apparent compressibilities). The compressibility of a single-phase gas or liquid can be calculated by the methods mentioned before. For a two-phase system, the compressibility of the mixture may be obtained either by computing the volume of the mixture at two different pressures:

$$v_{mix} = v_L + x \ (v_g - v_l \ ) \qquad 3.5$$

$$c = \frac{1}{v_{mix}} \left(\frac{\Delta v_{mix}}{\Delta p} \right)_{T or S} \qquad 3.6$$

or by differentiating an appropriate equation of state that would represent the two-phase volume. Note x represents mass quality in Eq. 3.5.

The compressibility caused by liquid mass transfer to vapor by boiling can be computed from the change in mass after a small change in pressure at constant total volume, i.e., a constant-volume flash, with the required production of higher and/or lower enthalpy fluids. The computation of the fluid compressibility and the compressibility effect from vaporization caused by boiling can be obtained from multicomponent vapor/liquid equilibrium in conjunction with energy influx from rocks and the consideration of production of fluid, when appropriate.

3.1. Vapor-Liquid Equilibrium Calculations

The thermodynamic model considered herein consists of a porous medium of fixed rock mass, m_r, and uniform porosity which contains an initial molar (feed) with m components at a given pressure, composition and enthalpy. The ftuid is flashed after a small drop in pressure into liquid and vapor. This model is a modification of the model presented by Prausnitz et al (1980).

The total molar and component molar balances are expressed by:

$$F = \bar{V} + L \tag{3.7}$$

$$F\omega_i = \bar{V}y_i + Lx_i \tag{3.8}$$

and an enthalpy balance:

$$Fh^F + Q = \bar{V}h^V + Lh^L \tag{3.9}$$

where Q is the external heat (enthalpy) addition from the porous medium, and is defined as:

$$Q = \left(1 - \Phi\right) V_{total} \quad \rho_r c_p \quad \Delta T \tag{3.10}$$

Rock heat capacity and density are considered constant throughout the flash processes. Addition of the rock contribution to the enthalpy balance is a modification of the enthalpy expression presented by Prausnitz et al. (1980). Thermodynamic relationships required for the flash calculations follows the description presented by Prausnitz et al. (1980), and are given here for the sake of completeness.

3.2. Phase equilibrium

Gibbs showed that at thermodynamic equilibrium the fugacity, pressure and temperature of each component are the same for each of the coexisting phases (Smith et. al., 1975):

$$f_i^V = f_i^L \tag{3.11}$$

where:

$$f_i^V = \varphi_i^V y_i \; p \tag{3.12}$$

and:

$$f_i^L = \varphi_i^L x_i p = \gamma_i x_i f_i^{OL} \tag{3.13}$$

$$\gamma_i = \frac{f_i^L}{x_i f_i^{OL}} \tag{3.14}$$

by definition equilibrium ratios *are:*

$$K_i = \frac{Vi}{x_i} \tag{3.15}$$

or:

$$K_i = \frac{\gamma_i f_i^{\,OL}}{\varphi_i\, p} \tag{3.16}$$

additional restrictions required are:

$$\sum_{i=1}^{m} x_i = 1 \tag{3.17}$$

$$\sum_{i=1}^{m} y_i = 1 \tag{3.18}$$

Combining a total mass balance, component mass balances, and the definition of equilibrium ratios in the conventional **way** for flash calculations, the following expressions are obtained:

$$x_i = \frac{\omega_i}{(K_i-1)\,\alpha + 1} \tag{3.19}$$

and:

$$y_i = \frac{K_i\,\omega_i}{(K_i-1)\,\alpha + 1}, \tag{3.20}$$

where the fractional vaporization, $\frac{V}{F'}$ is represented by α, and ω_i represents the initial molar fraction.

Using the Rachford and Rice **(1952)** procedure, the following expression is obtained:

$$\sum_{i=1}^{(m)} \frac{(K_i-1)\omega_i}{(K_i-1)\alpha+1} = 0 \qquad \textbf{3.21}$$

which can be solved for a iteratively, given K_i values.

For determination of the separation temperature, an enthalpy balance should **be** solved simultaneously with Eq. **3.21.** Furthermore, vapor-liquid equilibrium problems can be represented by:

Component Mass Balance:

$$G_1(T,x,y,\alpha)=\sum_{i=1}^{(m)} \frac{(K_i-1)\omega_i}{(K_i-1)\alpha+1} = 0 \qquad \textbf{3.22}$$

Enthalpy Balance:

$$G_2(T,x,y,\alpha,Q/F)=1+\frac{Q}{F}h^F - \alpha\frac{h^V}{h^F} - (1-a)\frac{h^L}{h^F} = 0 \qquad \textbf{3.23}$$

$$\frac{Q}{F} = \frac{1-\Phi}{\Phi}\,\frac{\rho_r c_p}{PF}\,AT \qquad \textbf{3.24}$$

Equations **3.22** and **3.23** may **be** solved simultaneously for a and T, with the corresponding thermodynamic functions to give equilibrium ratios and enthalpies.

3.3. Equilibrium Ratios

The different components of the equilibrium ratios can be computed as follows. The fugacity coefficient of component i, is related to the fugacity coefficient of the vapor phase of the same component i by the following expression:

$$\varphi_i = \frac{f_i^V}{y_i P} \qquad 3.25$$

The connection between the fugacity of a component in a vapor phase and the volumetric characteristics of that phase can be achieved with the help of an equation of state (EOS). An equation of state describes, Martin, J.J,(1967), the equilibrium relationship (without special force fields) between pressure, volume, temperature, and composition of a pure substance or a homogeneous mixture. l'he EOS can be made to be volume explicit, pressure explicit, or temperature explicit. The temperature explicit equations are not practical. and are generally discarded. In looking for an appropriate equation of state, three decisions must be made. The first concerns the amount and kind of data necessary to obtain the equation parameters. The second concerns the range of density to be covered, and the third concerns the precision with which pVT data can be represented.

Simple, short equations are adequate for a low density range. However long complicated equations are required if a broader range of density must be covered. As an illustration, Martin (ibid), reports that an equation covering data accurately to a fiftieth of the critical density requires only two constants. To get to onc half thc critical density, four or five constants are needed. Six or more constants are required to continue to the critical density, and many more constants are required if the desired density goes beyond the value of the critical density.

For low or moderate density ranges, a suitable equation of state for gases is the virial equation of state, Eq. **3.26.** This equation has a theoretical basis.

$$Z = \frac{p\,v}{R\,T} = 1 + \frac{B\,p}{R\,T} + C\left(\frac{p}{R\,T}\right)^2 + \ldots \qquad 3.26$$

Statistical mechanics methods can be used to derive the virial equation and indicate physical meaning for the virial coefficients. The second virial coefficient, B, considers interactions between molecular pairs. The third virial coefficient, C, represents three-body interactions, and so on. Two-body interactions are more common than three-body interactions, which are more abundant than four-body interactions, etc. The contributions of high-order terms diminish rapidly. Another important advantage of the virial equation of state is that theoretically-valid relationships exist between the virial coefficients of amixture and its components.

The virial equation of state, truncated after the second term, gives a good approximation for densities in the range of about one half of the critical density and below. Although, in principle, the equation may be used for higher densities, this requires additional higher-order virial coefficients that, unfortunately, are not yet available, Prausnitz et al. (1980).

The thermodynamic definition of the fugacity coefficient is (Smith et. al., **1975):**

$$\ln \varphi_i = \int_0^p \frac{\overline{z_i} - 1}{p}\,dp \qquad 3.27$$

where:

$$\overline{z_i} = \frac{p\overline{v_i}}{R\ T} \qquad 3.28$$

and:

$$\overline{v_i} = \left(\frac{\partial v}{\partial n_i}\right)_{T,p,n_j} \qquad 3.29$$

$$B_{mix} = \sum_{i=1}^{m}\sum_{j=1}^{m} y_i y_j B_{ij} \qquad 3.30$$

When the virial equation of state, truncated after the second term, and the definition of the second virial coefficient, **Eq. 3.30** are substituted in the expression for the fugacity coefficient, the following expression is obtained Prausnitz, et al, (1980):

$$\ln \varphi_i = \left[2\sum_{j}^{m} y_j\ B_{ij} - B\right]\frac{p}{R\ T} \qquad 3.31$$

These equations, suitable for vapor mixtures at **low** or moderate pressures, are used throughout this work.

For the computation of vapor liquid equilibrium for polar mixtures, an activity coefficient method **is** advantageous. The ratio of fugacity of the component i, f , and the standard state fugacity, f^{OL}, **is called** the activity, a_i. The quantity known as "activity coefficient",which is an auxiliary function in the application of thermodynamics to vapor-liquid equilibrium is defined **as:**

$$\gamma_i = \frac{a_i}{x_i} \qquad 3.32$$

or:

$$\gamma_i = \frac{f_i^{\,L}}{x_i f_i^{\,OL}} \qquad 3.33$$

Activity coefficients were computed with the UNIQIJAC model, Prausnitz et al. (1980), from which individual activity coefficients were calculated from Gibbs molar excess energy.

With the preceding elements, the equilibrium ratios for each component can be obtained from the expression:

$$K_i = \frac{\gamma_i f_i^{\,OL}}{\varphi_i\, P} \qquad 3.34$$

Enthalpies were calculated following the procedure presented by Prausnitz et al. (1980), and were defined as follows:

Vapor enthalpy:

$$h_i^I = \int c_{p_i}^{\circ} dT \qquad 3.35$$

$$h^V = h^I + \Delta h \qquad 3.36$$

Liquid enthalpy:

$$h_L = h_I + \sum_{i=1}^{m} x_i \overline{\Delta h_i} \qquad 3.37$$

A combination of vapor-liquid equilibria with appropriate thermodynamic relationships to permit solution of material and energy balances is presented in the next section.

3.4. Flow Diagram For Flash Calculations

A flow diagram for solving Eqns. 3.22 and 3.23 simultaneously with a two-dimensional Newton-Raphson method to obtain fractional vaporization, a, and temperature, T. is given in Fig. 3.1. The thermodynamic definitions of equilibrium ratios and enthalpies were taken from the published routines from Prausnitz et al. (1980), and are included in the solution.

Single or multicomponent systems (up to 10 components) with heat interaction from a porous medium is represented by this method. The main limitation is that pressure must be less than about half the critical pressure for a particular system. Therefore, the maximum pressure considered is 100 bars. This procedure supplies the necessary information, molar composition of the vapor and liquid phases, temperature, and fractional vaporization €or multiphase, multicomponent compressibility calculations, which are described in the next section.

3.5. Compressibility Calculations

Procedures for calculating expansion compressibility and production compressibility for two different modes of production are presented in this section.

3.5.1. Expansion Compressibility

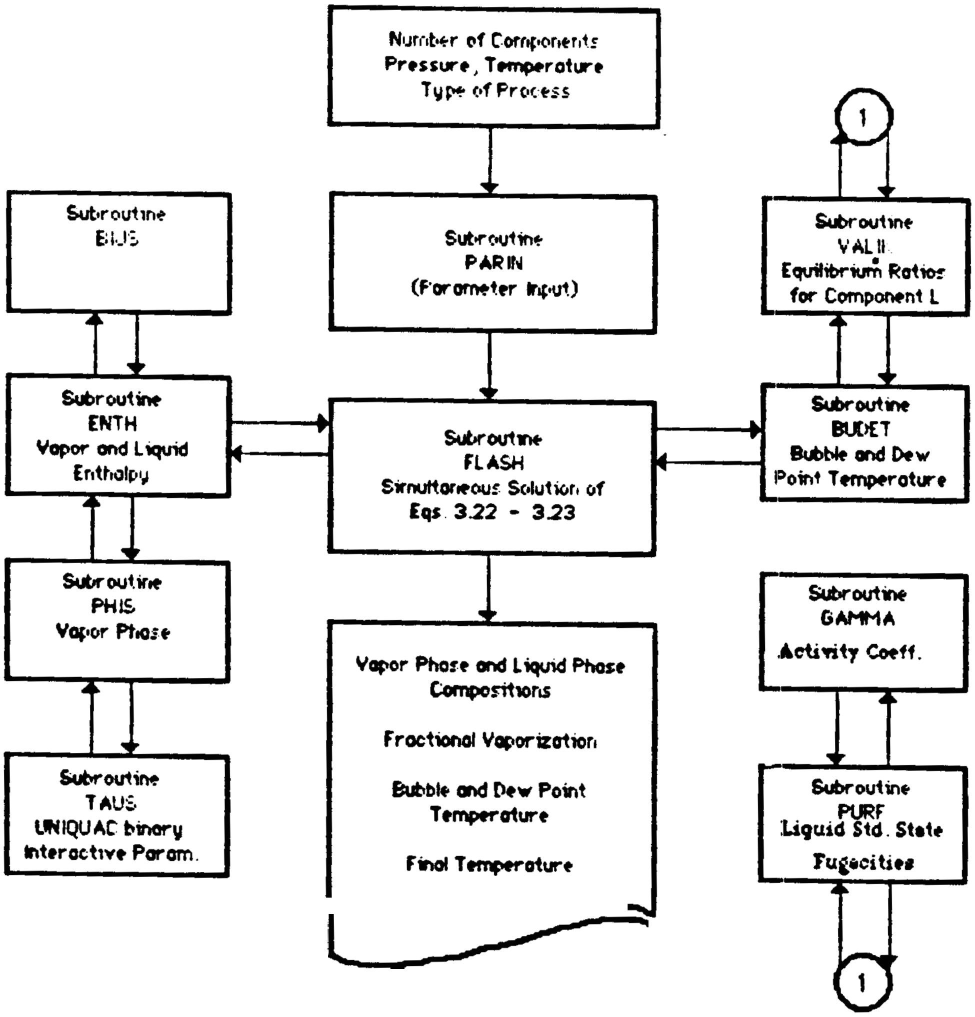


Fig. 3.1 Flow diagram from flash calculations (Prausnitz et al. (1980)).

Coupled with calculations described in the last section, compressibility computations are considered for either a single-component or multicomponent system with specified initial conditions of temperature, pressure, composition, and fractional vaporization. The volume of the vapor phase, liquid phase, and the volume of the mixture after a decrease in pressure can be computed in the following manner.

The gas specific volume can be computed from the truncated virial equation of state:

$$Z = \frac{p\ v_g}{R\ T} = 1 + \frac{B\ p}{R\ T} \tag{3.38}$$

in which the second virial coefficient, B, may be calculated at the initial conditions.

Then:

$$v_g = \frac{R\ T\ Z}{p} \tag{3.39}$$

which corresponds to the gas specific volume, for either single or multicomponent systems.

The liquid specific volume of single component-systems can be computed from published routines, e.g., routines published by Reynolds (1979) for pure water, which are based on correlations of thermodynamic data.

Once the liquid mole fractions are known, the liquid specific volume for a multicomponent system is given by:

$$v_l = x_i v_i \tag{3.40}$$

The specific volumes of the individual components, v_i , can be obtained from published data. The specific volume of the mixture, or the two-phase specific volume, liquid and gas. can be approximated by:

$$v_{mix} = v_l + x\ (v_g - v_l\ ) \qquad 3.41$$

Combining a change in mixture volume with a change in pressure, divided by the arithmetic average of the volume of the mixture at the initial and final pressures of the pressure change, gives the fluid compressibility:

$$c_{2\varphi} = -\frac{1}{\overline{v_{mix}}}\ \frac{v_2 - v_1}{p_2 - p_1} \qquad 3.42$$

where v_1 and v_2 correspond to the specific volumes of the mixture at pressures p_1 and p_2, respectively. Equation 3.42 represents the two phase compressibility due to expansion and without production.

A comparison of the two-phase compressibility and the compressibility of the gaseous mixture, Eq. 3.43, can be made. The gas compressibility is:

$$c_g = \frac{1}{p} - \frac{1}{Z}\left(\frac{\partial Z}{\partial p}\right)_T \qquad 3.43$$

where:

$$\left(\frac{\partial Z}{\partial p}\right) = \frac{B}{R\ T} \qquad 3.44$$

as obtained from the virial equation of state, Eq. *3.313.*

Calculation of two-phase compressibility caused by withdrawal of fluids from a reservoir block can be approached in several ways depending on production from the system. This is the subject of the following section.

3.6. Production Compressibility

Production compressibility was computed with two production modes, gas production, and multiphase production. **A** description of the two production modes is presented in the following sections.

3.6.1. Gas Production

After a pressure drop within a reservoir block, there is a phase change in the system because some of the liquid changes to vapor, causing a volume increase and expulsion of fluids from the reservoir block. Production in this case considers that only gas **is** produced. **A** schematic representation of this process is shown in Fig. **3.2.**

Production compressibility can be described as follows:

$$c = \frac{1}{V_{pore}} \frac{\Delta V_{prod.}}{\Delta p} \qquad 3.45$$

where $\Delta V_{prod.}$ corresponds to the initial fluid volume after the flash in the reservoir minus the fluid volume remaining after production, which gives the volume produced. The V_{pore} term represents the pore volume.

For the present case of gas production and referring to *Fig.* **3.2,** $\Delta V_{prod.}$ can **be** represented as:

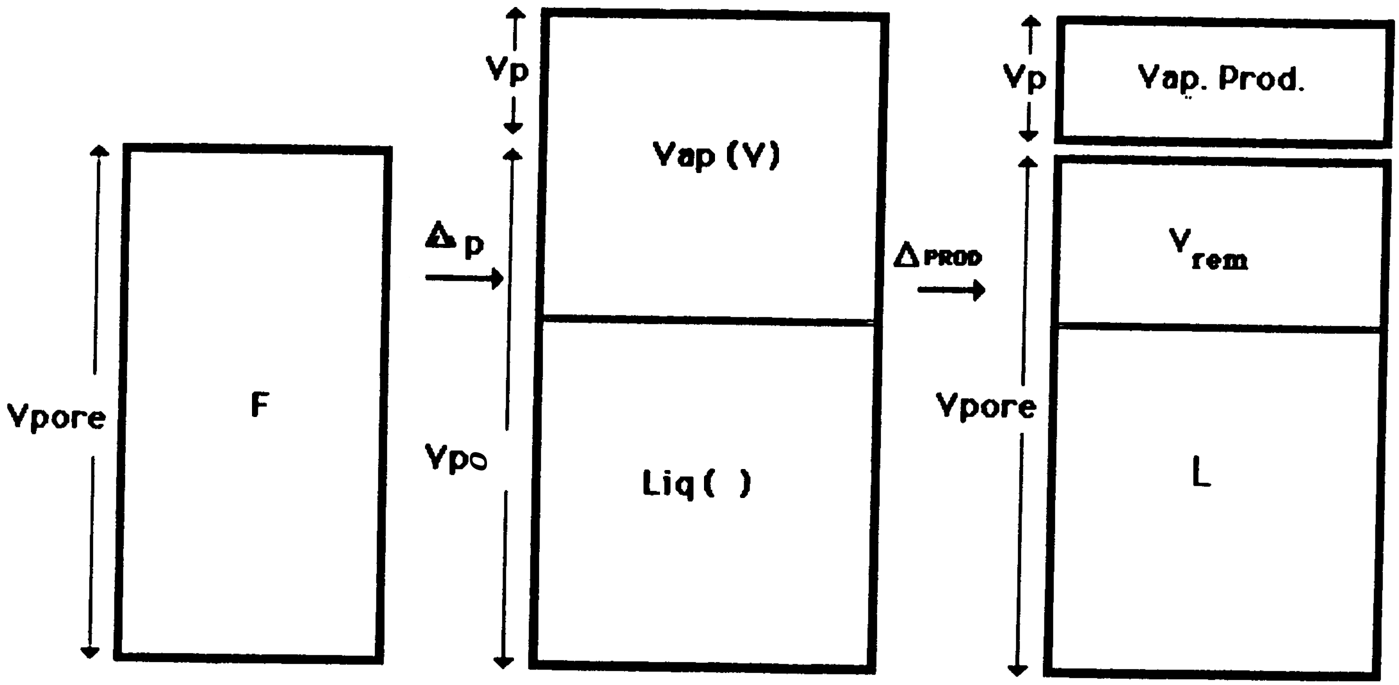


Fig. 3.2 Gas production.

$$\Delta V_{prod.} = V_{initial} - V_{rem}$$

or:

$$\Delta V_{prod.} = (F - L)\, v_g - (F - L)\, v_w \qquad 3.46$$

which represents the moles of feed changing to vapor times the specific molar volume of the gaseous phase less the initial volume of the vaporized feed. The remaining gas volume can be obtained from a volumetric balance as follows:

$$V_{rem} = V_{pore} - V_l \qquad 3.47$$

where V_{pore} is considered a constant, and V_l is the liquid volume after the flash, and is given by:

$$V_l = (1 - \alpha)F\ v_l \qquad 3.48$$

Expressing the change in moles for the system as the initial liquid moles minus the final liquid moles (with no liquid production), or in equation form:

$$\Delta N = F - L = \overline{V} = \alpha F \qquad 3.49$$

Substituting Eq. 3.49 in Eq. 3.46 gives:

$$V_p = \Delta N(v_g - v_l) \qquad 3.50$$

where v_g and v_l are the specific molar volumes of gas and liquid respectively, and alpha is the fractional vaporization obtained from the flash routine.

The two-phase compressibility caused by production of gas is given by:

$$c = \frac{1}{V_{pore}} \frac{\alpha F (v_g - v_l)}{\Delta p} \qquad 3.51$$

Expansion compressi ility ɔr the individual phases is ignored in this derivation. A comparison between the production compressibility and the gas compressibility can be made. For the next pressure drop, the new fractional vaporization is:

$$\frac{\bar{V}}{F} = \frac{\frac{V_g}{v_g}}{\frac{V_g}{v_g} + \frac{V_l}{v_l}} \qquad 3.52$$

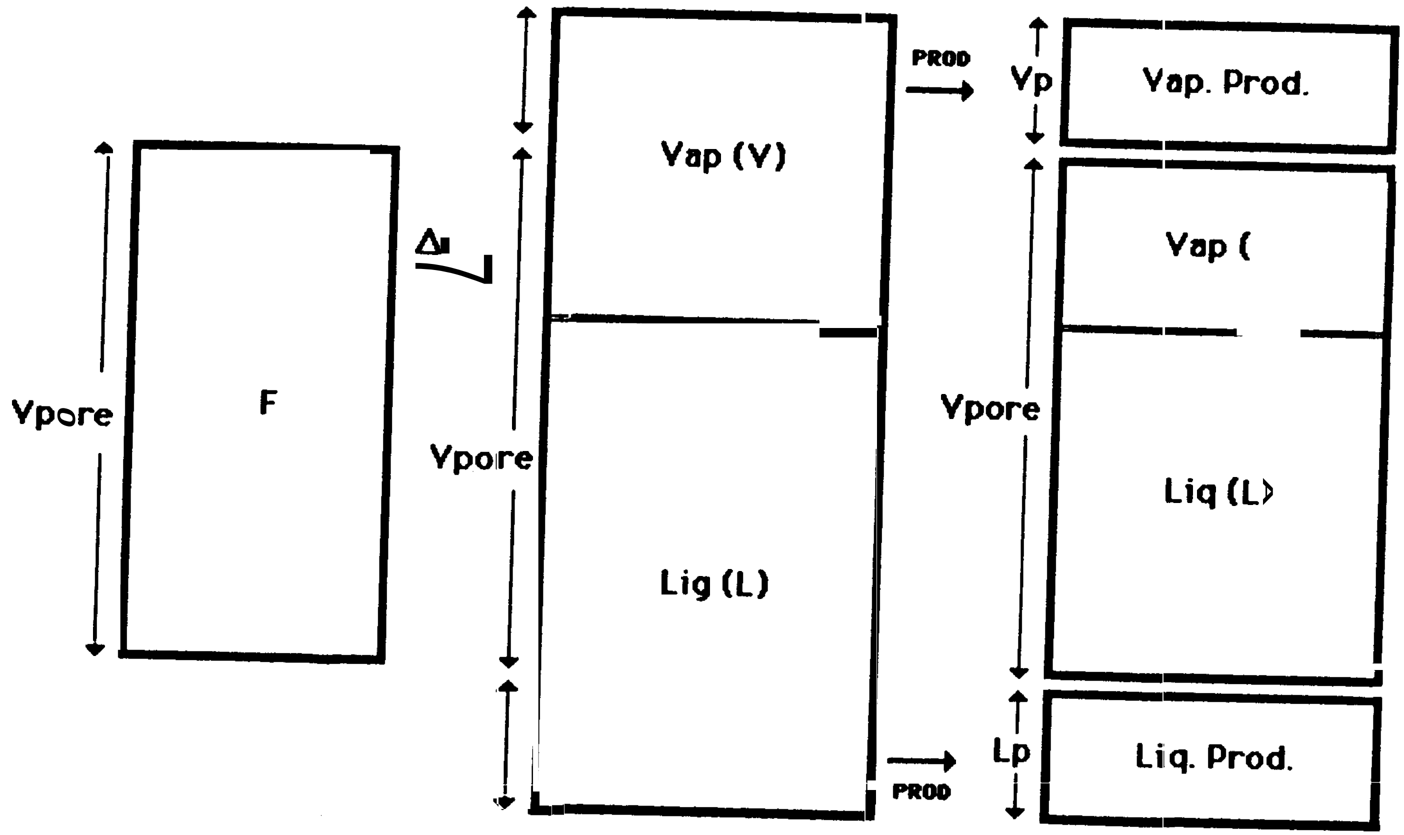
The process may be repeated, taking as initial conditions the conditions at the last pressure **drop.** Production compressibility for other than one fluid production mode is considered the next section.

3.6.2. Multiphase Fluid Production

In this case, it was considered that after a given pressure drop from a reservoir, fluids **will** be produced according to a relative permeability-saturation relationship for flow in a porous medium. A diagram for the process **is** shown in Fig. **3.3.** Gas saturations in this cases are given by:

$$S_g = \frac{v_g}{v_l + x\,(v_g - v_l)} \qquad 3.53$$

Production is computed by:



Note: $\frac{Vp}{Lp} = \frac{kg}{kl}$

Fig. 3.3 Multiphase fluid production according to relative permeability-saturation relationships.

$$q_w = \frac{k\ k_{rw}\ A}{\mu_w\ \Delta x}\ \Delta p \qquad 3.54$$

and:

$$q_g = \frac{k\ k_{rg}\ A}{\mu_g\ \Delta x}\ \Delta p \qquad 3.55$$

The volume of vapor remaining after production is:

$$V_g = \left(F\ \alpha\right) v_g - q_g\ \Delta t \qquad 3.56$$

The volume of liquid remaining after production is:

$$V_l = \left(F\ \left(1 - \alpha\right)\right) v_l - q_l\ \Delta t \qquad 3.57$$

The term At is varied in every pressure drop case to match the fixed pore volume, thus:

$$V_{pore} = V_g + V_l = constant \qquad 3.58$$

The moles of liquid produced, ΔN_l, is the initial moles of liquid after the flash **less** the final moles of liquid in the porous medium **or:**

$$\Delta N_l = F\left(1 - \alpha\right) - \frac{V_l}{v_l} \qquad 3.59$$

The moles of gas produced, ΔN_g, is the initial moles of gas after the flash less the final moles of gas in the porous medium or:

$$\Delta N_g = F a - \frac{V_g}{v_g} \qquad 3.60$$

where a, is the fractional vaporization calculated from the flash routine, and v_g and v_l are the gas and liquid specific volumes, also computed from the flash routine. Then the production compressibility, following Eq. 3.45 may be computed as:

$$c = \frac{1}{V_{pore}} \frac{\Delta N_l v_l + \Delta N_g v_g}{\Delta p} \qquad 3.61$$

Expansion compressibility for the individual phases is ignored in this derivation. A comparison may be made between the production compressibility and the gas compressibility. For the next pressure drop, the new fractional vaporization is:

$$\frac{\bar{V}}{F} = \frac{\frac{V_g}{v_g}}{\frac{V_g}{v_g} + \frac{V_l}{v_l}} \qquad 3.62$$

The process may be repeated, taking as initial conditions the conditions at the last pressure drop.

Compressibility calculations combined with flash calculations constitutes a model to study multiphase, multicomponent systems under pressure expansion conditions, and several production modes: production of a high enthalpy fluid, and production of multiphase Auid governed by relative permeability-saturation relationships.

Figure **3.4** is a flow diagram of the complete calculation method using the flash calculation procedure and compressibility calculations. In the event of finding no solution from a flash calculation (Fig. **3.1)** because of a temperature higher than the bubble point temperature, T_B, or lower than the dew point temperature, T_D, (single- phase conditions, or no solution possible because of a high pressure drop imposed on the system), then the initial data should be revised and the flash computation started again.

When a solution is found for a system in queslion, dala that will be used for compressibility calculations is obtained. Depending on whether production is considered or not, the appropriate compressibility calculations are chosen followed by checking whether the system pressure has reached the final pressure. If the system pressure is higher than the final pressure, **a** new pressure drop is taken, and the process is repeated until the Anal pressure **is** reached.

A flow diagram for fluid expansion compressibility calculations is shown on Fig. **3.5.** Gas, liquid, and two-phase specific volumes are computed in order to obtain the two-phase expansion compressibility. The final conditions of pressure, temperature. phase compositions and fractional vaporization become the initial conditions **for** the next pressure drop.

Gas production calculations are depicted in Fig. 3.6 in which the required gas and liquid specific volumes, and change in moles are computed to obtain the required production compressibility. Since the pore volume is fixed. the gas volume which exceeds the volume of the vaporized liquid is considered to be "produced' from the total pore volume. The remaining moles of liquid and vapor are computed to obtain the new fractional vaporization for the next pressure drop.

Figure **3.7** shows a **flow** diagram for the computation of low and high enthalpy fluid production compressibility. Gas and liquid specific volumes are calculat-

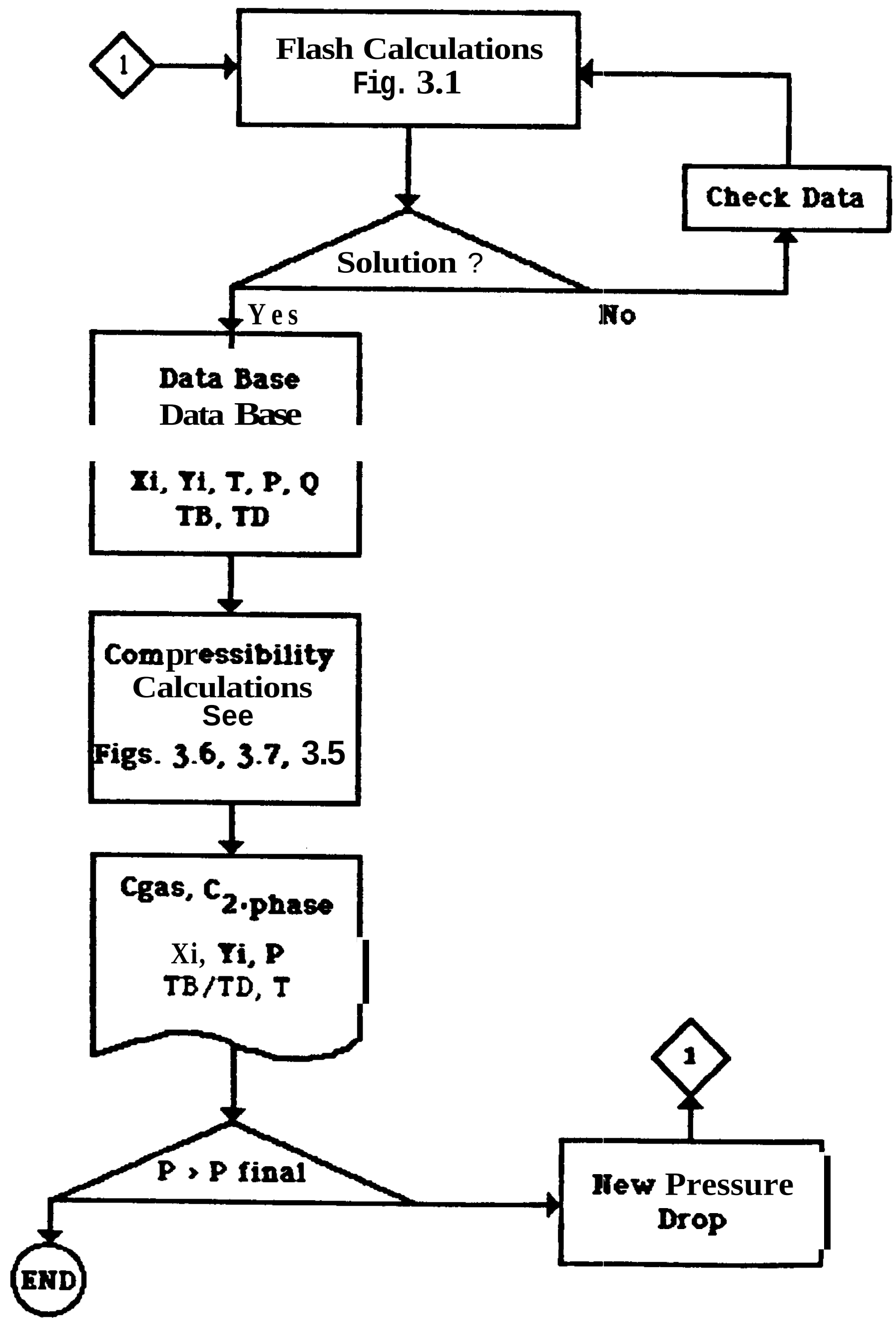


Fig. 3.4 **Flow** diagram of flash and compressibility calculations.

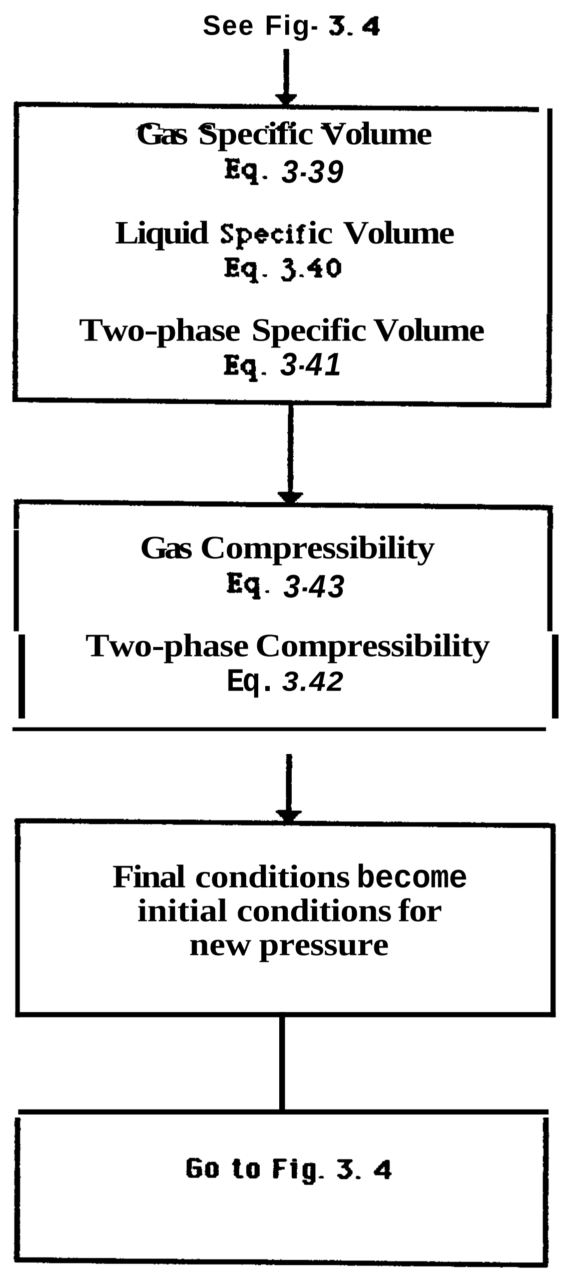


Fig. 3.5 Flow diagram for expansion compressibility calculations.

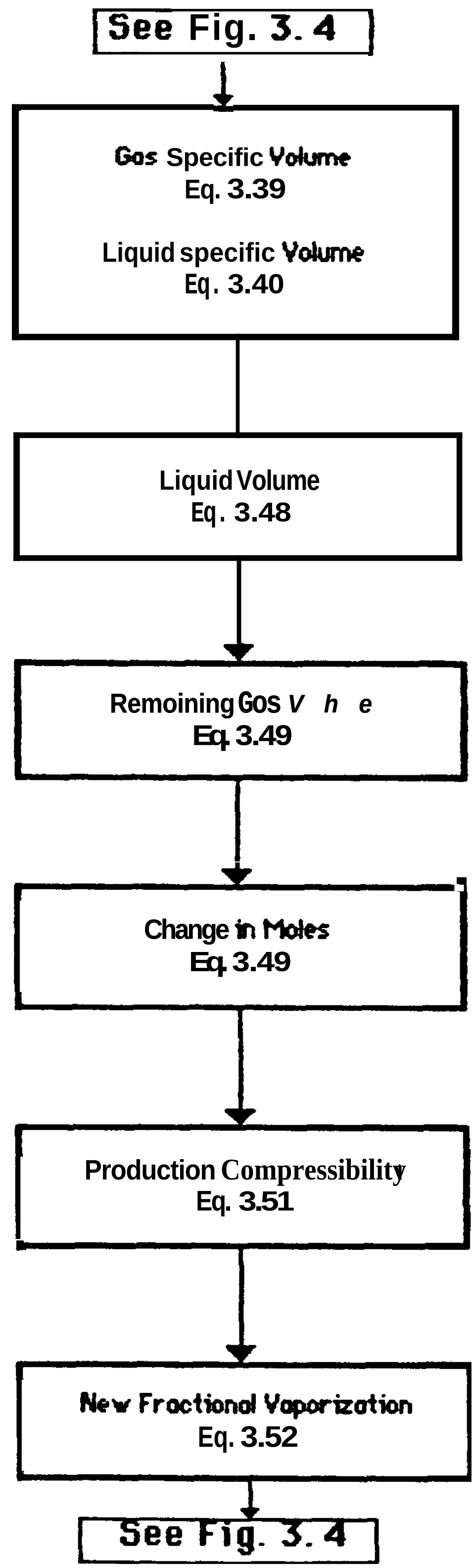


Fig. **3.6** Flow **diagram** of gas production compressibility calculations.

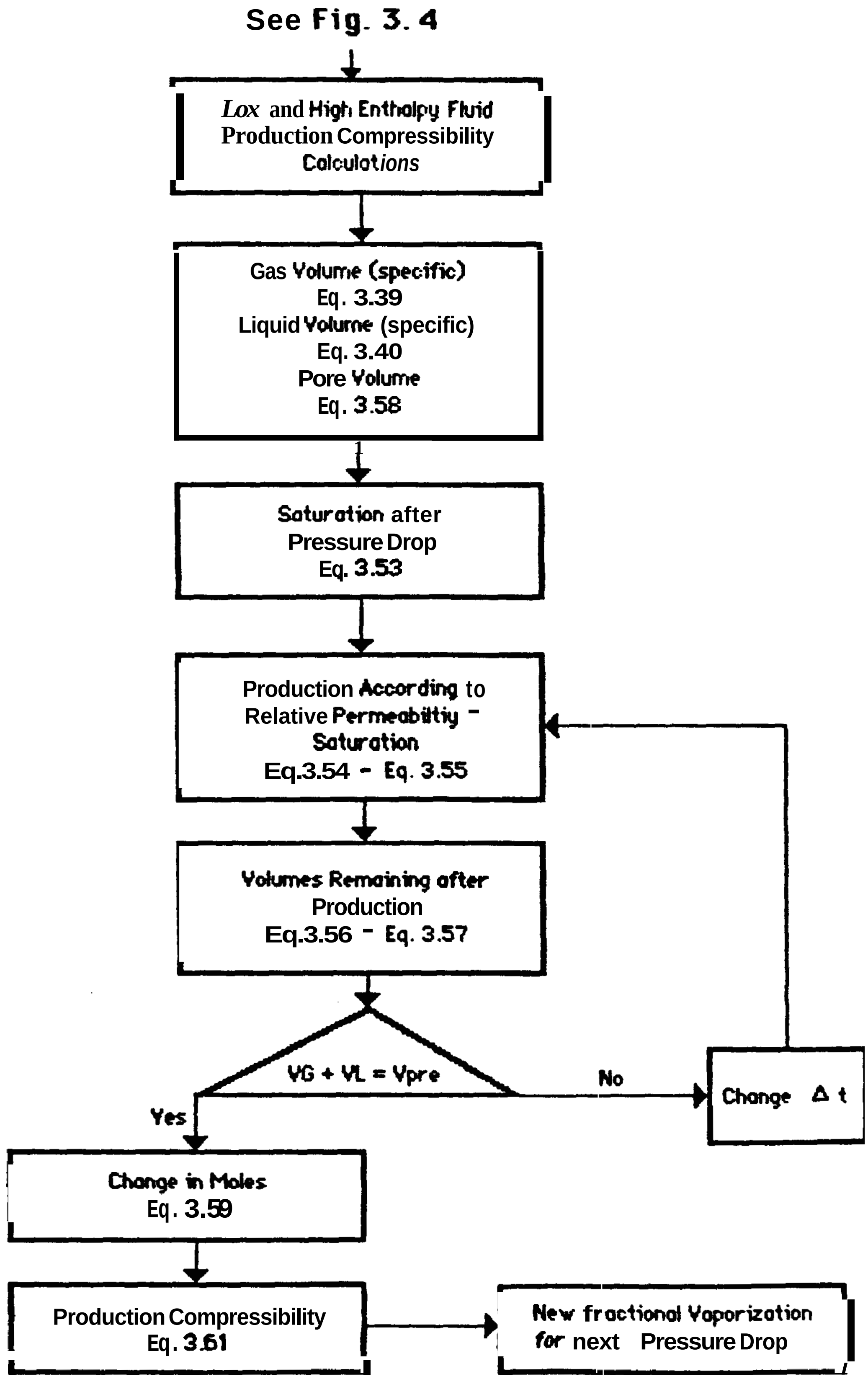


Fig. 3.7 **Flow diagram** of multiphase fluid production compressibility calculations.

ed Eollowed by the saturation value corresponding to that pressure and pressure drop. Saturation values after the first pressure drop are the arithmetic average between the last pressure drop saturation value, and the value corresponding to the new pressure drop. Production of liquid and vapor according to the relative-permeability-saturation relationship is obtained, and then the volumes of gas and liquid are calculated, checking that the summation of the two volumes (gas+liquid) are the same as the pore volume plus a tolerance. In the event of having a summation of volumes different from the pore volume plus a tolerance, the production time, At, is adjusted and the volumes recalculated. Next the change in moles is calculated followed by production compressibility and the new fractional vaporization for the new pressure drop.

The combination of flash process calculations and compressibility calculations, called the Flash Model, was used to study multiphase, multicomponent compressibility for a number of possible reservoir systems. Description of the systems, observations on these systems, and results are presented in the next section.

4. RESULTS

The Flash Model was used to study system compressibility for a number of possible fluid systems ranging from geothermal fluids to hydrocarbon systems. Table 4.1 lists thirteen systems considered. The systems included pure water, water carbon-dioxide, several simple multicomponent hydrocarbon systems, reservoir oil systems, and oil water systems. For systems studied by simple flash expansion, no porous medium was included in the calculations. The systems containing pure water and water-carbon dioxide were treated as adiabatic. The hydrocarbon and the hydrocarbon-water systems were considered to be isothermal. The results for each are presented in table 4.1.

Table 4.1 Systems studied by simple flash expansion

Single Component Systems		
System No.	Fluid	Initial Pressure (bar)
1	H_2O	100
2	H_2O	40
3	H_2O	9.3

Multicomponent [illegible]s		
S N	Fluid	Initial Pressure (bar)
4	$H_2O - CO_2$	50
5	$H_2O - CO_2$	70
6	$C_1 - C_3$	54
7	$C_1 - C_3$	50
8	$C_4 - iC_4 - nC_5 - C_{10}$	15
9	C_1 through nC_7	50
10	C_1 through nC_7	35
11	C_1 through $nC_7 - H_2O$	35
12	C_1 through $nC_7 - H_2O$	35
13	C_1 through $nC_7 - H_2O$	35

The model was also run in two production modes: production of the high enthalpy fluid (steam) from a geothermal system, and production from a geothermal system wherein both water and steam are produced as multiphase-flow relative permeability relationships would dictate. Table 4.2 lists these systems.

Table 4.2 Production–ontrolled compressibility systems

Higher enthalpy fluid production			
System No.	Fluid	Initial Pressure (bar)	Porosity (%)
14	H_2O	40.0	10
15	H_2O	40.0	25
16	H_2O	9.3	10
17	H_2O	9.3	25

Production According to Relative Permeability			
System No.	Fluid	Initial Pressure (bar)	Porosity (%)
18	H_2O	8.3	25
19	H_2O	40.0	25

Observations and discussion for the Flash Model results are presented for the systems studied. First, the fluid expansion cases are considered, then the production controlled systems.

4.1. FLUID COMPRESSIBILITY

Compressibility calculations were made following the thermodynamic definition for flashing systems allowing an increase in volume with a Axed decrease in pressure. Both single and multicomponent fluids were considered.

4.1.1. Single Component Systems

The systems modeled started at saturation pressure and temperature, allowing the pressure to decrease until the system was depleted. or at any other selected final pressure. Calculations of the individual phase volumes were made, and the two volumes were combined. Gas compressibility was calculated from the equation of state. Compressibility of the two phases was computed by taking the differences between the two molar volumes from two different pressures, and divided by the arithmetic average molar volume of the mixture and the pressure difference.

System No. 1 -- One-component system, adiabatic: compressibility of water at an initial pressure of 100 bars. Figure 4.1 presents pressure versus specific volume, and shows a very steep curve which indicates a small change in volume with a large change in pressure. followed by a decrease in slope to give a large change in volume with a small change in pressure. A comparison of the gas compressibility (in this case steam) and the adiabatic compressibility of the two-phase fluid, Fig. 4.2, shows that the compressibility of the two phases is larger than the compressibility of the gas phase at the same conditions, throughout most of the pressure range covered, even at very low qualities. This difference is better seen in a logarithmic graph of the same data, Fig. 4.3. Figure 4.4 presents quality versus pressure for this case.

System No.2 -- One-component-system, adiabatic compressibility for water at an initial pressure of 40 bars. The pressure versus specific volume graph, Fig. 4.5 for system No. 2, shows a steep curve, followed by a decrease in slope in the lower pressure range, as was the case previously presented. Again, the first part of the curve indicates a small change in volume with a large change in pressure. Figure 4.6 compares the two-phase adiabatic compressibility and the compressibility of the gas at the same conditions. It shows a larger two-phase compressibility than the compressibility of the gaseous phase. The two compressibilities approach each other at low pressures. Initially, the compressibility of the two phases decreases, and then increases as pressure decreases and quality in-

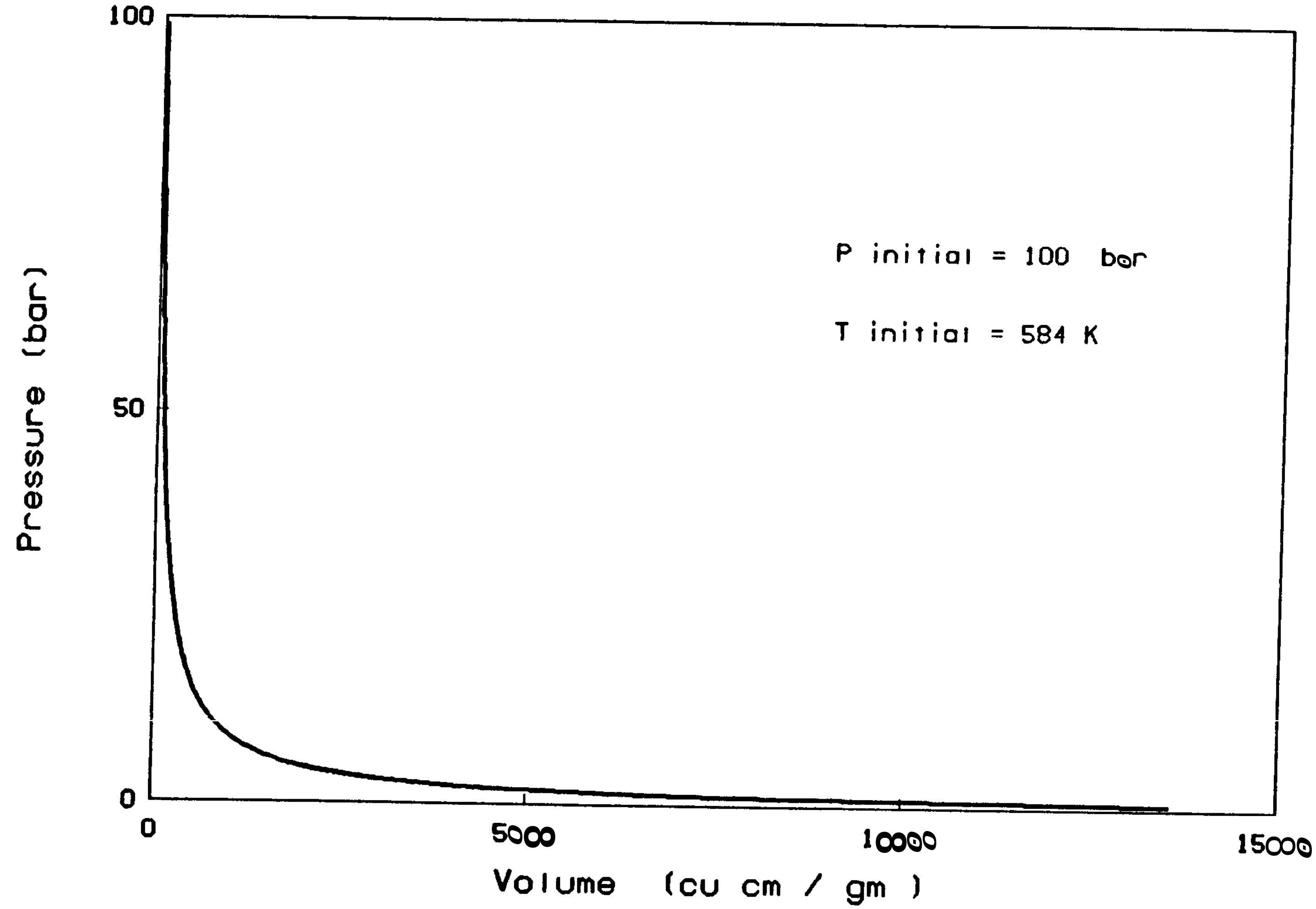


Fig. 4.1 Pressure versus Specific Volume, water System No 1

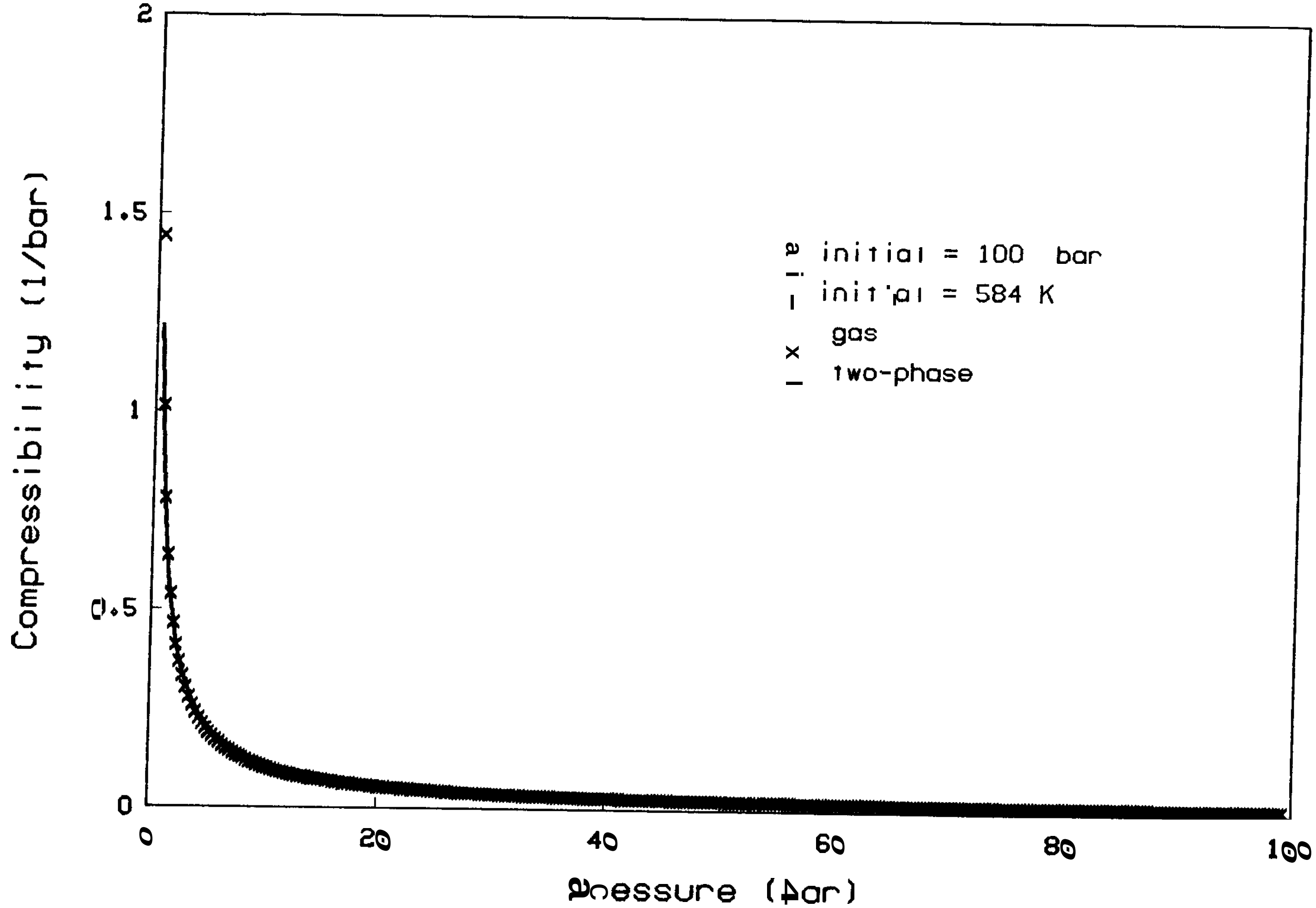


Fig. 4.2 Compressibility versus Pressure, water System No. 1

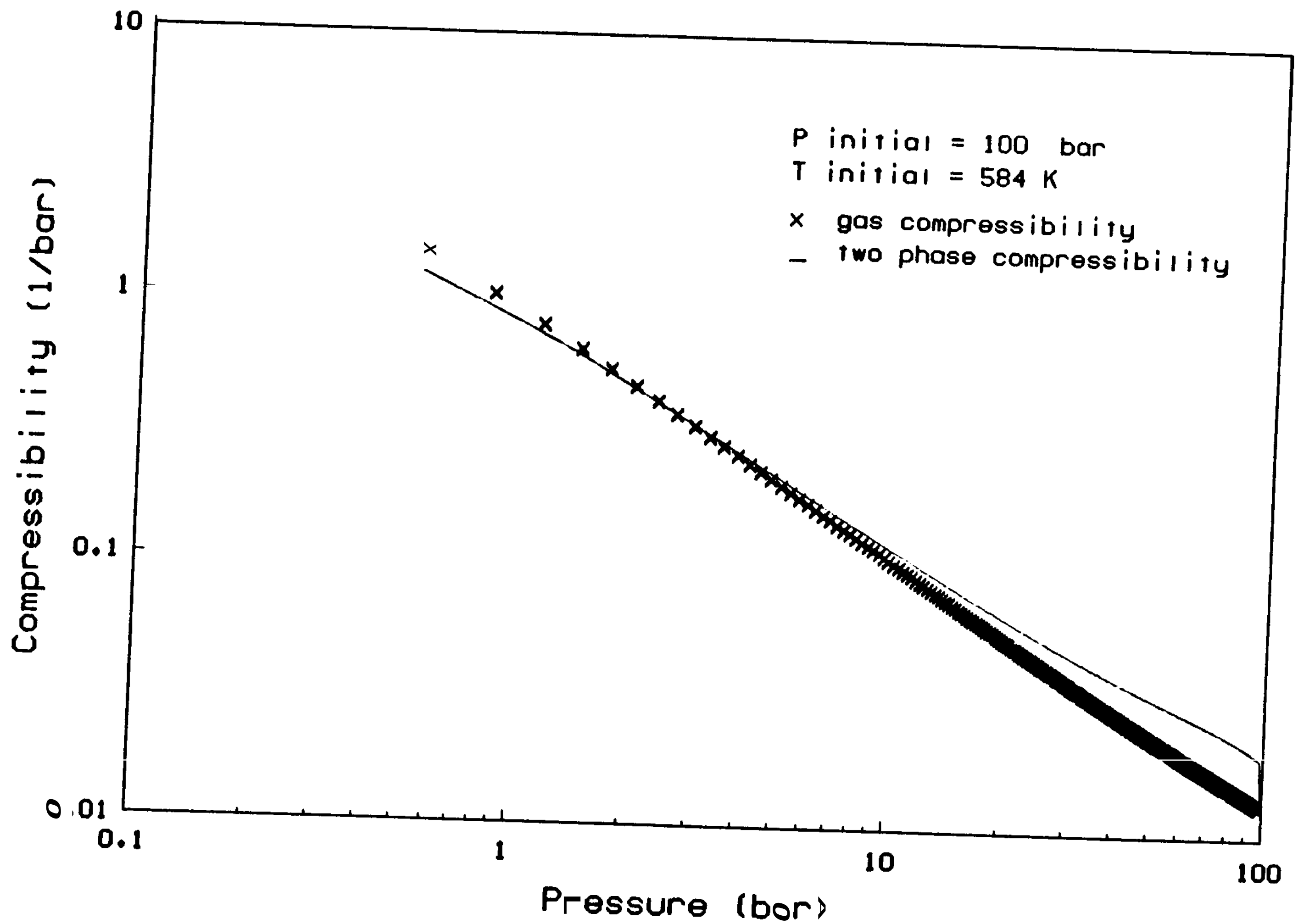


Fig. 4.3 Log -log graph of Compressibility versus Pressure, water System No 1

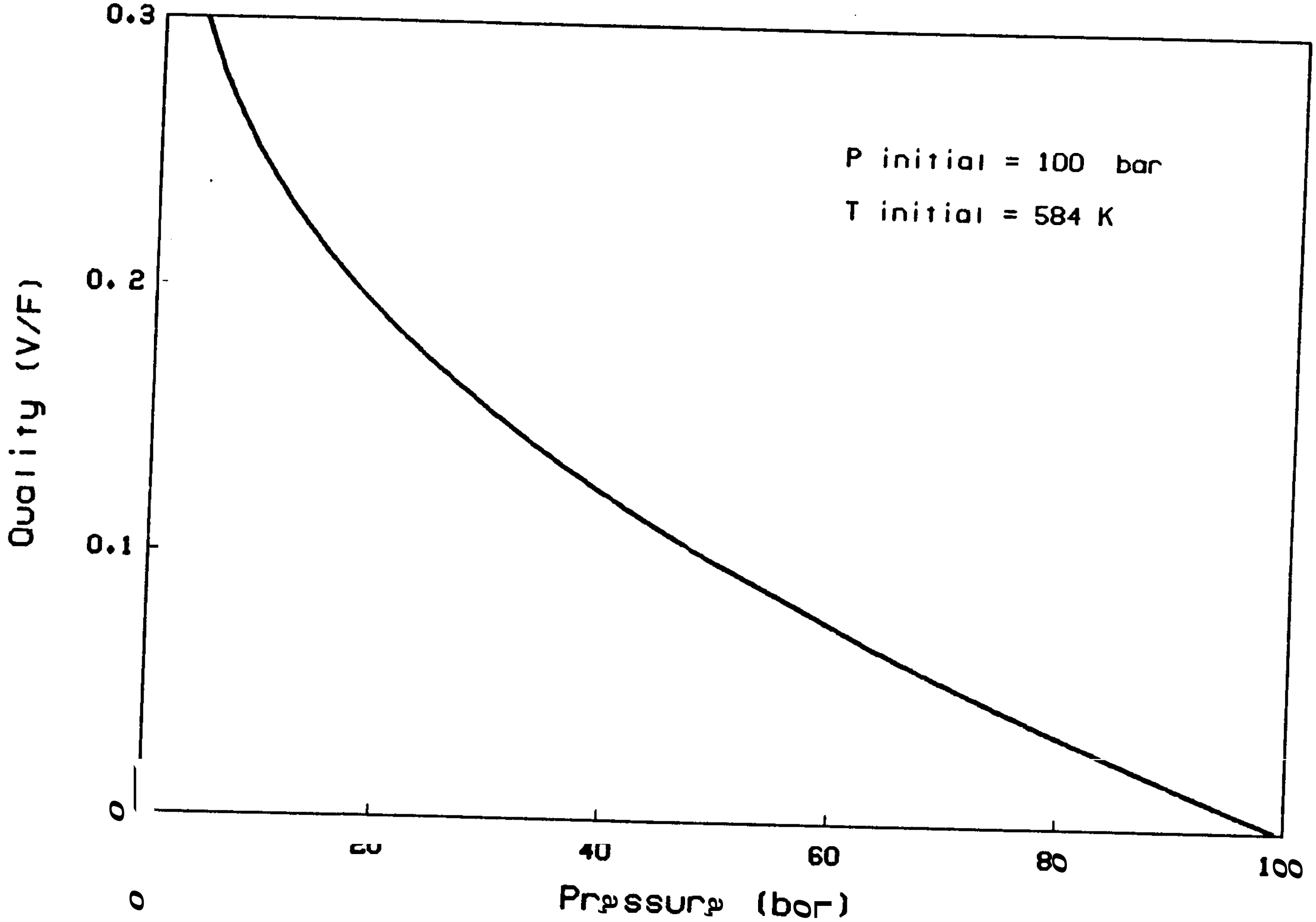


Fig. 4.4 Quality versus Pressure, water System No 1

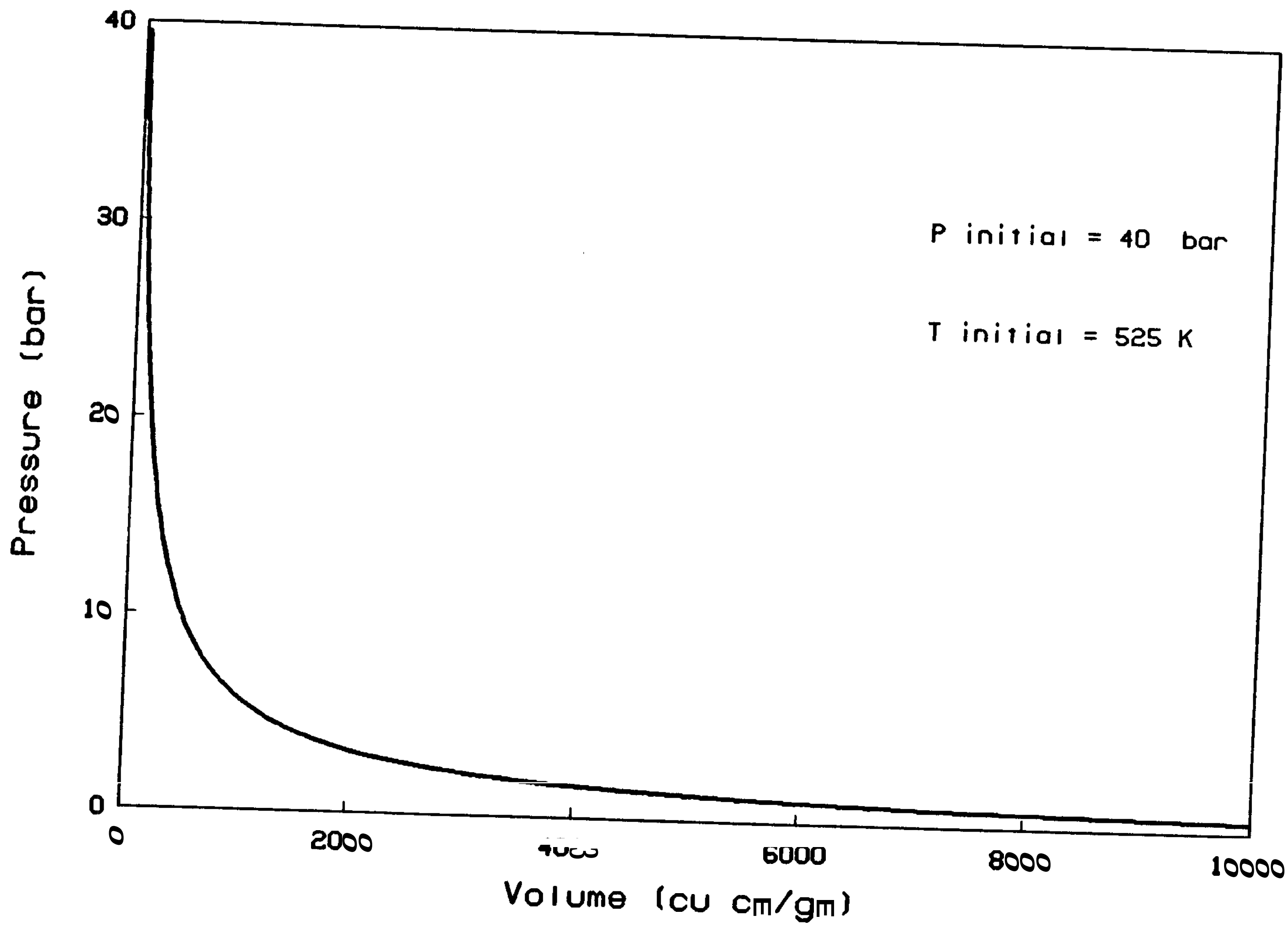


Fig. 4.5 Pressure versus Specific Volume, water System No 2

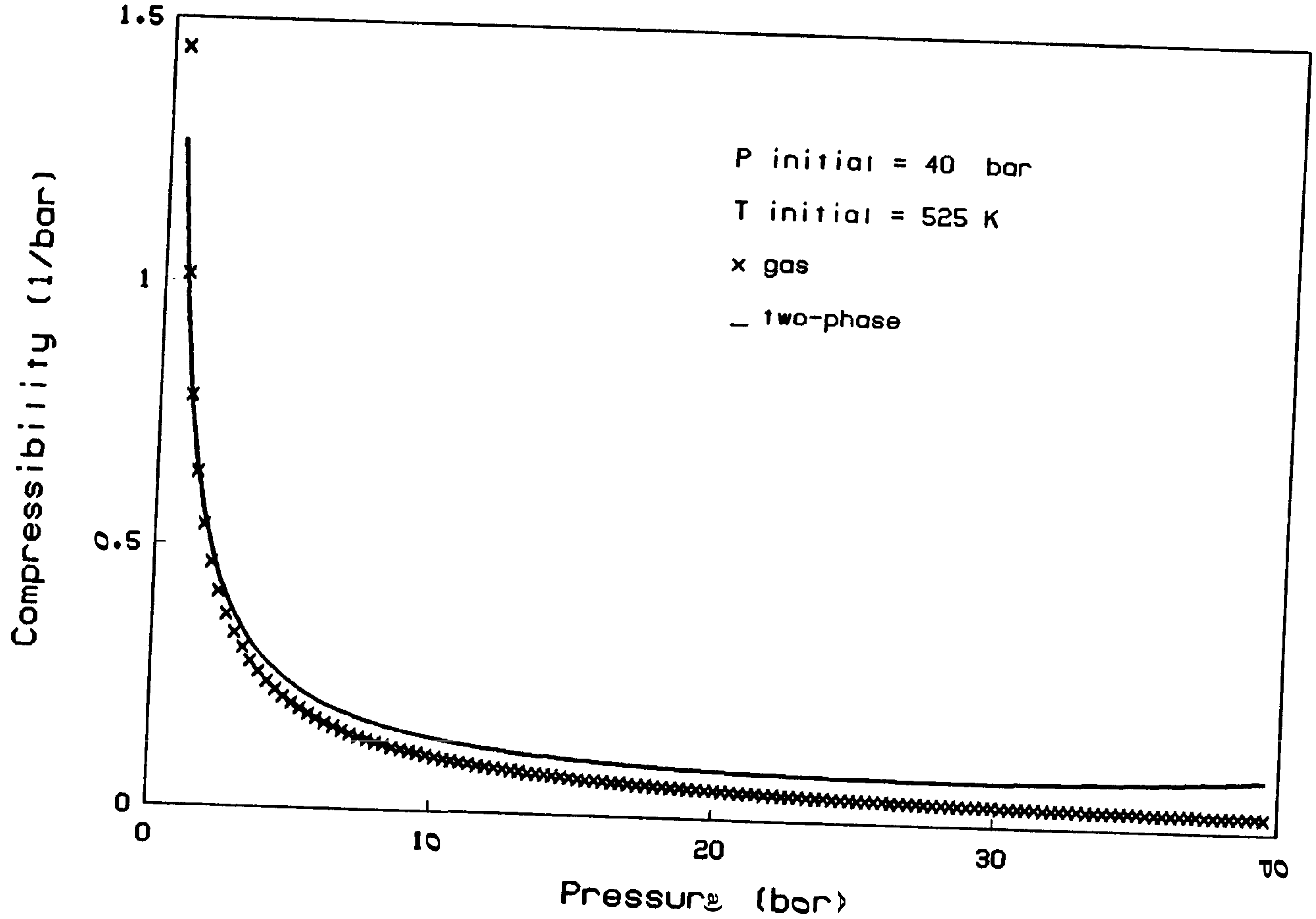


Fig. 4.6 Compressibility versus Pressure, water System No. 2

creases. This can be seen easier in Fig. 4.7. The quality versus pressure curve, Fig. 4.8, is similar to that for the previous case. That is, quality increases with pressure decrease. The highest quality for this case is not as large as that for system No. 1.

An important observation can be made at this point. Systems 1 and 2 are pure water starting expansion at different initial pressures: 100 bar lor system No.1, and 40 bar for system No.2. A comparison of the compressibility results €or the two cases at the same pressure can be made using Figs. 4.3 and 4.7. For example, the gas compressibility at 20 bar is clearly the same for both cases. However the two-phase compressibility is significantly greater for the System No.2, 40-bar initial pressure. The difference may be simply a result of different volumes of gas and liquid present. Figures 4.4 and 4.8 present the vapor molar fraction {quality) for the two cases. At a common pressure of 20 bar, the high pressure case has a much larger quality then the low pressure case. This would lead one to expect the high pressure case to exhibit the highest two-phase compressibility -- which is opposite the actual result. Clearly vaporization and initial pressure have a large impact on the effective system compressibility.

System No.3 -- One-component system, adiabatic compressibility for water at an initial pressure of 9.3 bars. The pressure versus specific volume curve, Fig. 4.9, follows a less steep behavior for the initial part of the graph than the behavior of the systems at higher pressures (Systems 1 and 2). The initial change in pressure with respect to volume is large, followed by a rapid change in volume with a smaller change in pressure.

A comparison of the two-phase compressibility and the gas compressibility, Fig. 4.10, shows an interesting pattern. The compressibility of the two phases is much larger than the compressibility of the gaseous phase. The two compressibilities approach each other as pressure decreases and quality increases. The

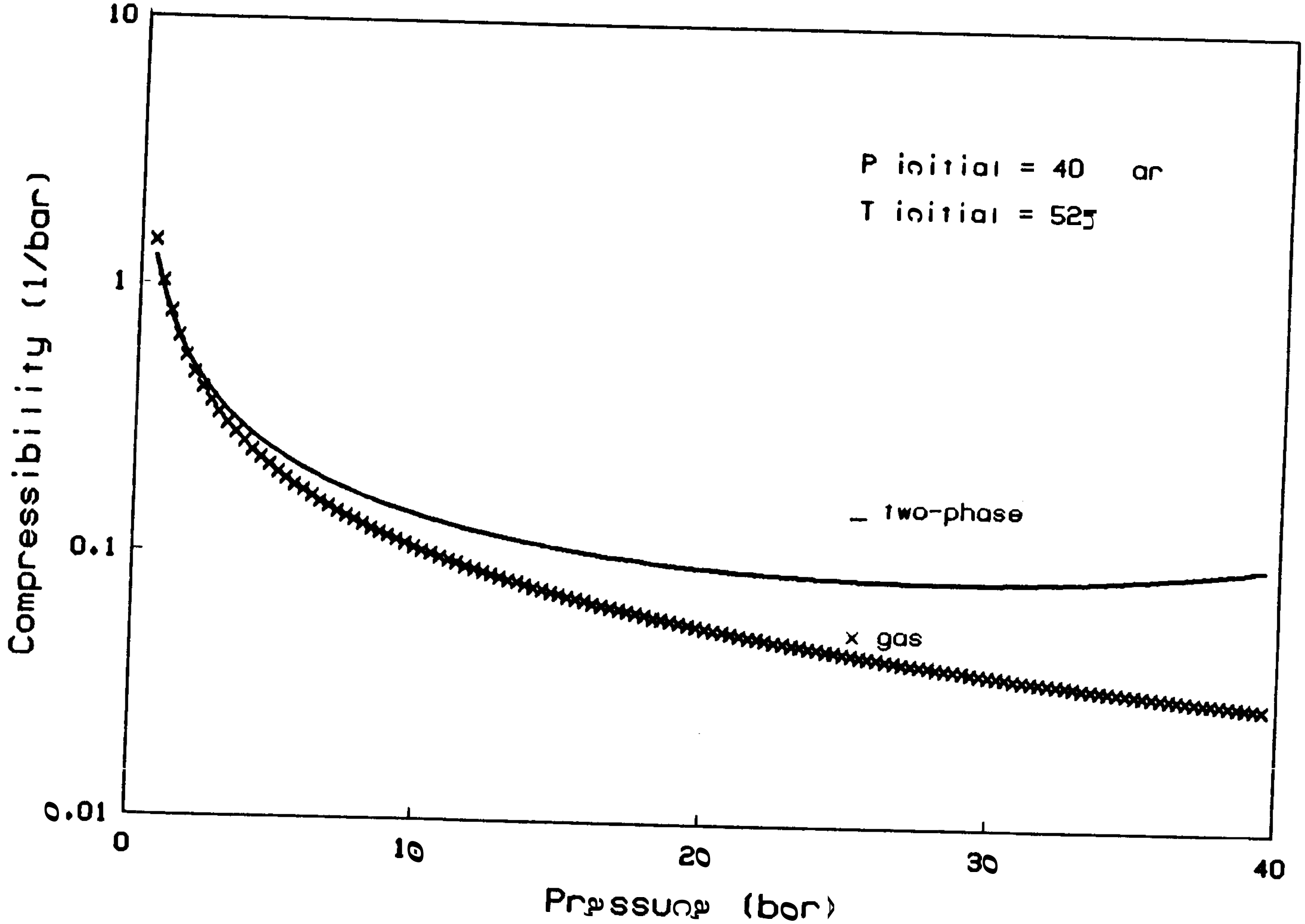


Fig. 4.7 Semilog graph of Compressibility versus Pressure, water System No 2

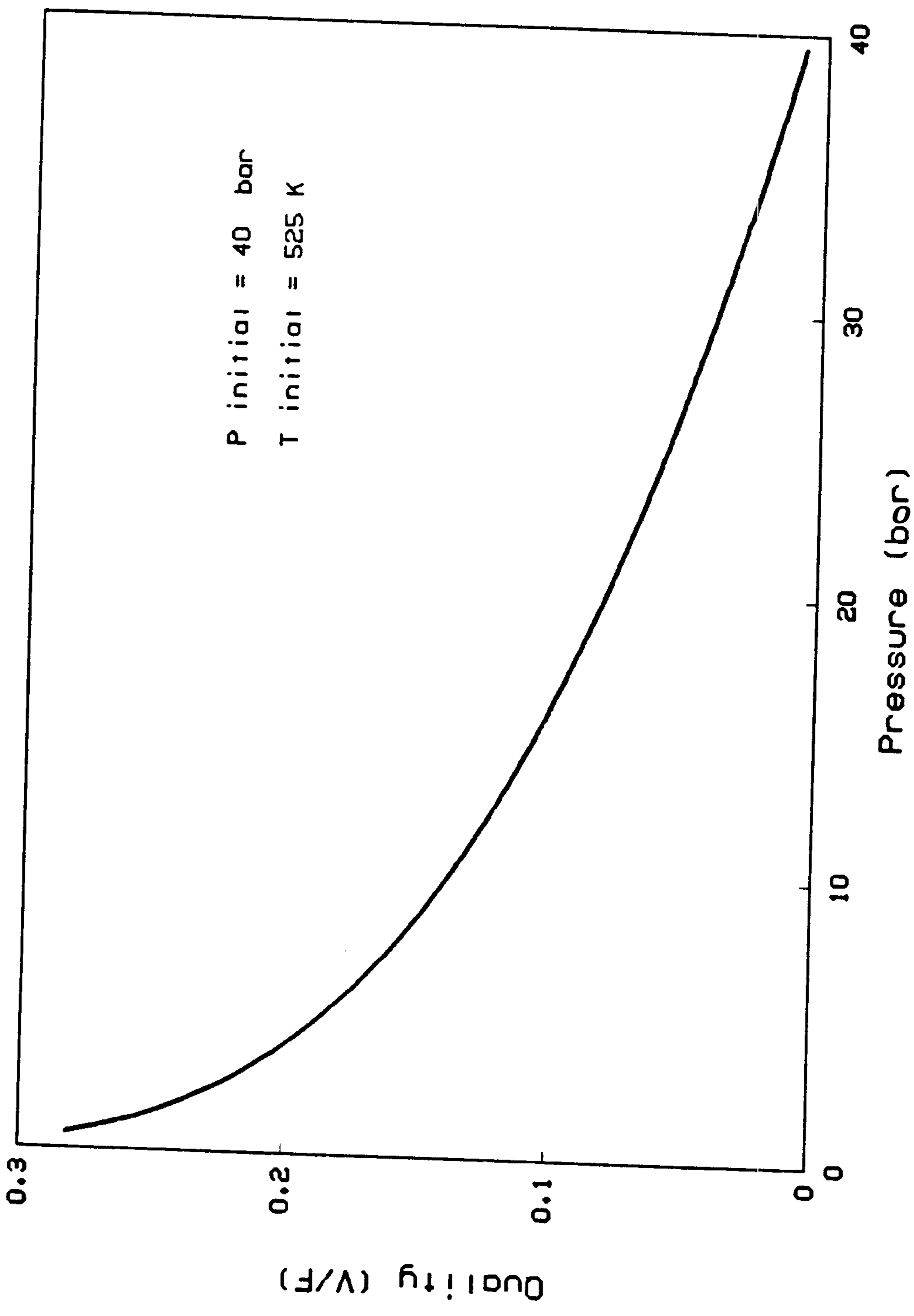


Fig. 4.8 Quality versus Pressure, water System No 2

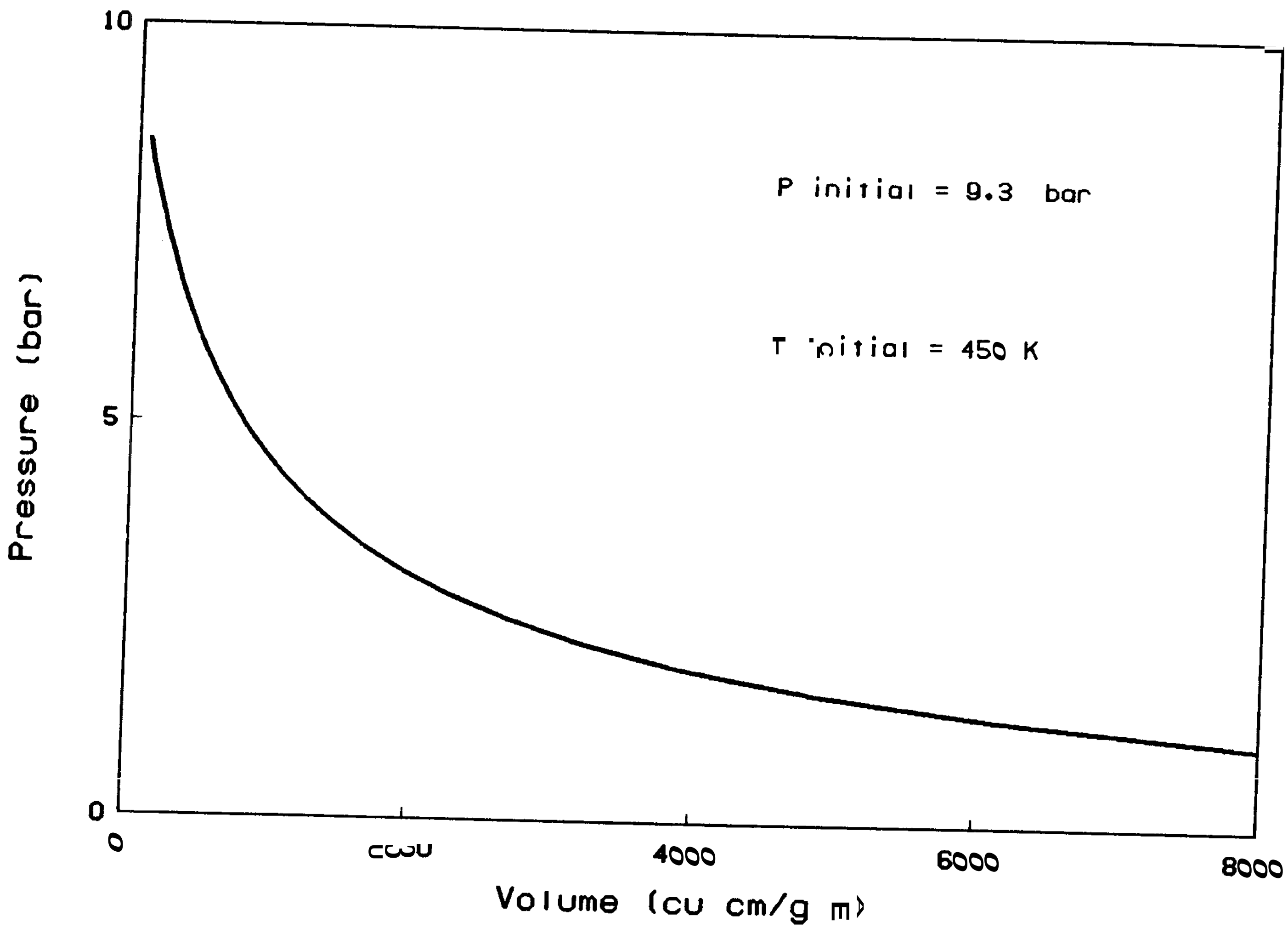


Fig. 4.9 Pressure versus Specific Volume, water System No 3

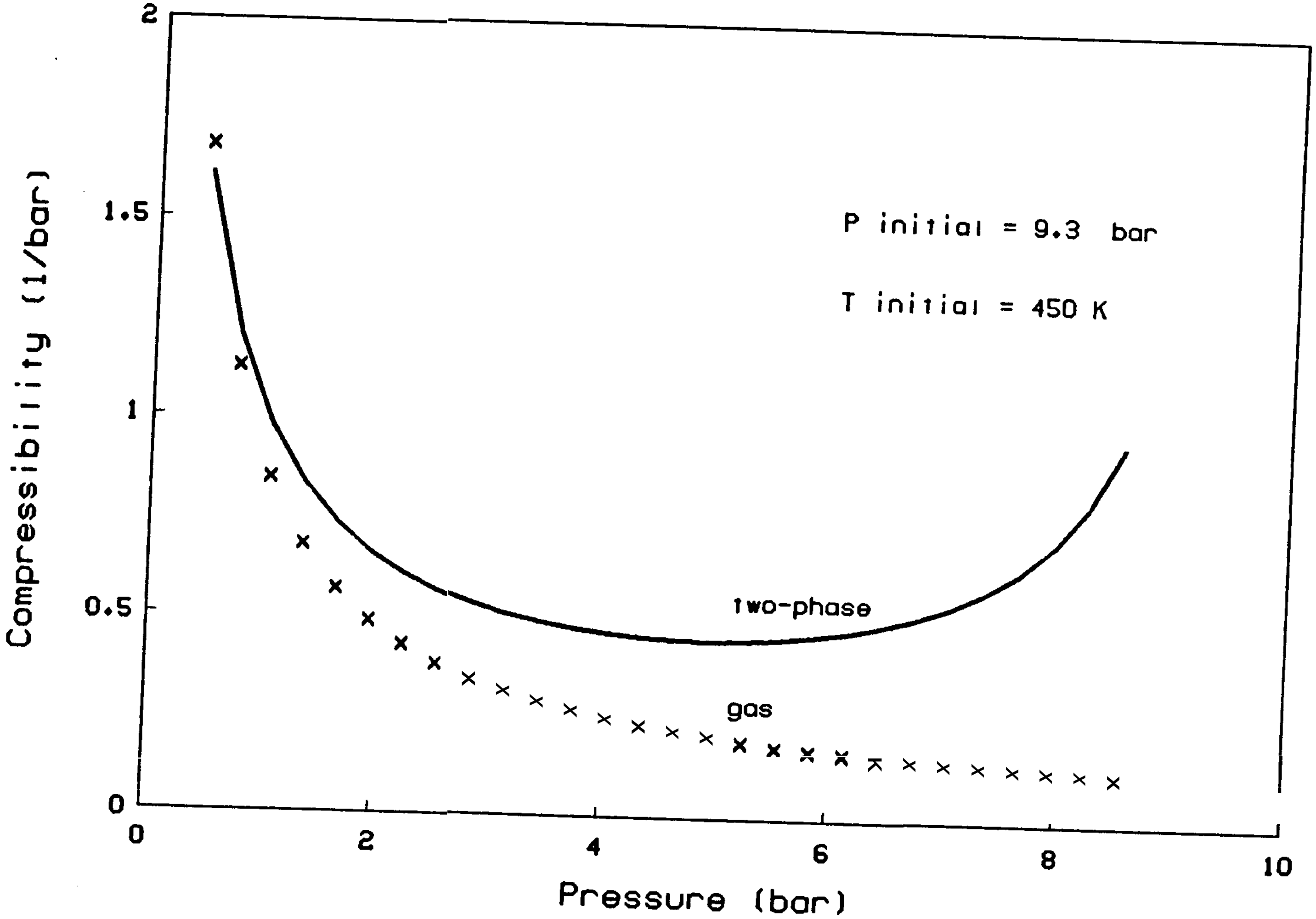


Fig. 4.10 Compressibility versus Pressure, water System No. 3

two- phase compressibility shows a rapid decrease with respect to pressure decrease. The initial compressibility is larger than the compressibilities at lower pressures and larger qualities. This behavior was observed in the other systems (1 and 2), but was not as obvious.

As in the previous cases, the quality increases as pressure decreases, see Fig. 4.11. The highest value of quality is lower than in the two previous systems. See Figs. 4.4, 4.8, and 4.11.

4.1.2. Multicomponent Systems

Calculations of two-phase specific volume, two-phase compressibility, and quality were made for two-component, four-component, seven-component and eight-component systems. Observations of the results for the different systems follow.

System No.4 -- Two-component system, adiabatic conipressibility for water-carbon dioxide with an initial mole fraction CO_2 of 0.005, initial temperature of 550 °K .and initial pressure of 50 bar.

For the pressure range considered, the pressure-specific molar volume curve in Fig. 4.12 shows a moderate increase in volume with pressure reduction. The adiabatic compressibility computed from this p-V data shows a larger compressibility for the two phases. Fig. 4.13, than the compressibility of the gas phase. The quality change with pressure showed a slight increase with pressure reduction, following a quasi-linear behavior, Fig. 4.14.

On another run, this same system was expanded to a lower pressure, Fig. 4.15. The result was similar to that for System No.2, but the compressibility for the two phases was lower for the two-component system (System No.4), than for a single-component pure water system (System No.2).

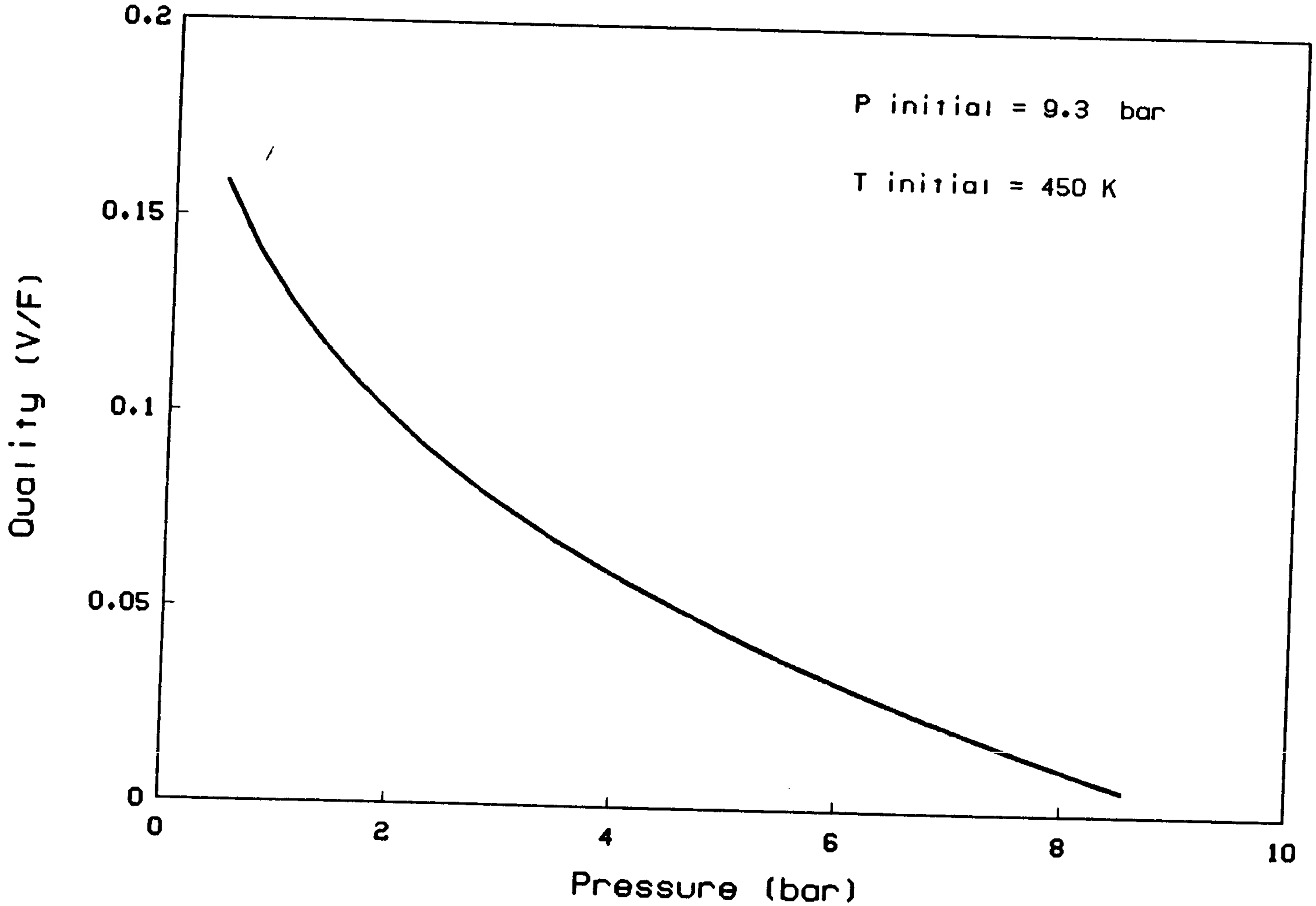


Fig. 4.11 Quality versus Pressure, water System No.3

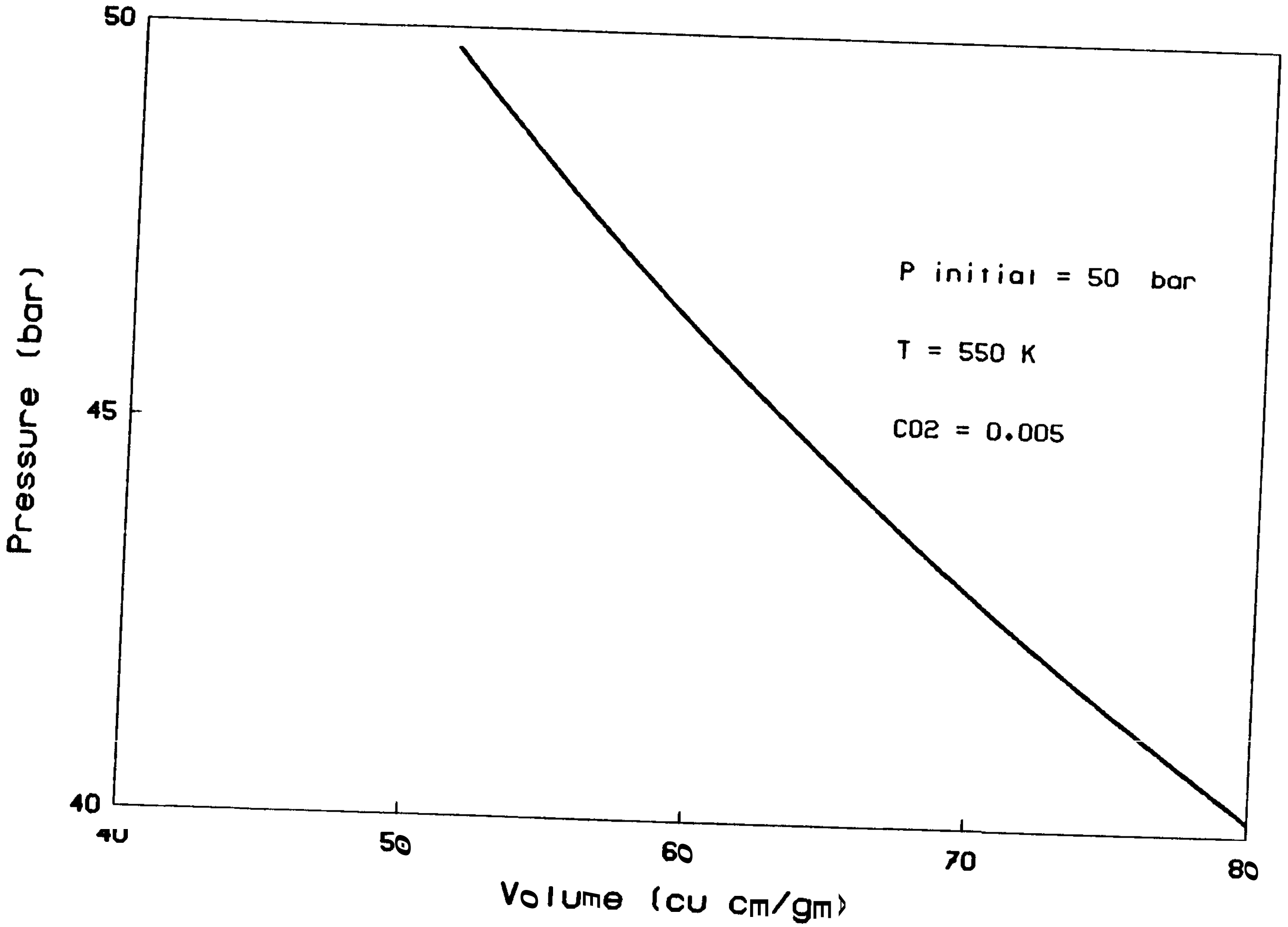


Fig. 4.12 Pressure versus Specific Volume, $H_2O - CO_2$ System No. 4

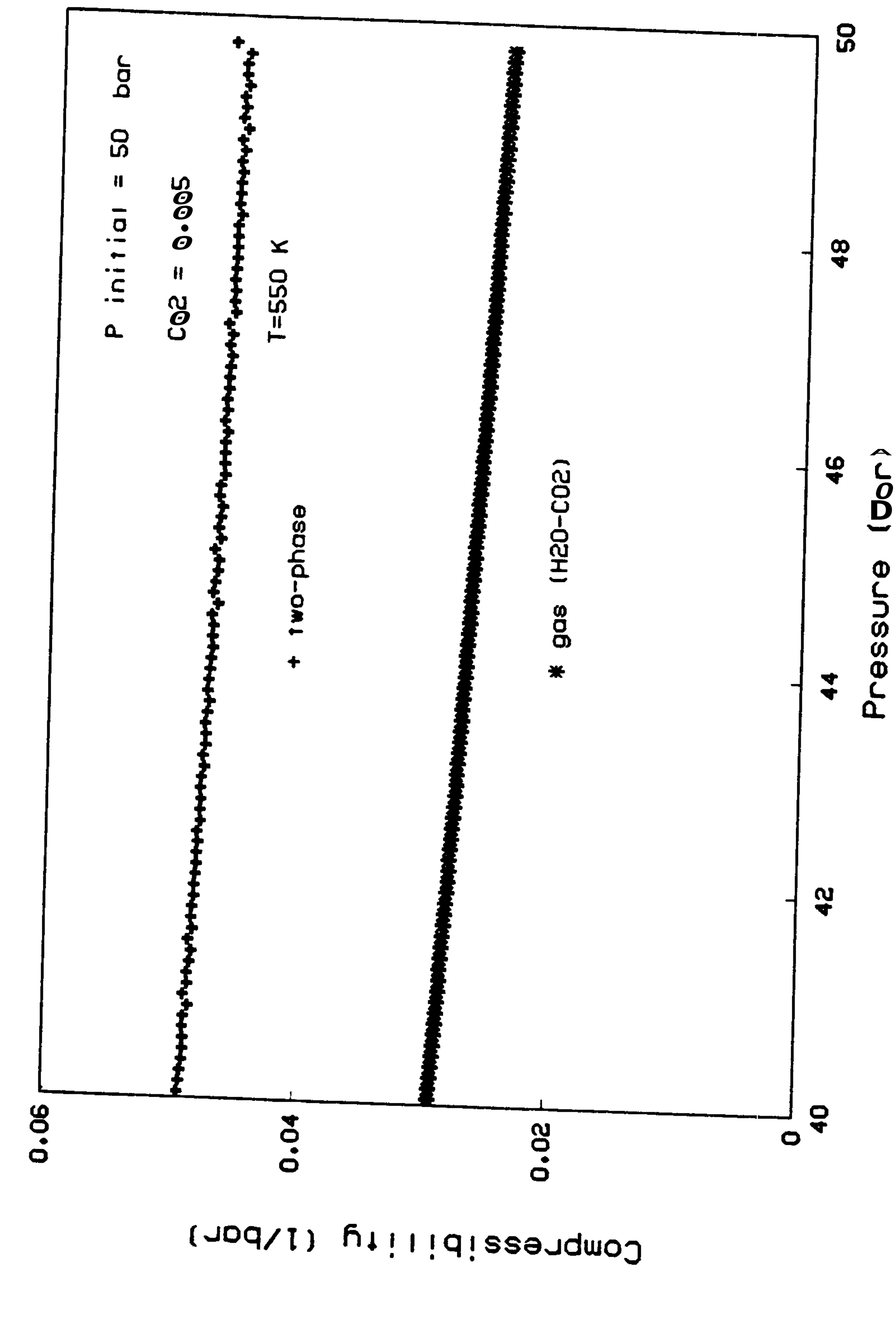


Fig. 4.13 Compressibility versus Pressure, $H_2O - CO_2$ System No 4

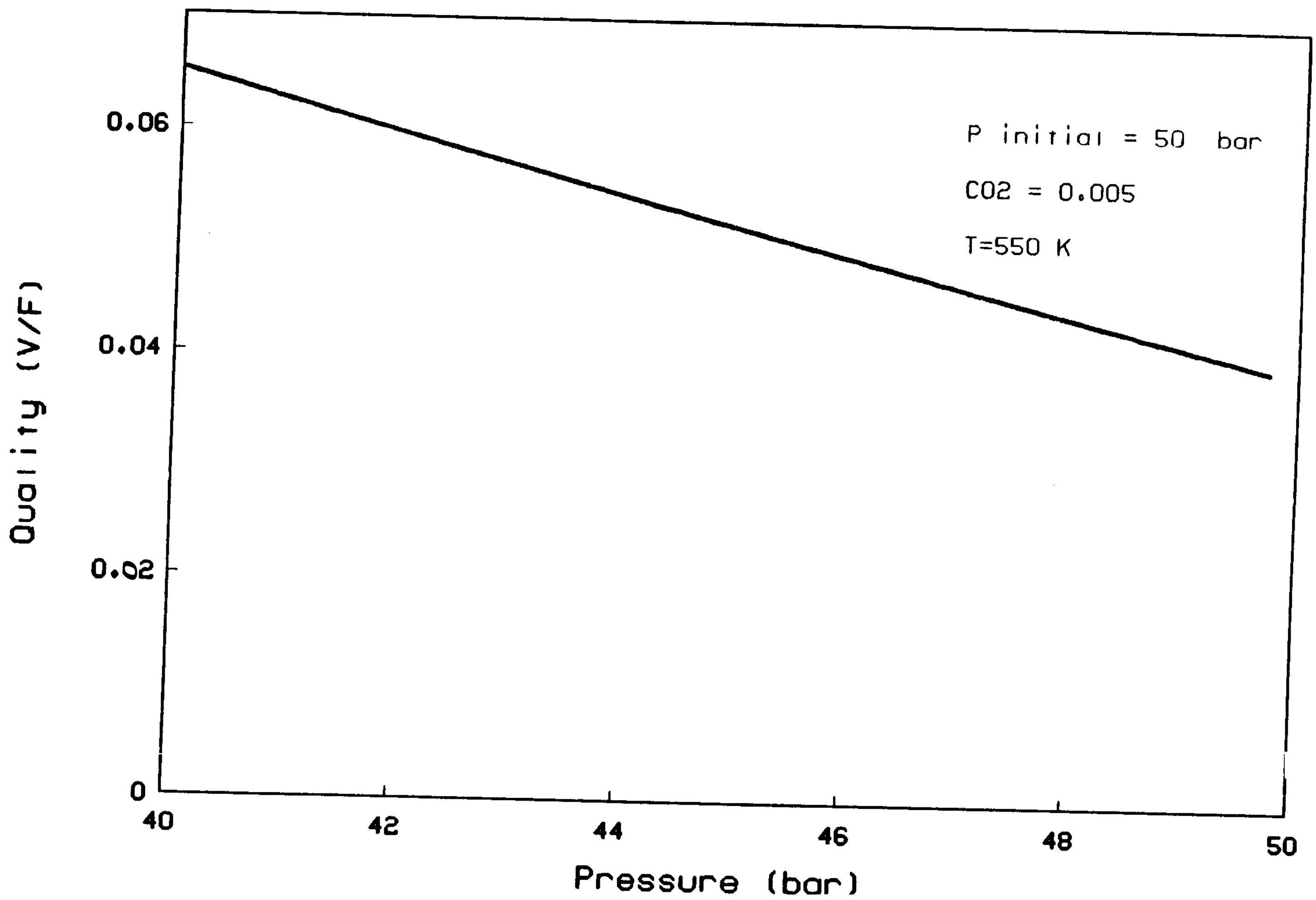


Fig. 4.14 Quality versus Pressure, $H_2O - CO_2$ System No.4

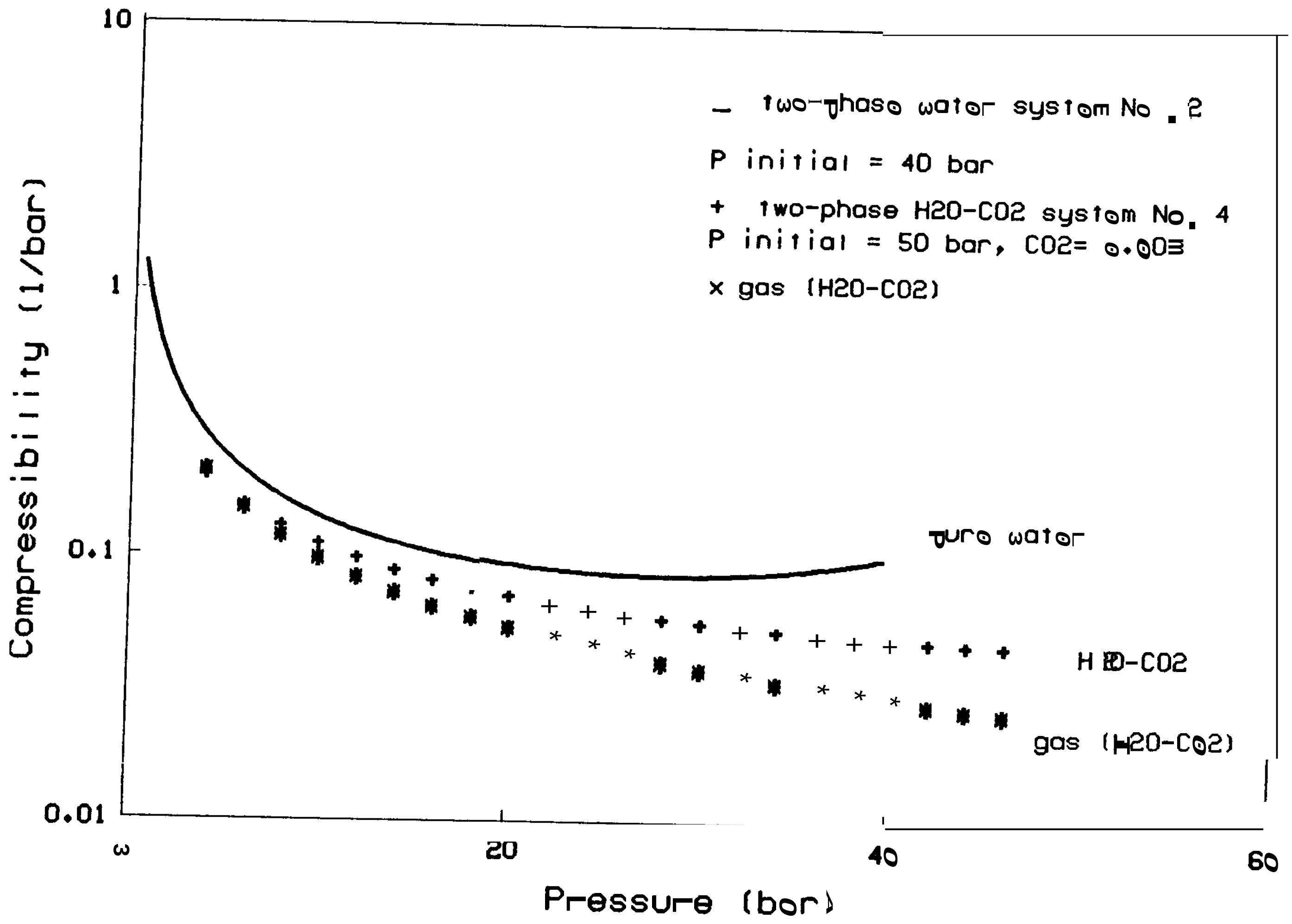


Fig. 4.15 Compressibility versus pressure a comparison of expansion compressibility and gas(steam) compressibility for water and water-carbon dioxide systems.

System No.5 -- Two-component system, adiabatic compressibility for water-carbon dioxide with an initial mole fraction CO_2 of 0.05, initial temperature of 550 °K, and initial pressure of 70 bar.

The initial amount of carbon dioxide for this case was increased from the previous case, and the effect of the increased concentration can be observed in the increased curvature of the pressure-specific molar volume graph, Fig. 4.16. A comparison of Figs. 4.13 and 4.17 reveals a decrease in separation between the two-phase compressibility and the compressibility of gas.

This system was also allowed to expand to a lower pressure showing the same type of result as the previous case (System No.4), Fig. 4.18. Quality versus pressure is shown in Fig. 4.19.

System No.6 -- Two-component methane-propane system, isothermal compressibility for initial liquid molar fraction of methane of 0.2, initial pressure 54 bar, and T = 329°K.

For this composition, values of pressure and specific molar volume were compared with experimental results from *Sage et al.* (1933), for similar conditions, Fig. 4.20. Results from the flash model compared favorably with the experimental values, specially for lower pressures. The initial value from the model and the value reported experimentally were slightly different.

The two-phase compressibility, Fig. 4.21 was larger than the gas compressibility at the same conditions, and showed a slight initial decrease followed by an increase, departing from the gas compressibility as pressure decreased. Figure 4.22 presents quality versus pressure.

System No.7 -- Two-component rnethane-propane isothermal system, for initial liquid molar fraction of methane of 0.3, and initial pressure of 51 bar, and T = 329 °K. This case was similar to the last system (System No.6). Results are presented in Figs. 4.23-4.25.

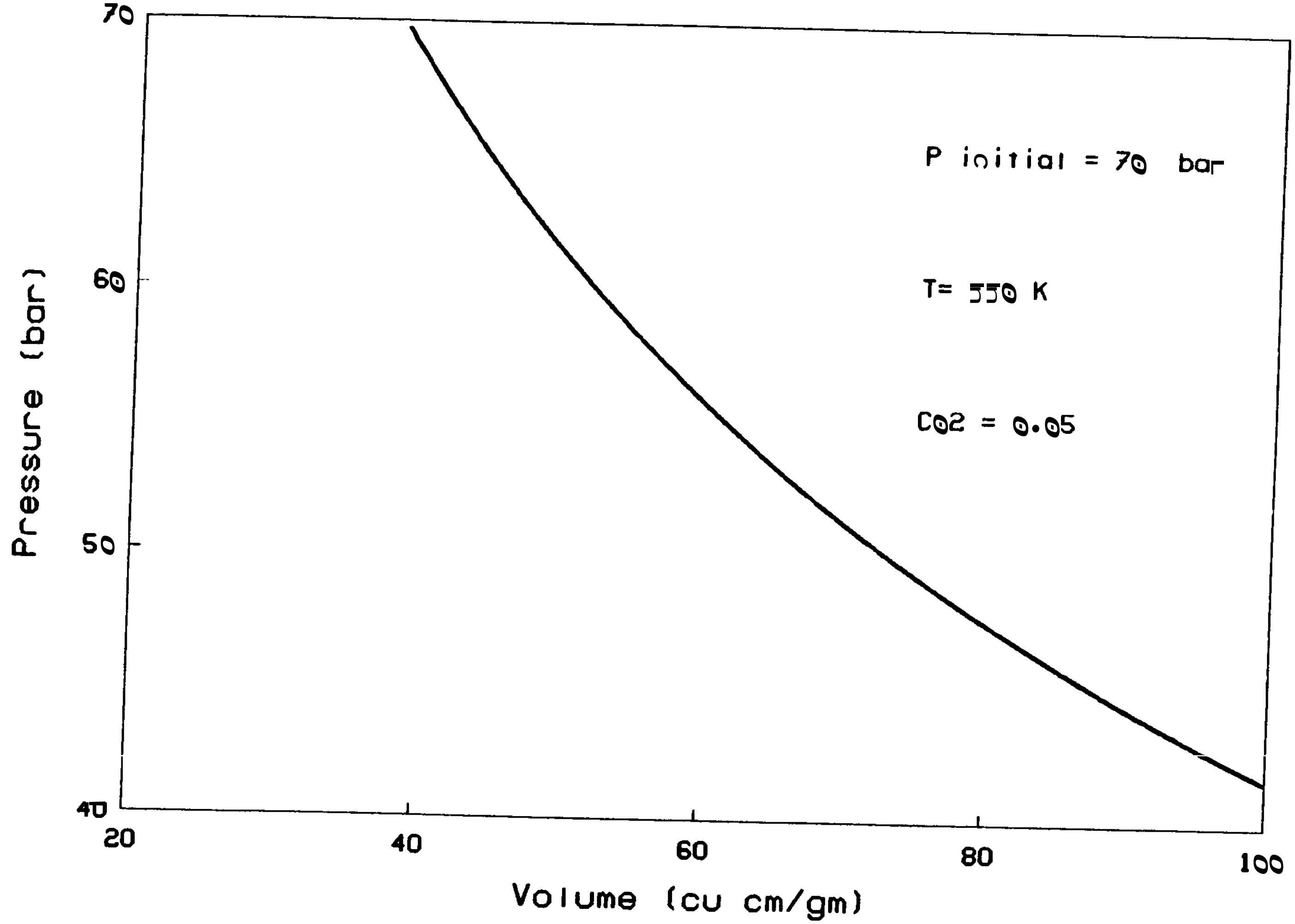


Fig. 4.16 Pressure versus Specific Volume, $H_2O - CO_2$ System No 5

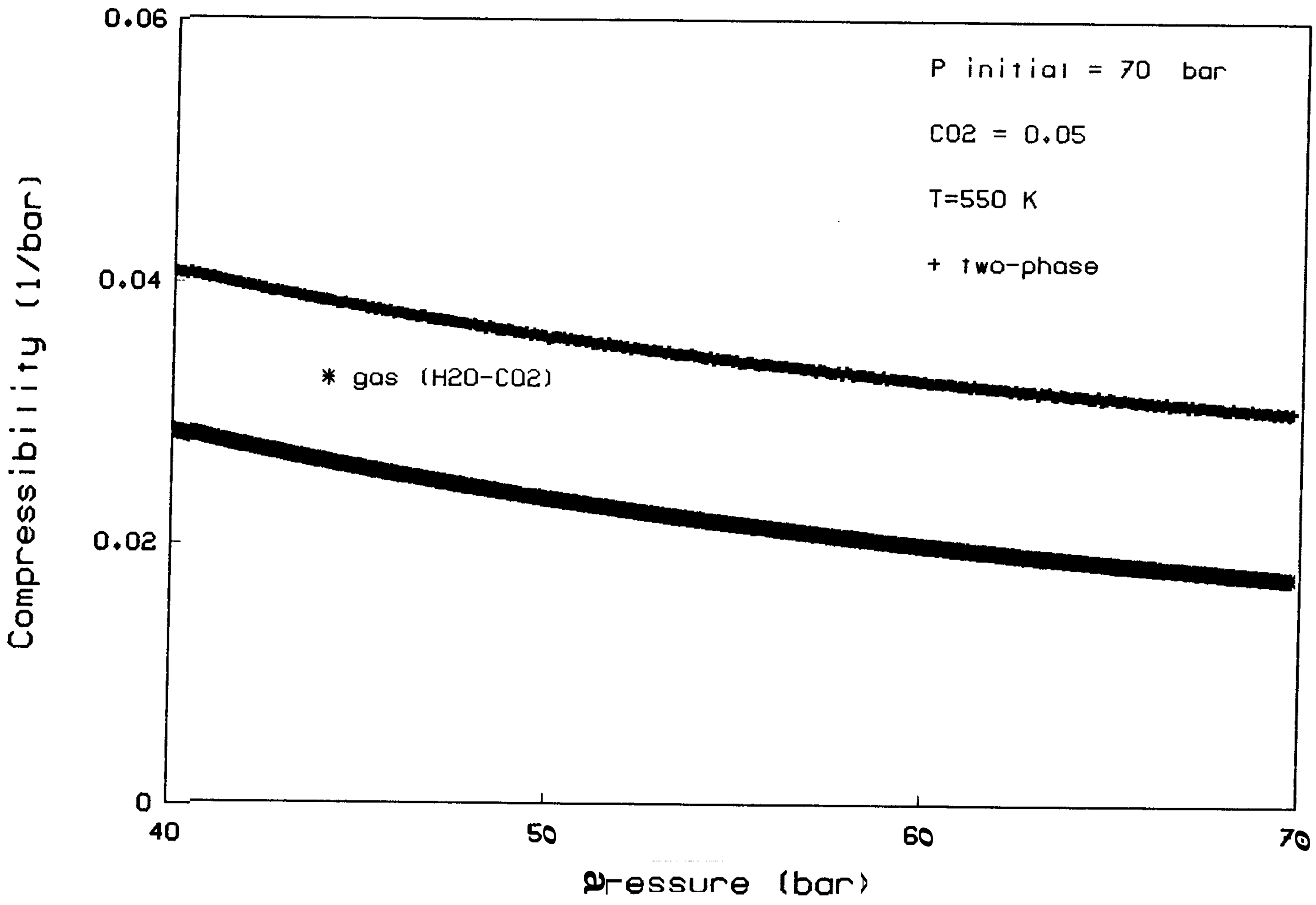


Fig. 4.17 Compressibility versus Pressure $H_2O - CO_2$ System No. 5

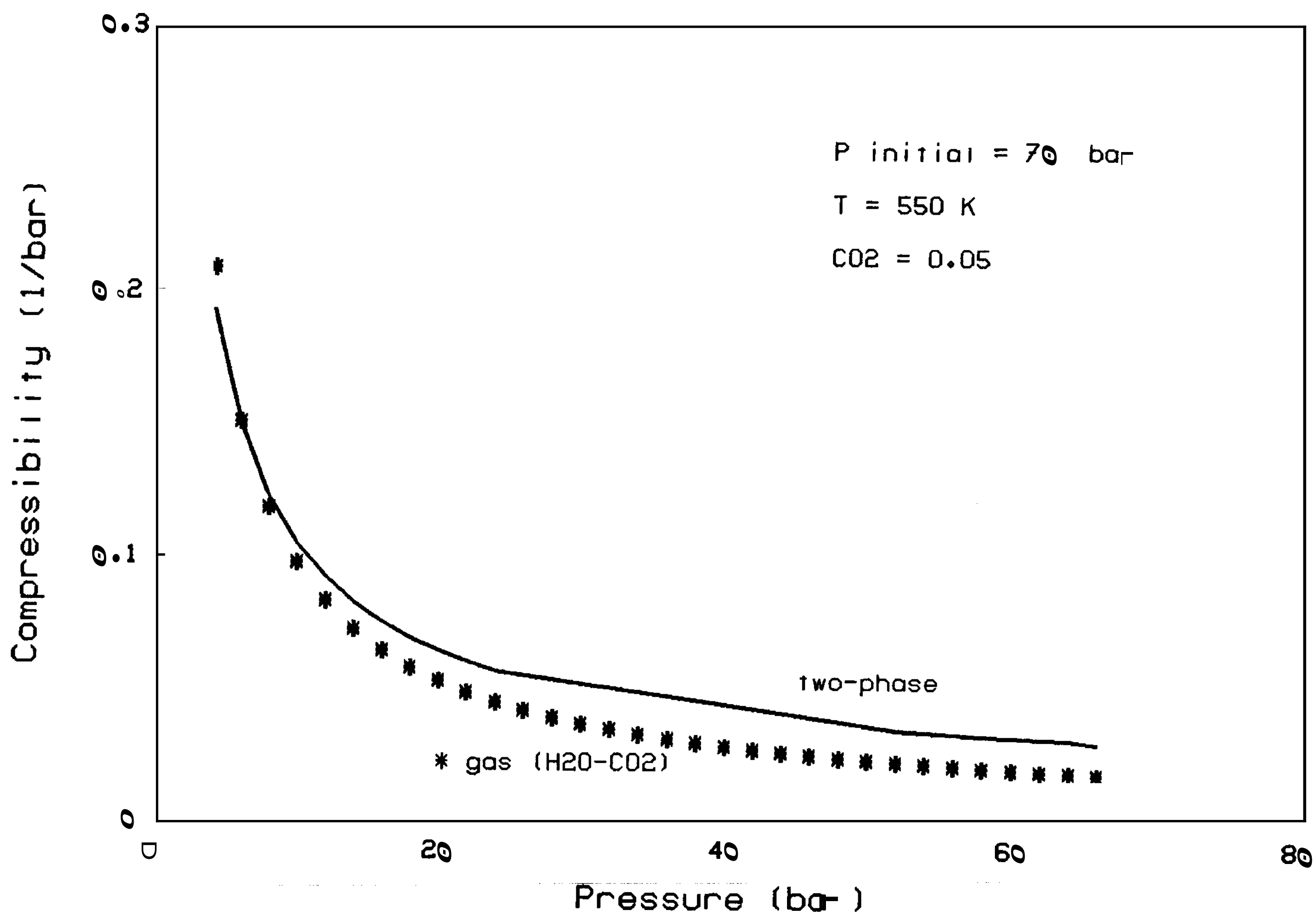


Fig. 4.18 Compressibility versus Pressure, $H_2O - CO_2$ System No. 5

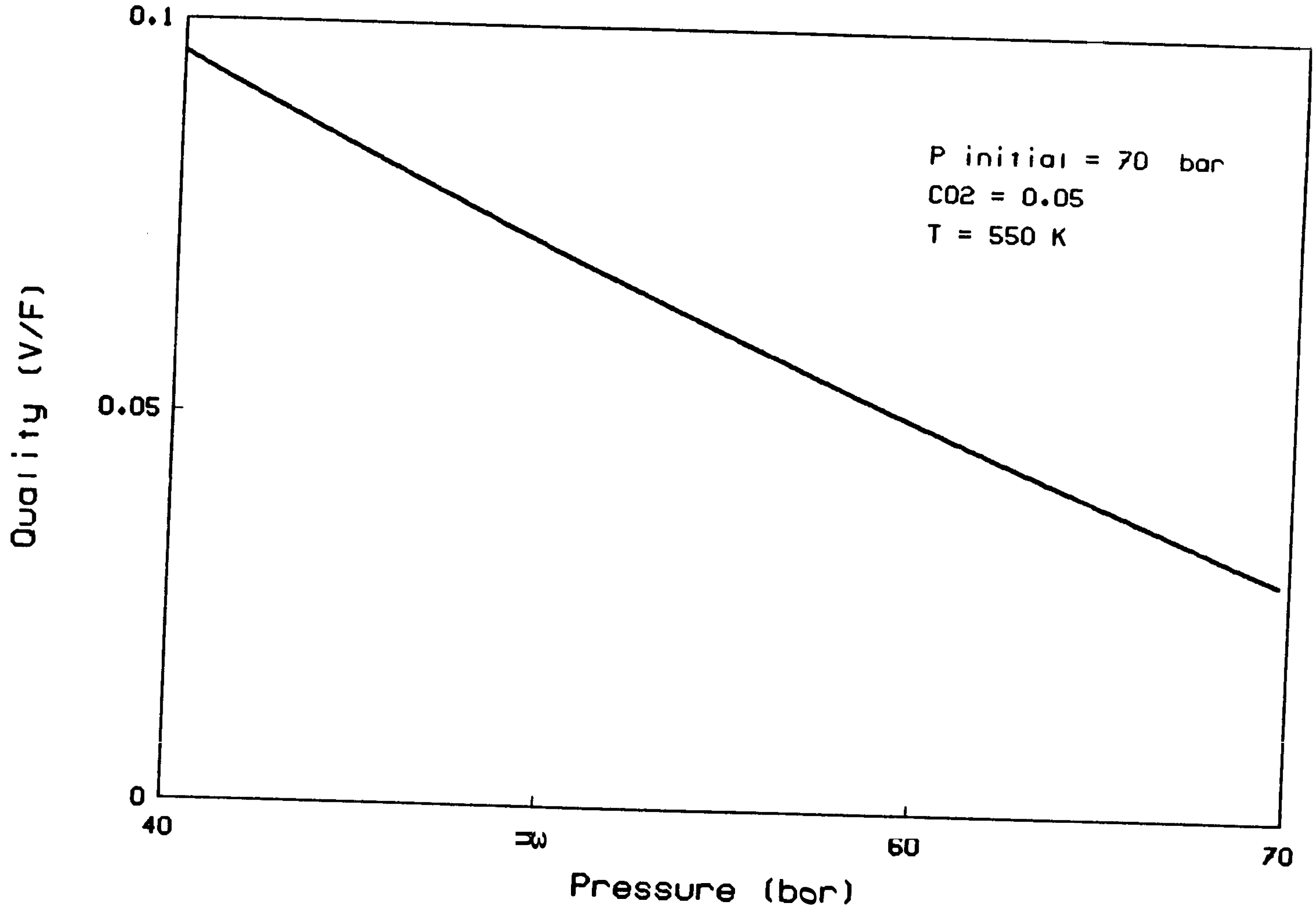


Fig. 4.19 Quality versus Pressure, $H_2O - CO_2$ System No.5

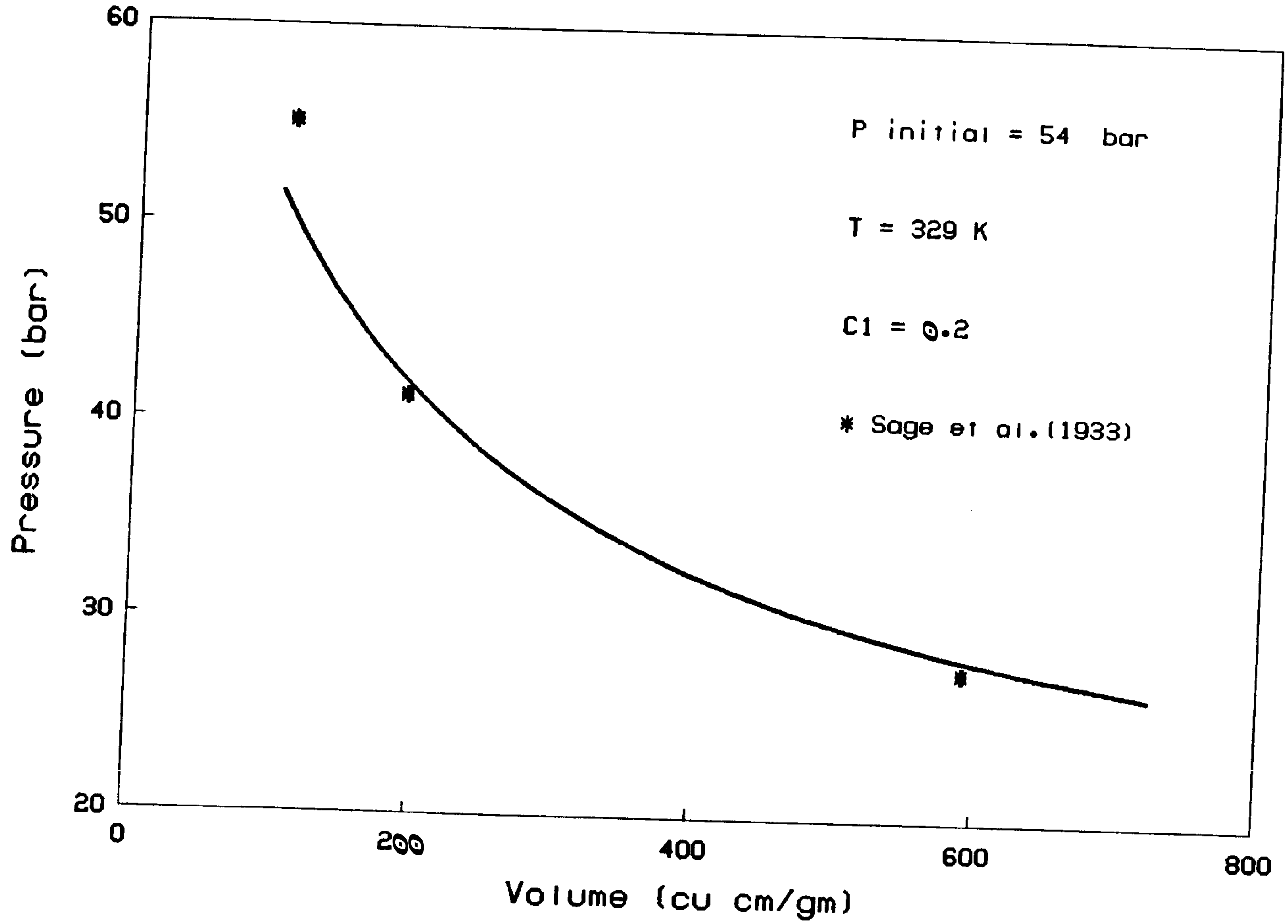


Fig. 4.20 Pressure versus Specific Volume, hydrocarbon System No. 6

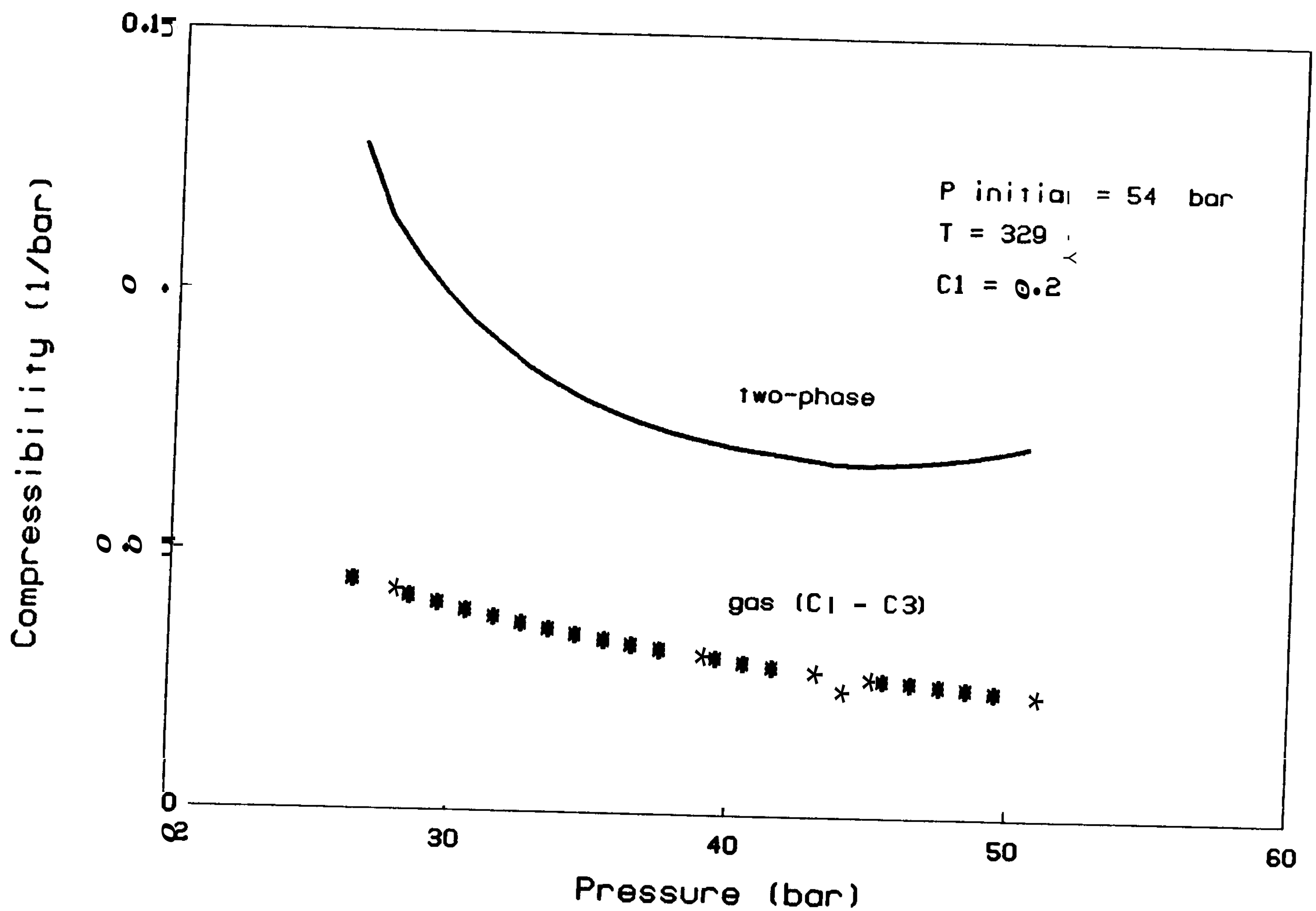


Fig. 4.21 Compressibility versus Pressure, hydrocarbon System No. 6

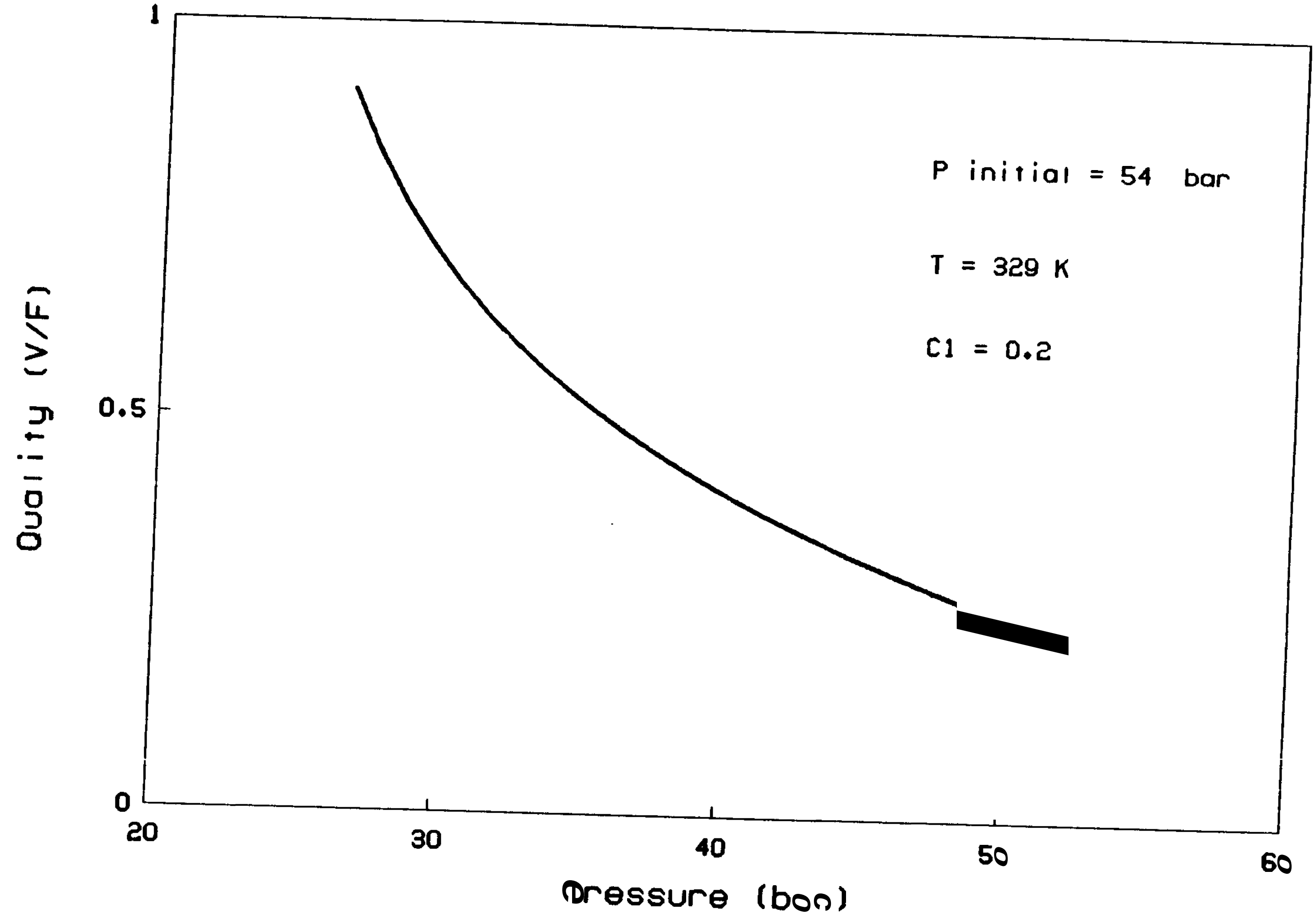


Fig. 4.22 Quality versus Pressure, hydrocarbon System No 6

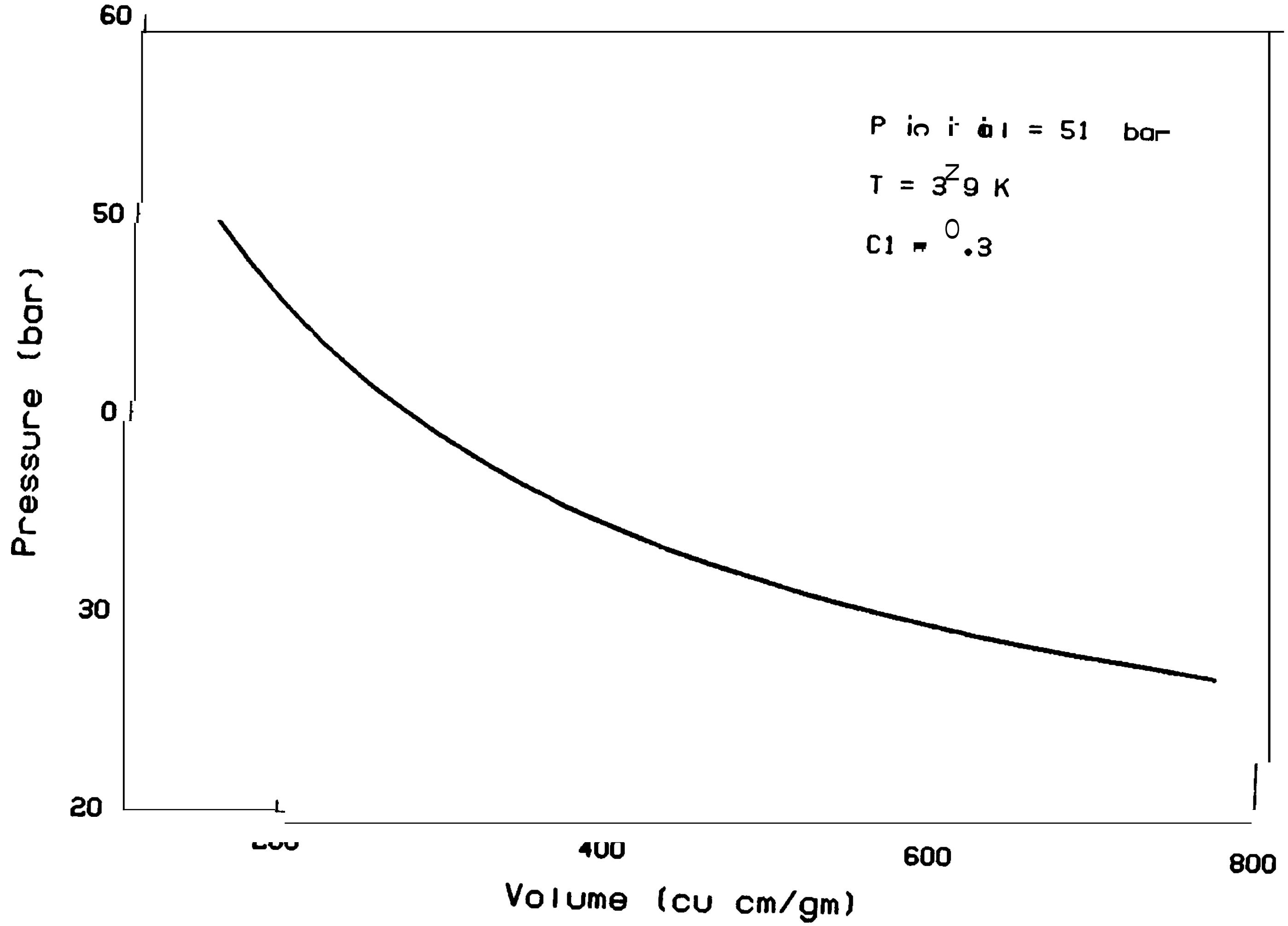


Fig. 4.23 Pressure versus Specific Volume, hydrocarbon System No. 7

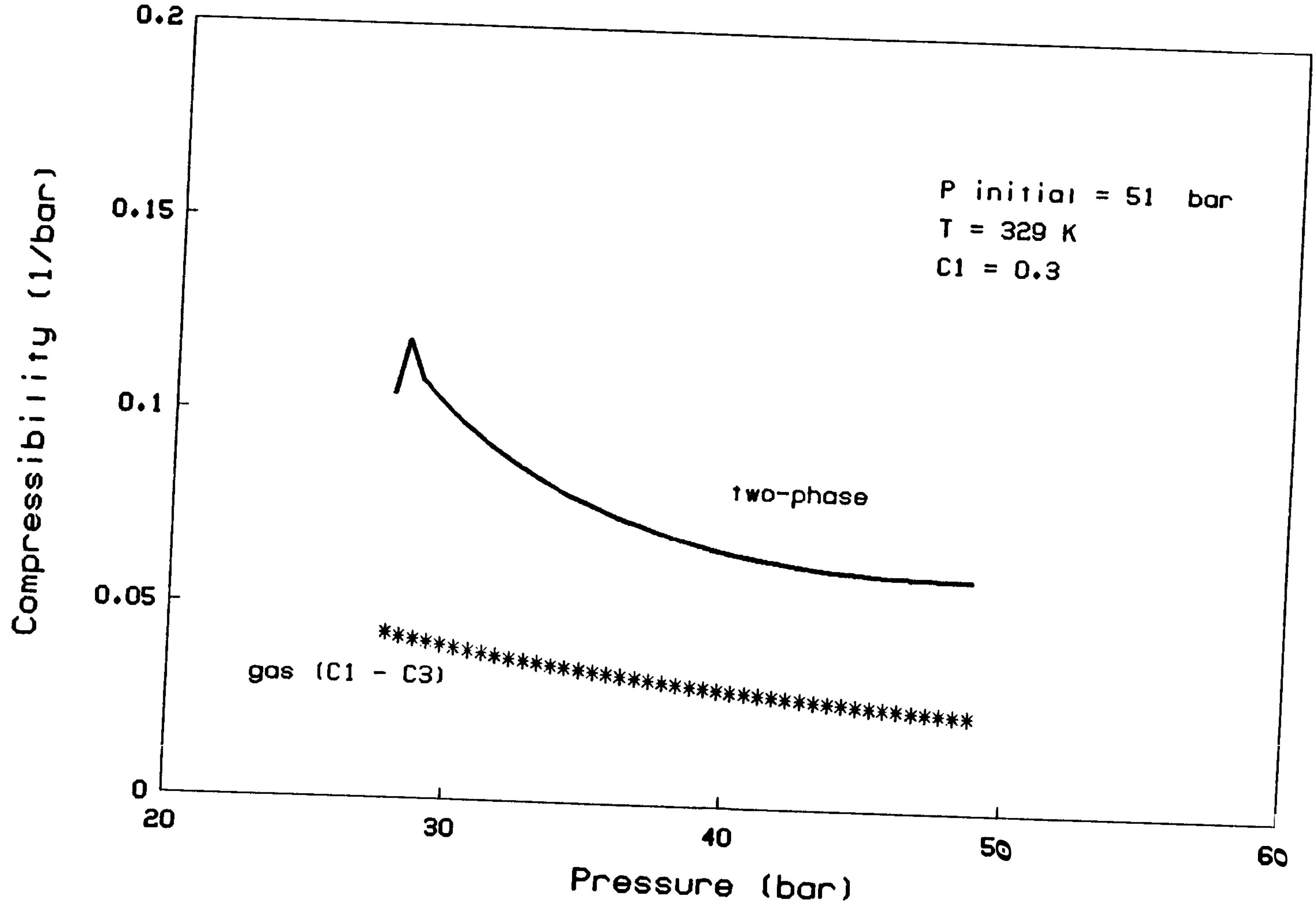


Fig. 4.24 Compressibility versus Pressure, hydrocarbon System No. 7

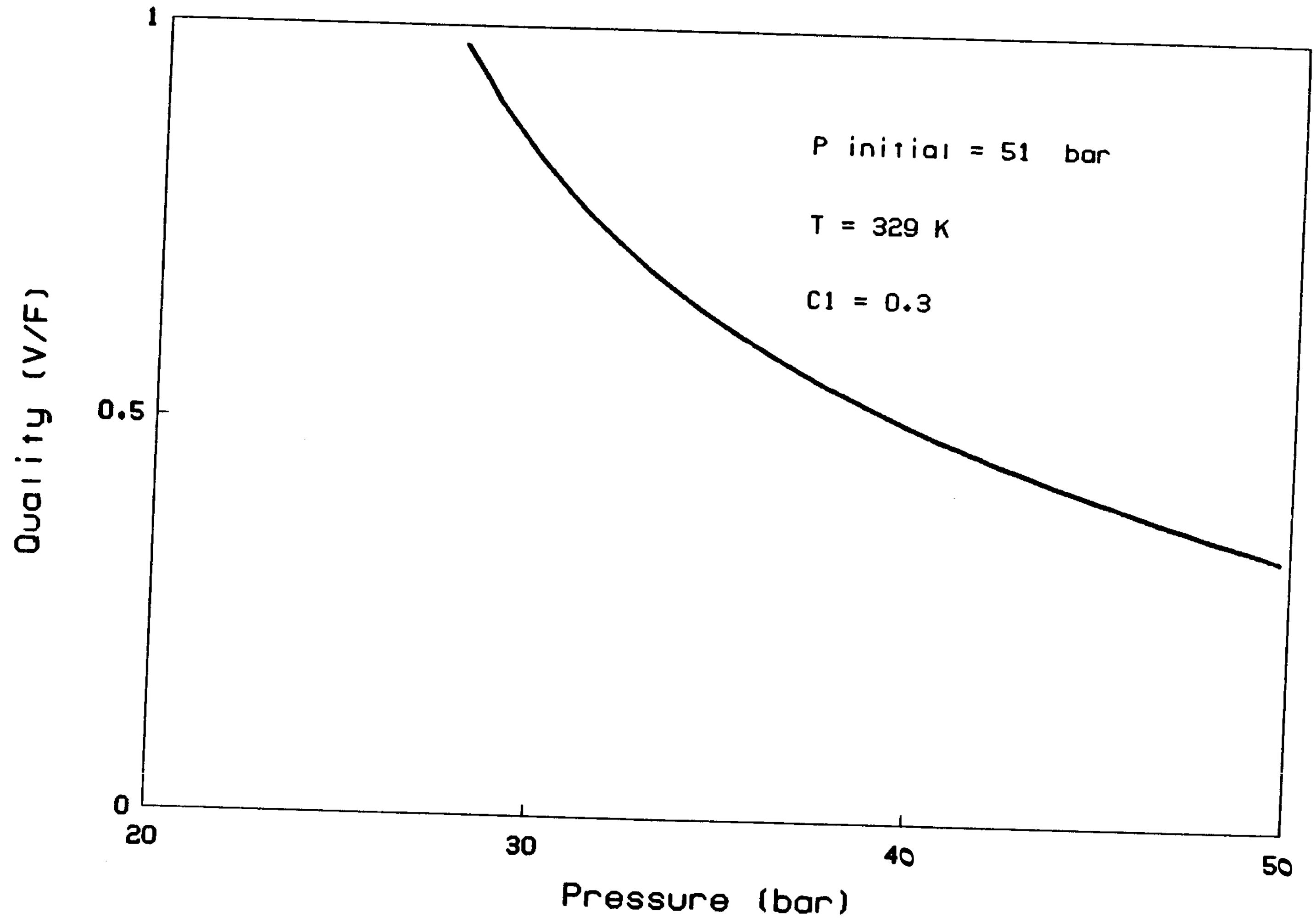


Fig. 4.25 Quality versus Pressure, hydrocarbon System No.7

System **No.8** -- Four-component hydrocarbon isothermal system, initial liquid molar fractions: $nC_4 = 0.25$, and $iC_4 = 0.15$, $nC_5 = 0.10$, and $C_{10} = 0.50$, and $P_{initial} = 15$ **bar,** $T = 470\,°K$. The results for this case are presented in Figs. 4.26-4.28. The pressure versus specific molar volume for this system shows an initial drop in pressure with volume that is fairly steep, followed by a flattening of the curve as pressure decreases. The compressibility of the gas phase is smaller than the compressibility of the two phases for the entire pressure interval.

System No.9 -- Seven-component hydrocarbon isothermal system, liquid composition mole fractions **of:**

$$C_1 = 0.040,\ C_2 = 0.043.\ C_3 = 0.041,\ C_4 = 0.028,\ C_5 = 0.017$$
$$C_6 = 0.229,\ C_7 = 0.602$$

initial pressure of 50 bar, and $T = 377°K$.

The results are presented in Figs. 4.29-4.31. The pressure vs. specific molar volume isotherm for this system shows behavior typical of a multicomponent system (Fig. 4.29). The compressibility of the two phases remains larger than the compressibility of the gaseous phase €or the pressure range considered (Fig. 4.30). As before, the two compressibilities differ more in the high pressure, low quality range than at the low pressure, high quality range. The change in quality with respect to pressure follows an almost linear trend for the pressure interval considered (*Fig.* 4.31).

System **No.** 10 – Seven-component hydrocarbon isothermal system, liquid composition mole fractions of

$$C_1 = 0.040,\ C_2 = 0.043,\ C_3 = 0.041,\ C_4 = 0.028,\ C_5 = 0.017$$
$$C_6 = 0.229,\ C_7 = 0.602$$

initial pressure **of 35** bar, and $T = 500°K$.

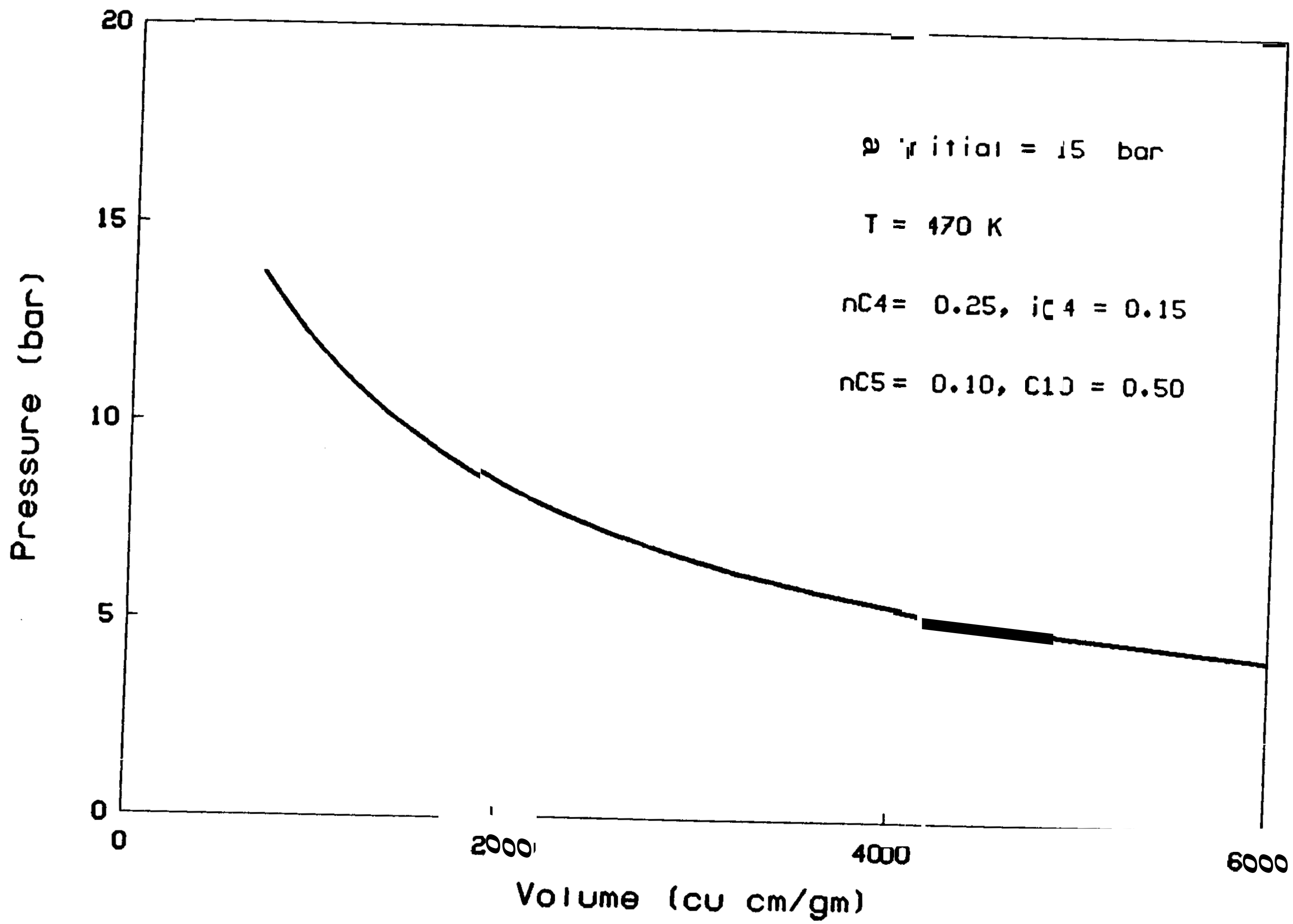


Fig. 4.26 Pressure versus Specific Volume, hydrocarbon System No. 8

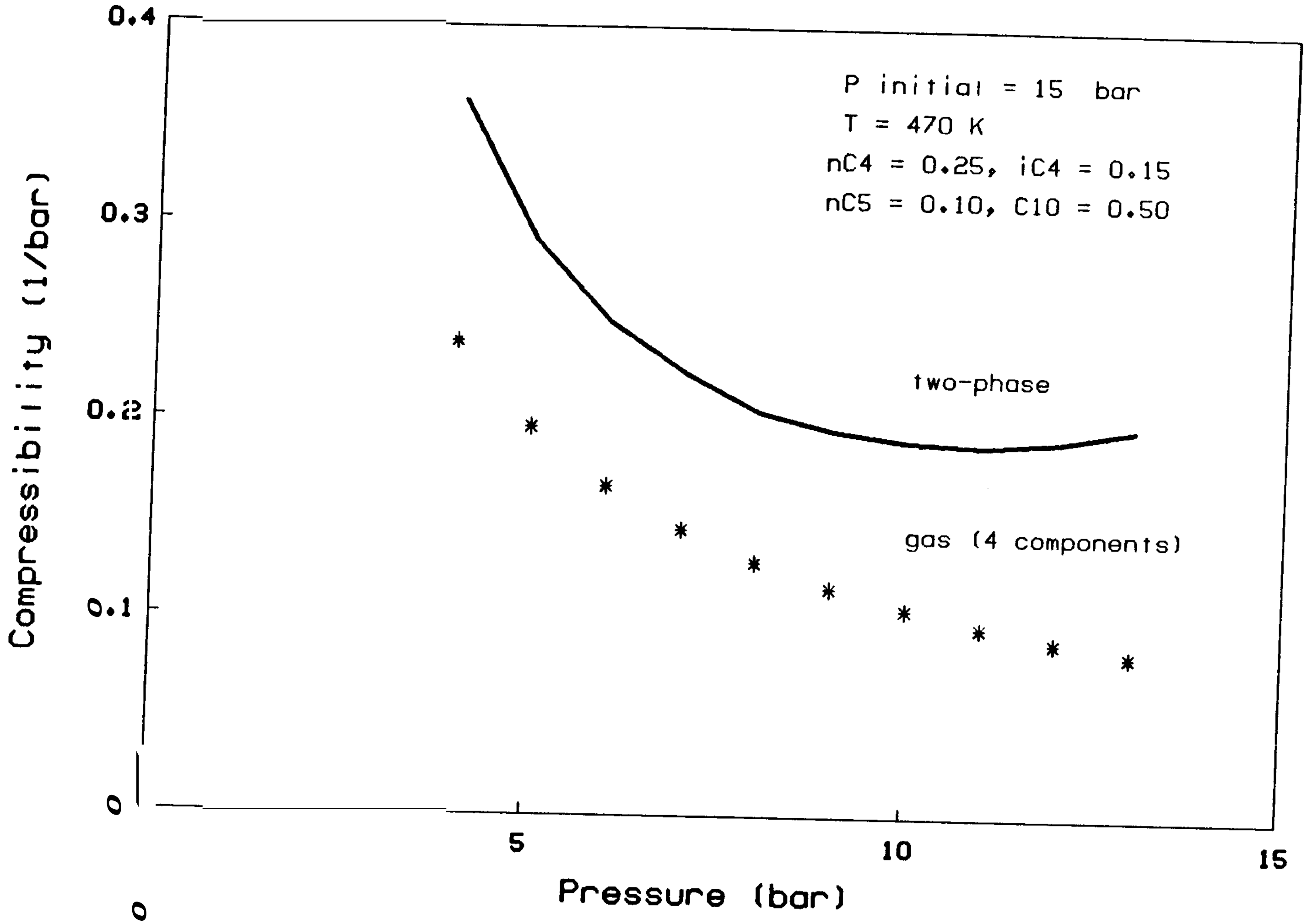


Fig. 4.27 Compressibility versus Pressure, Hydrocarbom System No 8

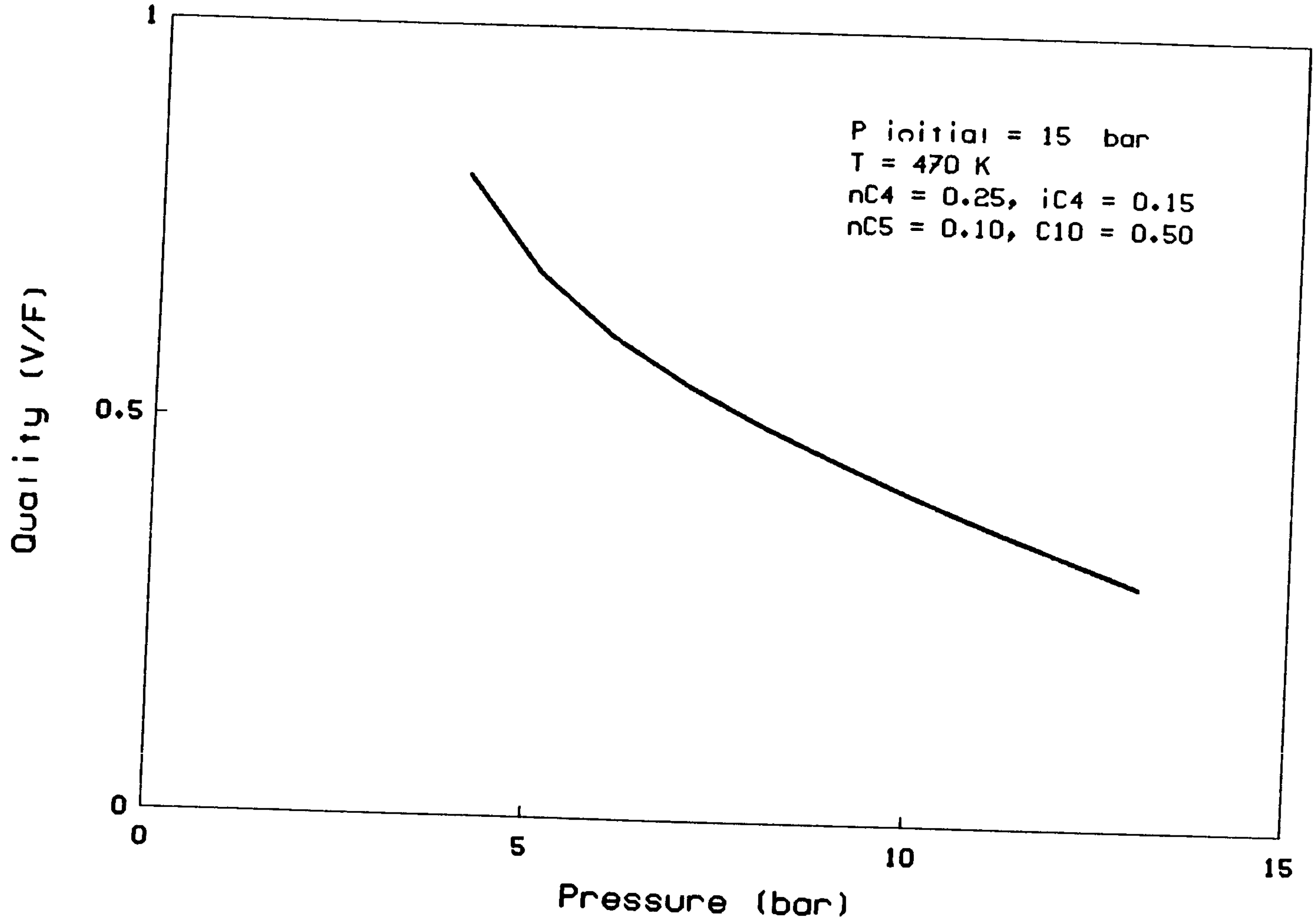


Fig 4.28 Quality versus Pressure, hydrocarbon System No.8

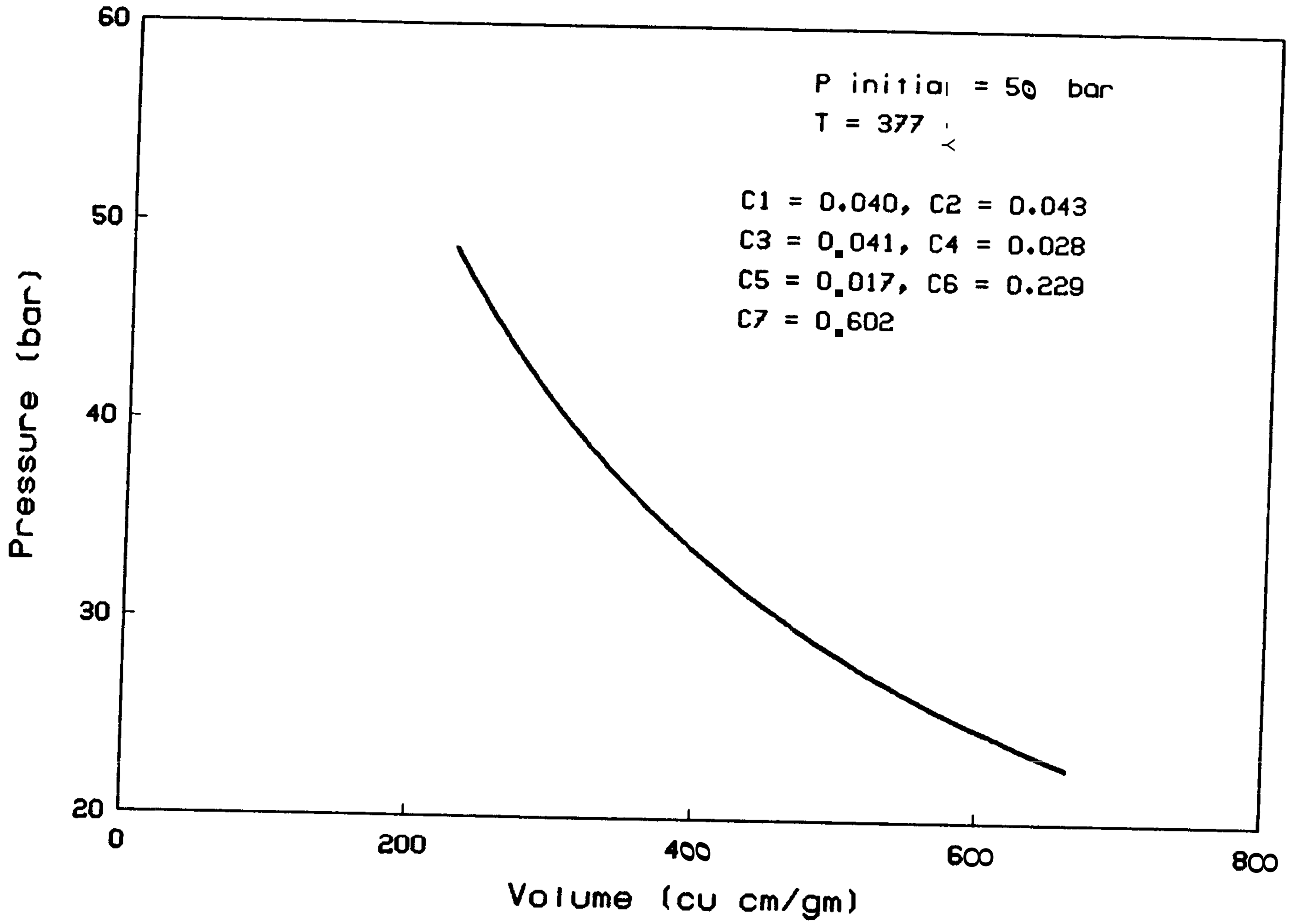


Fig. 4.29 Pressure versus Specific Volume, hydrocarbon System No 9

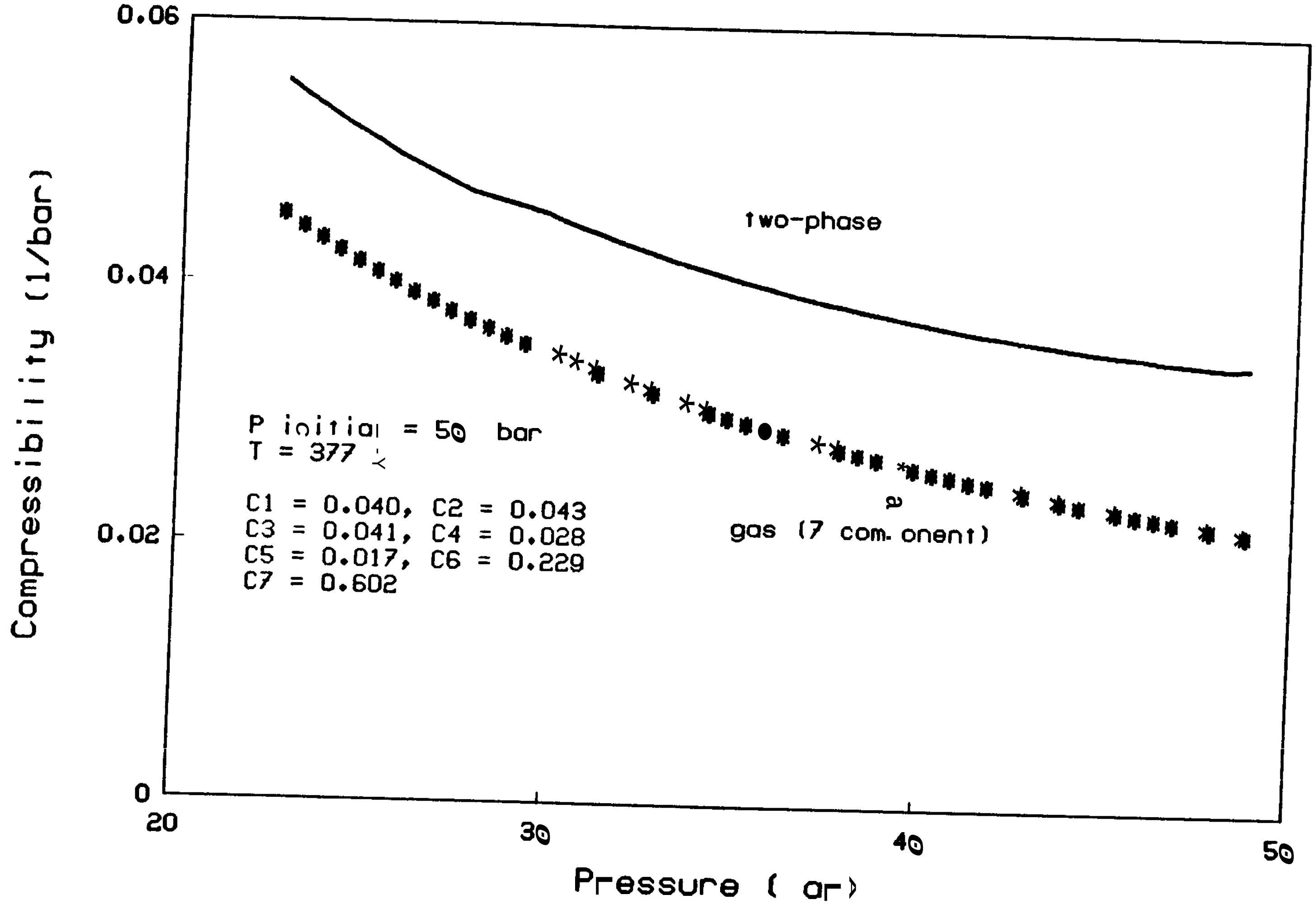


Fig. 4.30 Compressibility versus Pressure, hydrocarbon System No 9

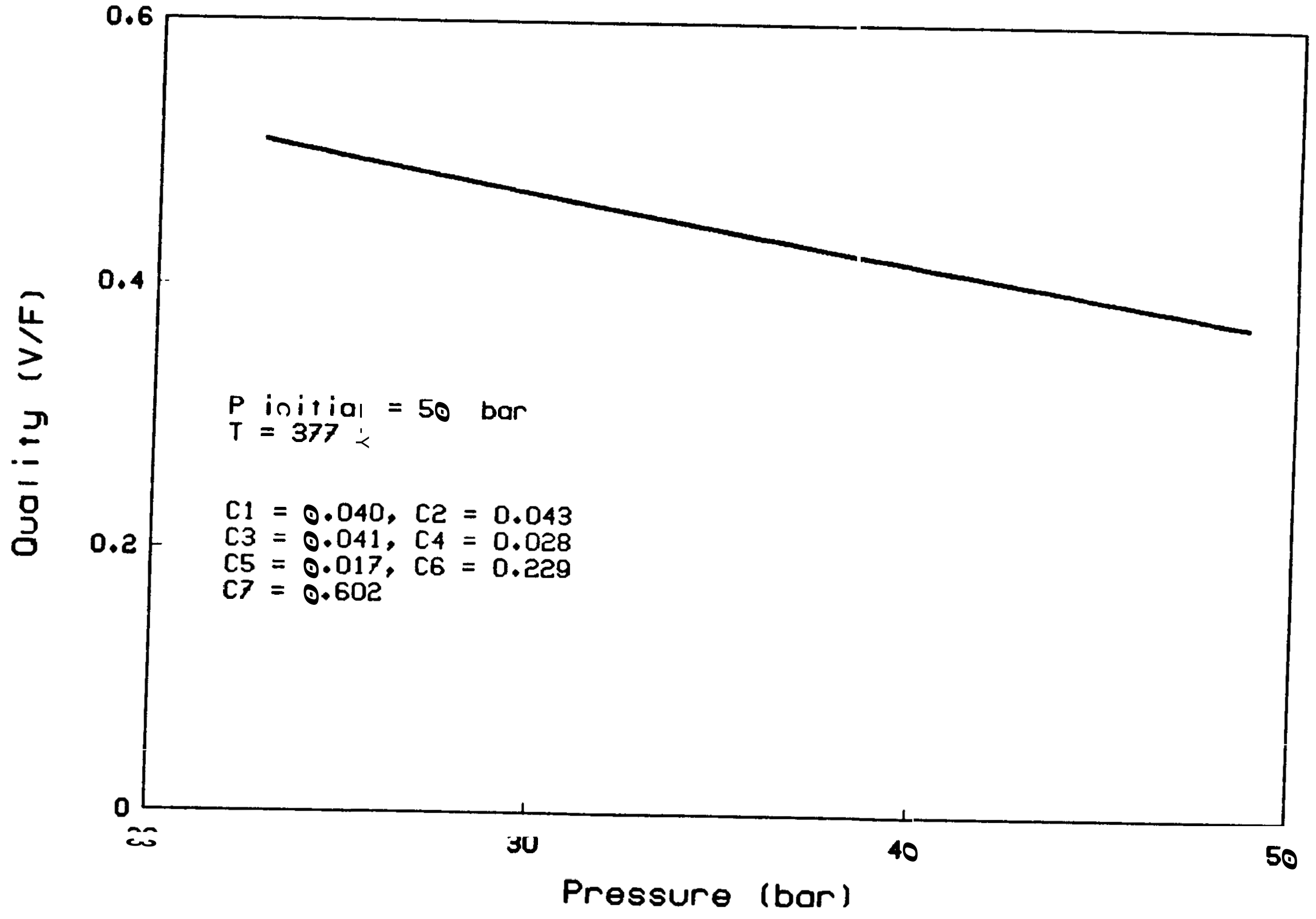


Fig. 4.31 Quality versus Pressure, hydrocarbon System No 9

The results for this case are presented in Figs. **4.32-4.34.** The pressure-specific molar volume isotherm showed a steep initial decline which changes to a flattening of the curve for the lower pressures considered (Fig. **4.32).** The two-phase compressibility showed an initial high value, followed by a sharp decline and then leveling **off,** proceeding to a slight increase towards the lower pressure values. The two-phase compressibility was **larger** than the compressibility of gas, showing a decline in the separation between the two compressibilities (Fig. **4.33).** The quality change with pressure was initially flat, followed by rise in value as the pressure declined (Fig. **4.34).**

System No. 11 -- Eight-component water-hydrocarbon isothermal system, liquid composition mole fractions of:

$$C_1 = 0.340,\ C_2 = 0.043,\ C_3 = 0.041,\ C_4 = 0.028,\ C_5 = 0.017$$
$$C_6 = 0.029,\ C_7 = 0.302,\ H_2O = 0.200$$

initial pressure of **35** bar, **and** $T = 311°K$.

This system is similar in composition to System No. 9 for seven hydrocarbon components. As before, the pressure-specific molar volume (Fig. **4.35)** isotherm behaves similarly to the previous systems. The same can be said for a comparison **of** the compressibility **of** the two phases and the **gas** compressibility. The compressibility of the two-phases is larger than the gas compressibility for the pressure range considered **(Fig. 4.36).** The quality change with pressure is linear as **was** the case in System No. 10 **{Fig. 4.37).**

System No. 12 -- Eight-component hydrocarbon-water isothermal system, liquid composition mole fractions of:

$$C_1 = 0.340,\ C_2 = 0.043,\ C_3 = 0.041,\ C_4 = 0.028,\ C_5 = 0.017$$
$$C_6 = 0.029,\ C_7 = 0.402,\ H_2O = 0.1$$

initial pressure of **35** bar, and $T = 311$ "K.

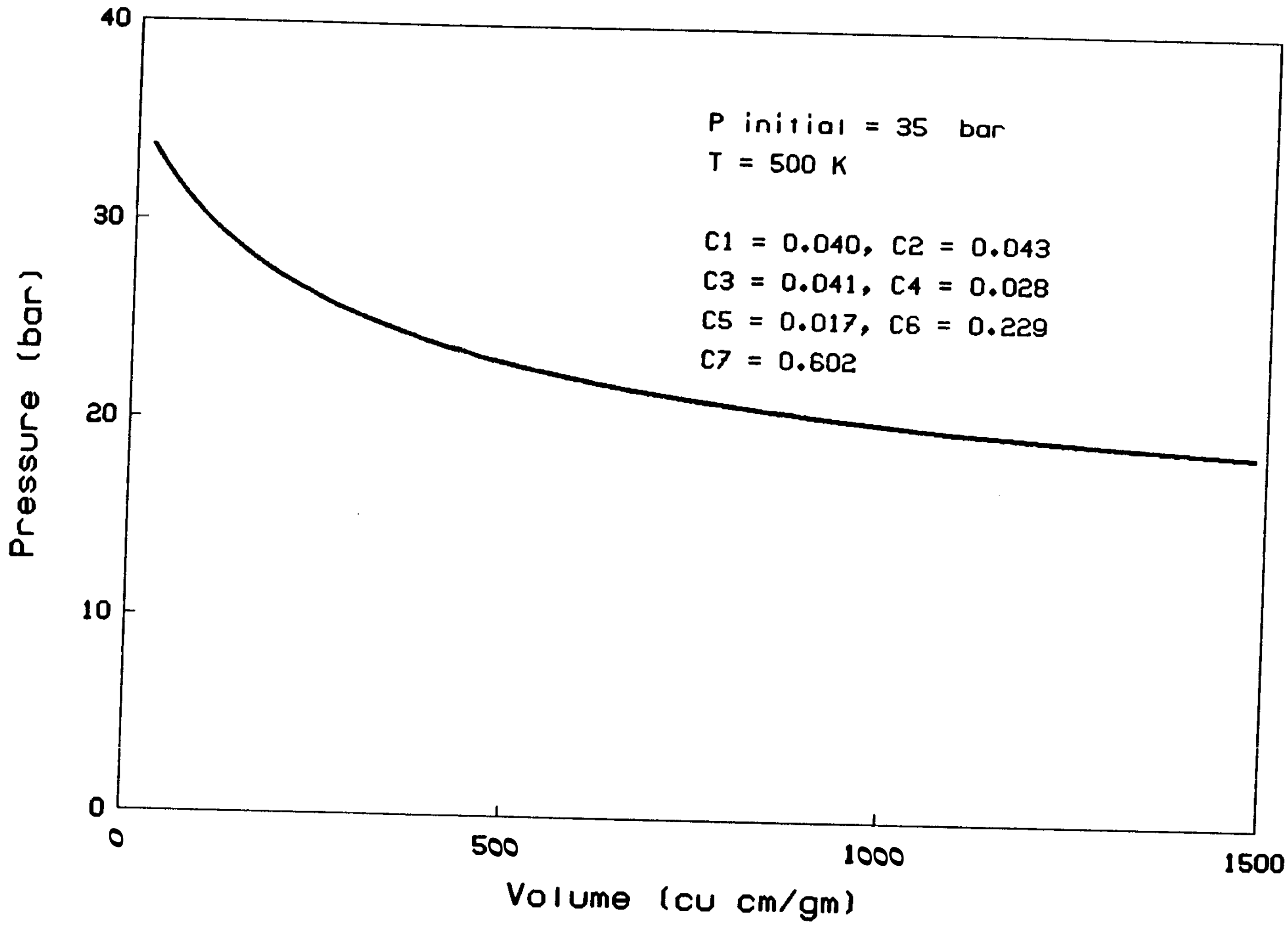


Fig. 4.32 Pressure versus Specific Volume, hydrocarbon System No 10

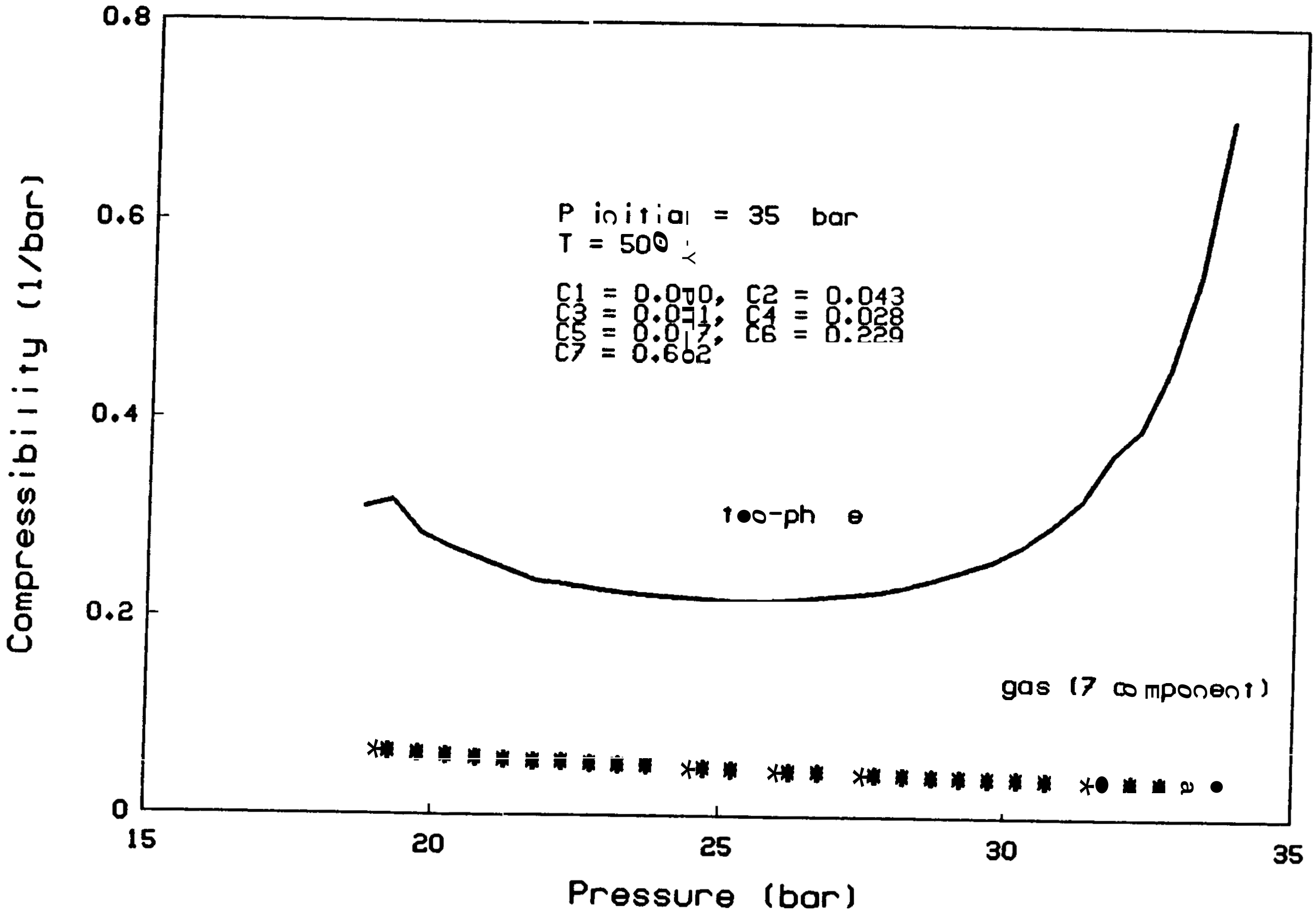


Fig. 4.33 Compressibility versus Pressure, hydrocarbon System No. 10

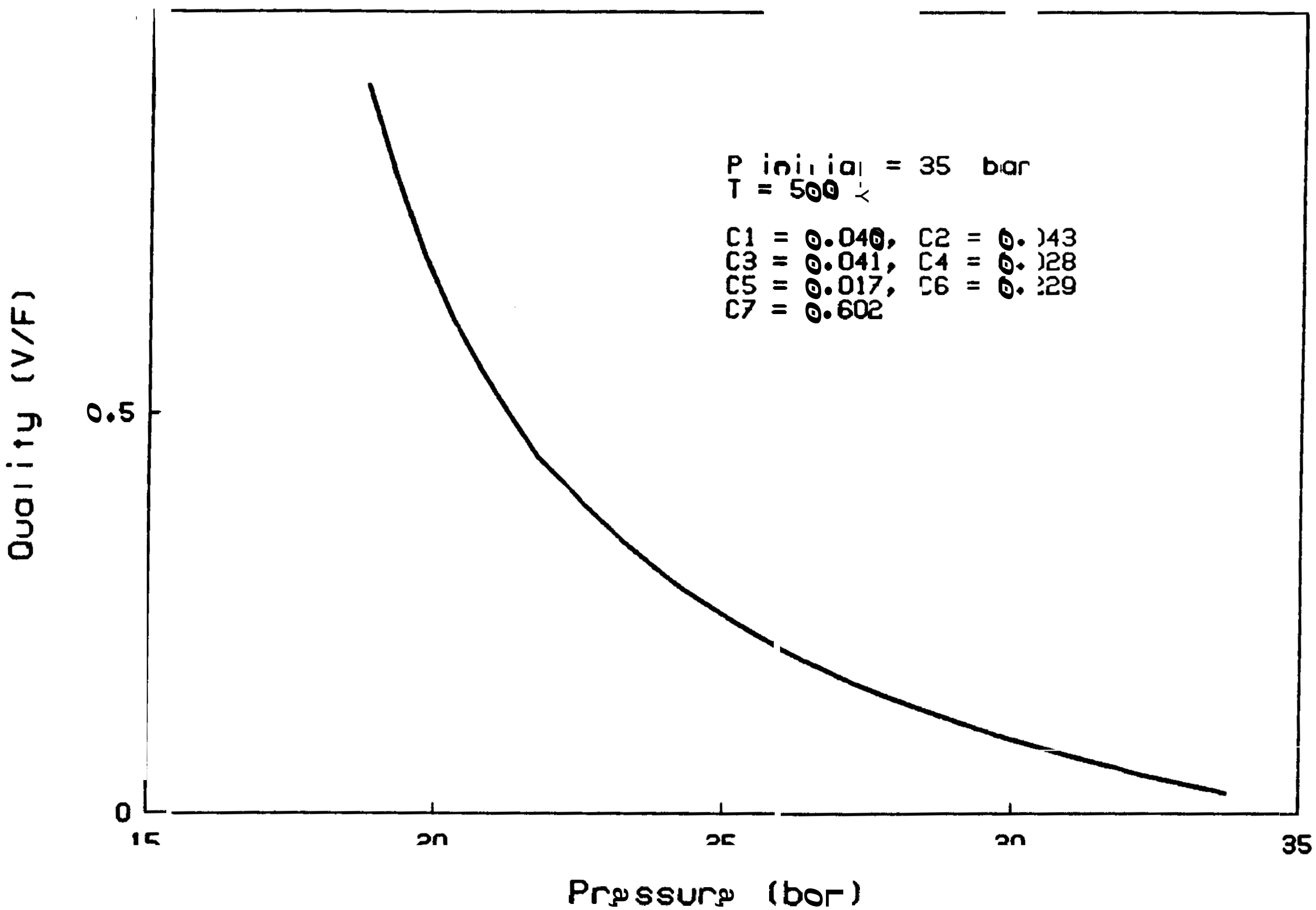


Fig. 4.34 Quality versus Pressure, hydrocarbon System No.10

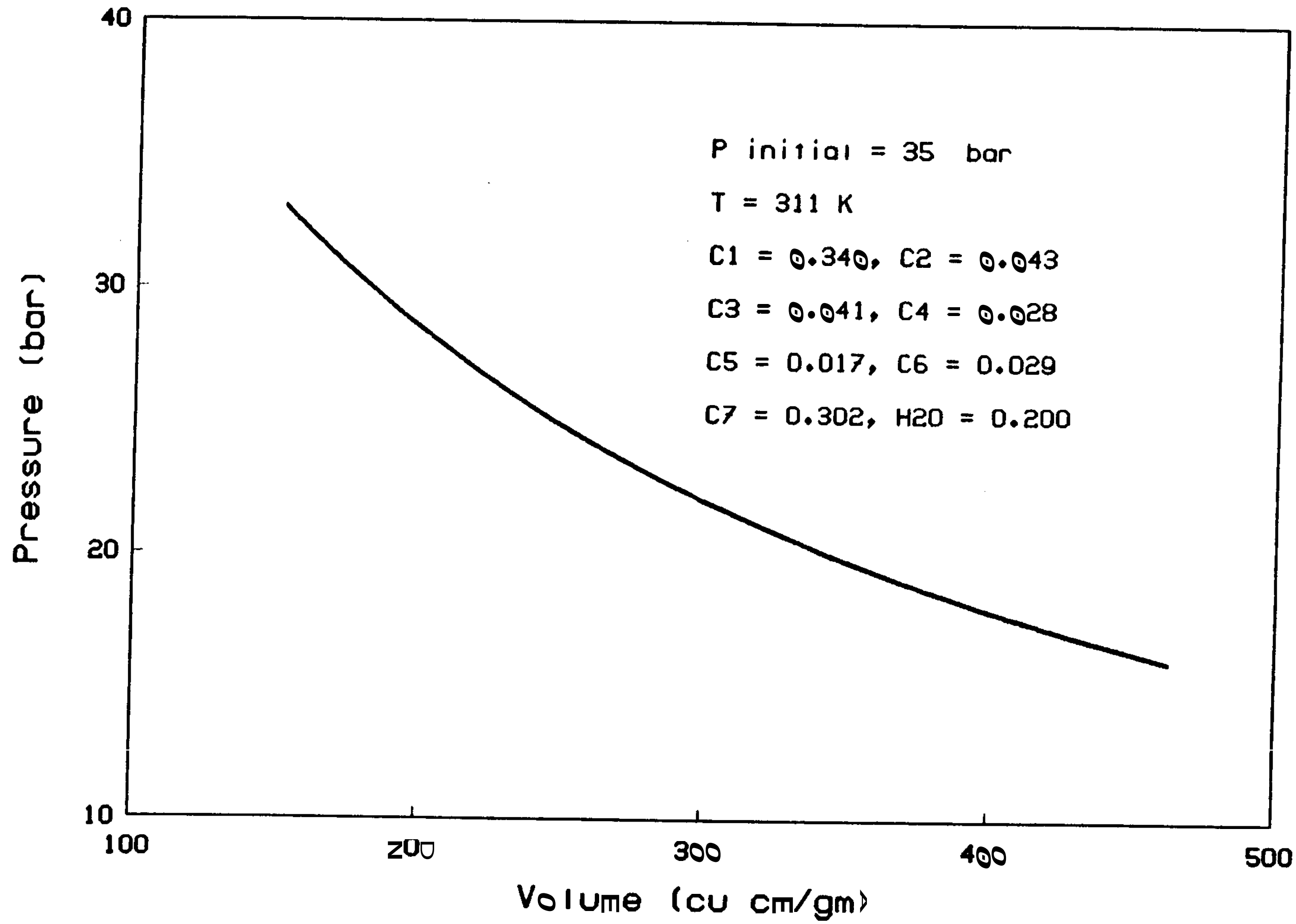


Fig. 4.35 Pressure versus Specific Volume, hydrocarbon System No 11

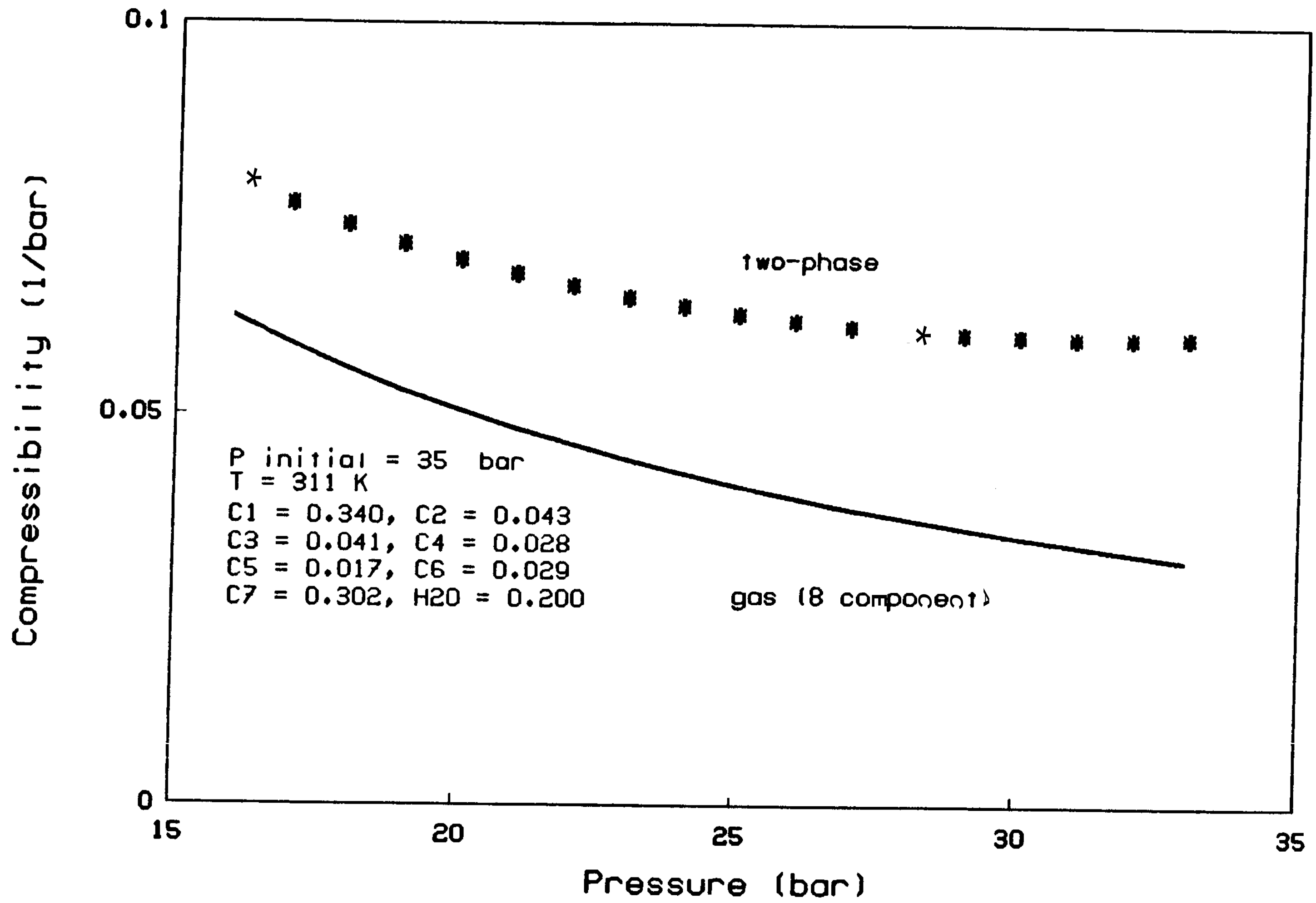


Fig. 4.36 Compressibility versus Pressure, hydrocarbon System No 11

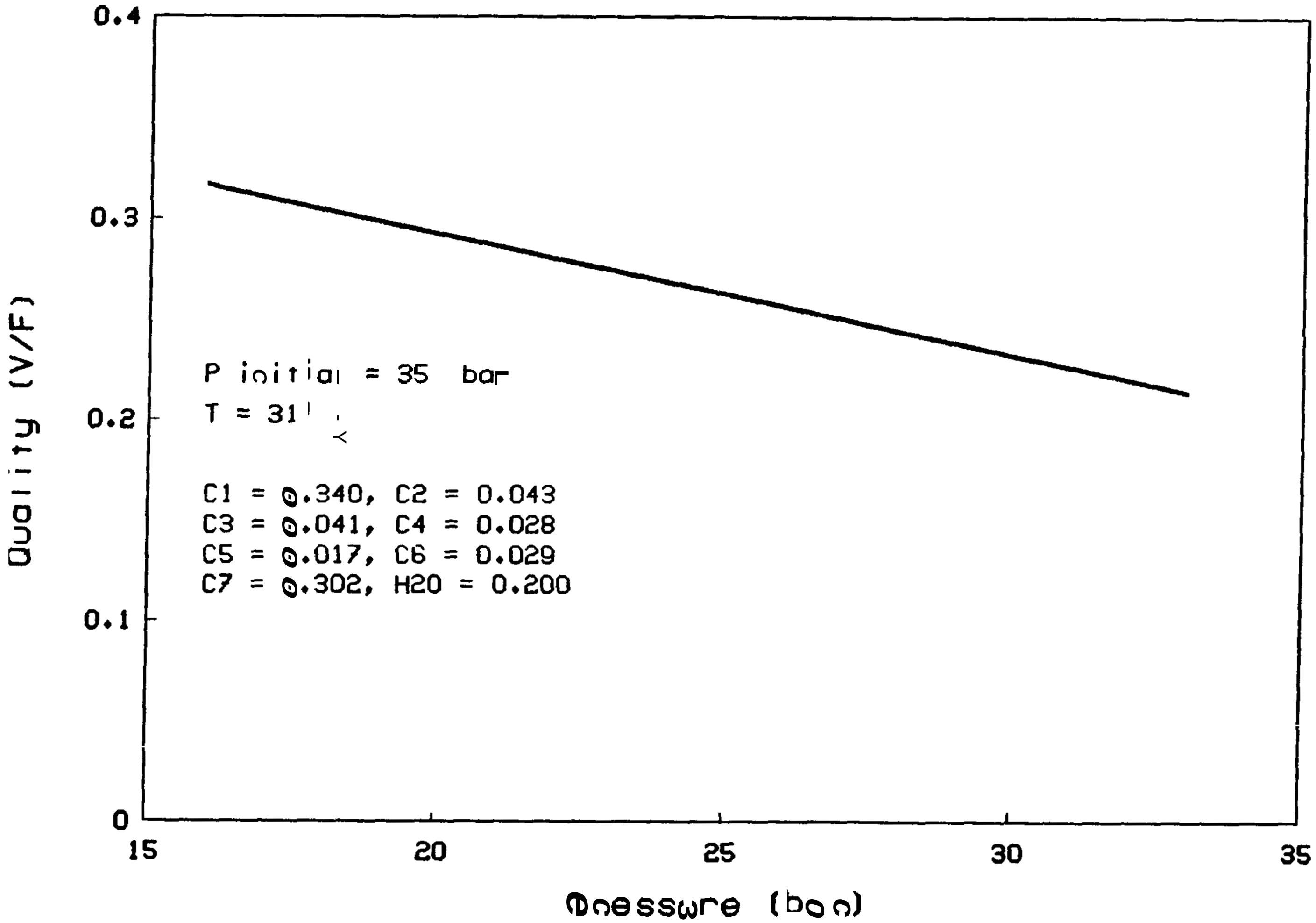


Fig. 4.37 Quality versus Pressure, hydrocarbon System No.11

The amount of water was decreased, and the quantity of C_7 was increased by the same amount, to fabricate a system that behaved essentially in the same manner as System No.11, and having also a two-phase compressibility larger than the compressibility of the gas for the pressure and temperature range considered (Figs. 4.38-4.40).

System **No.13** -- Eight-component hydrocarbon-water isolhermal system, liquid composition:

$$C_1 = 0.440,\ C_2 = 0.043,\ C_3 = 0.041,\ C_4 = 0.028,\ C_5 = 0.017$$
$$C_6 = 0.029.\ C_7 = 0.302,\ H_2O = 0.1$$

initial pressure of 35 bar, and $T = 311\,°K$.

The quantity of C_1 was increased by the same amount as the decrease of the C_7 from the previous system No.12. As before, this system had a behavior similar to the previous cases, the main difference being: in the value of compressibility, which was lower than the previous case. The quality was larger than the quality in the other systems (Figs. 4.41-4.43).

Systems **1-13** have considered only fluid expansion with no heat contribution from porous medium. In the following, we consider the effect of the production mode on the system effective compressibility.

4.2. PRODUCTION COMPRESSIBILITY

In order to consider the effect of production on effective compressibility, excluding the expansion term, two production modes were considered:

(a) gas (high enthalpy) production, and

(b) production of liquid and gas according to relative permeability relationships.

We will consider rock heat effects for these cases.

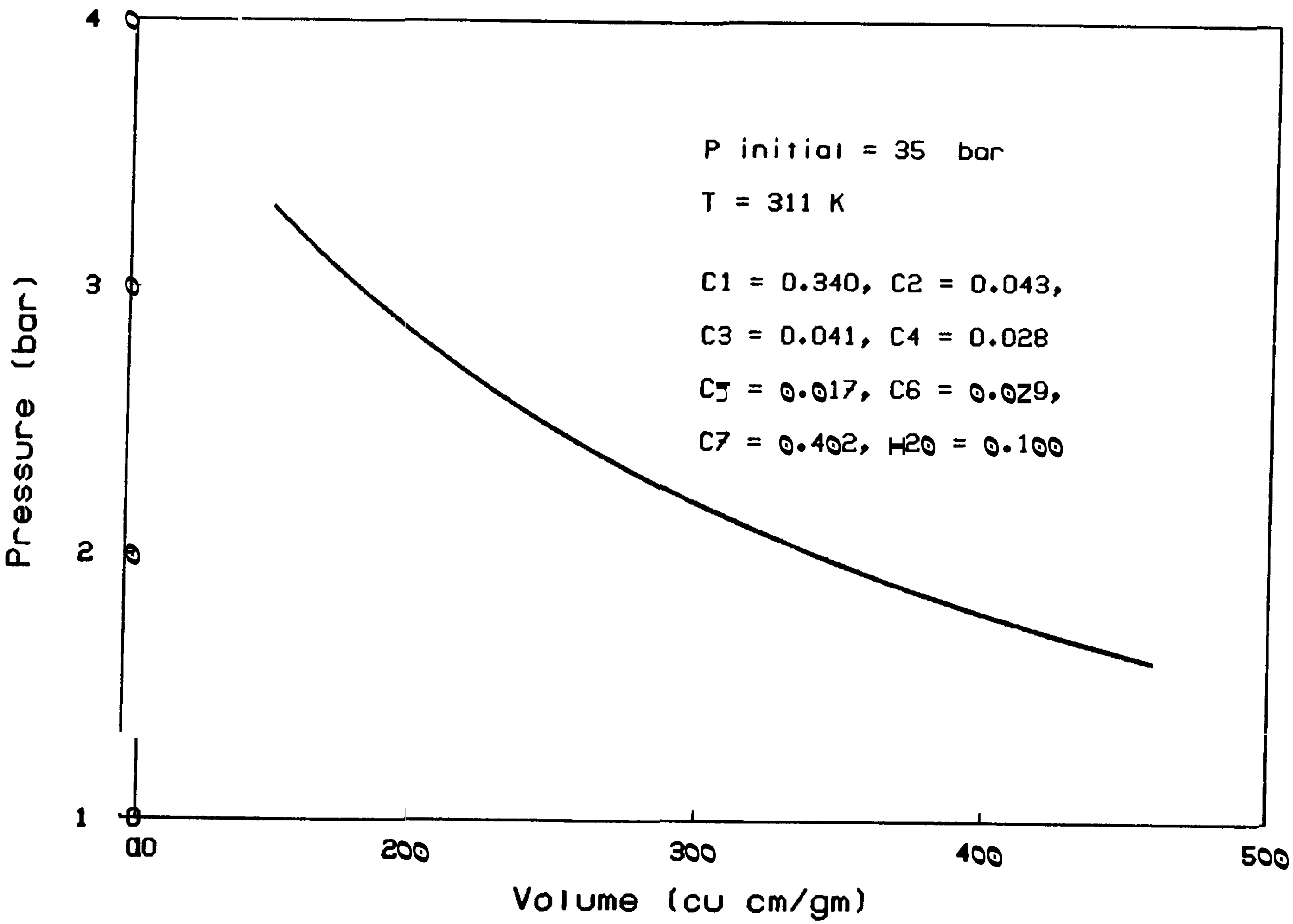


Fig. 4.38 Pressure versus Specific Volume, hydrocarbon System No. 12

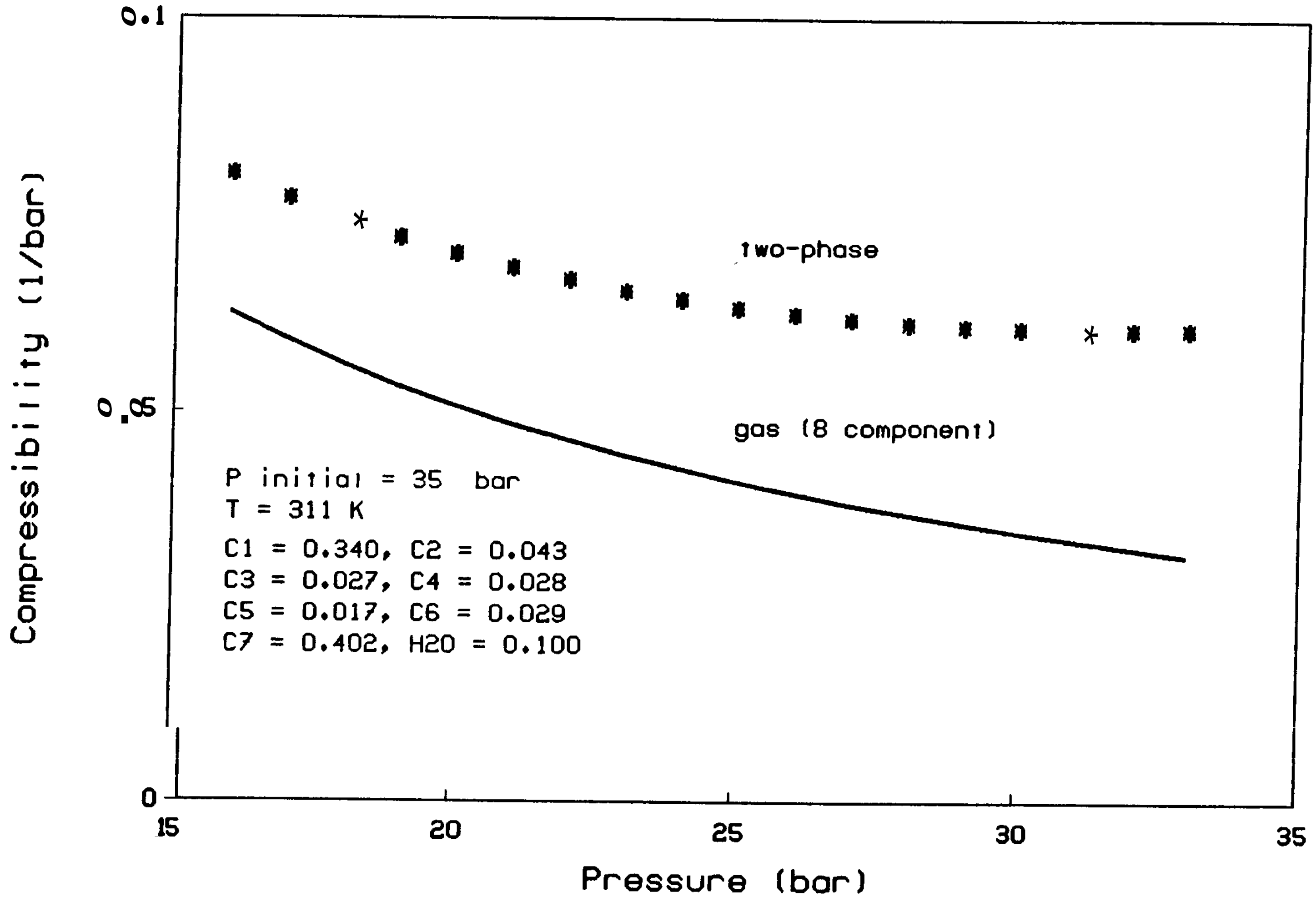


Fig. 4.39 Compressibility versus Pressure, hydrocarbon System No. 12

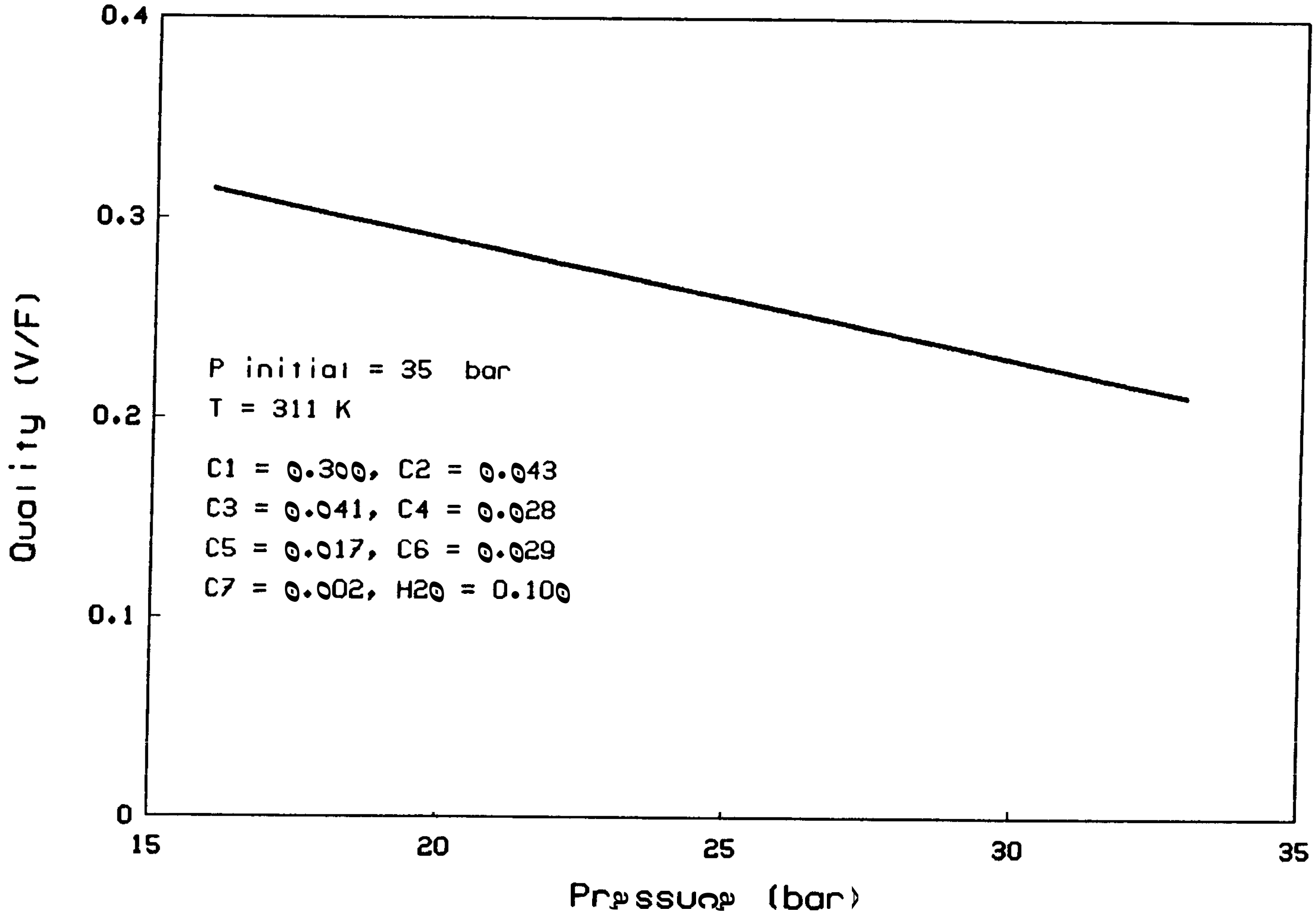


Fig. 4.40 Quality versus Pressure, hydrocarbon System No.12

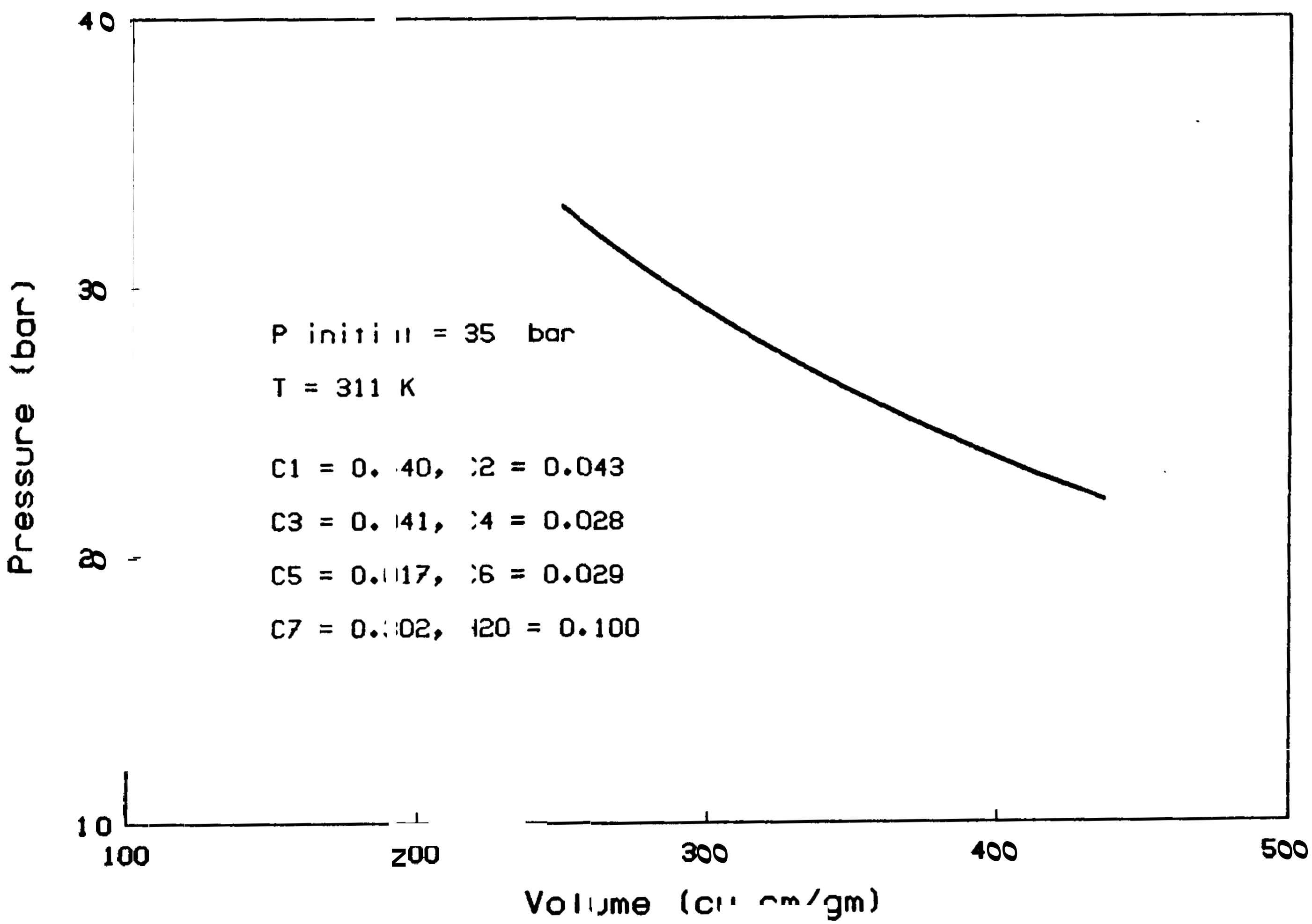


Fig. 4.41 Pressure versus Specific Volume, hydrocarbon System No. 13

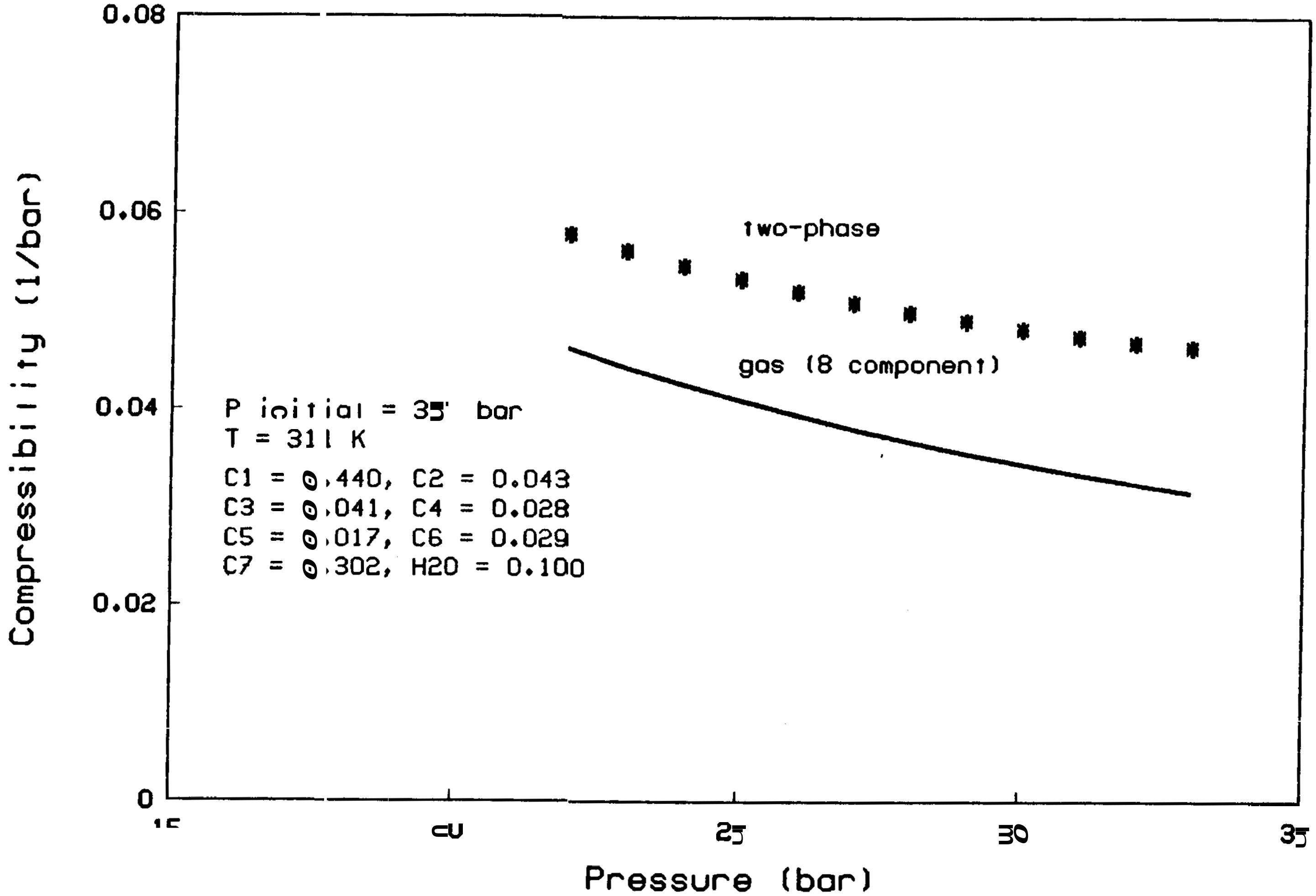


Fig 4.42 Compressibility versus Pressure, hydrocarbon System No 13

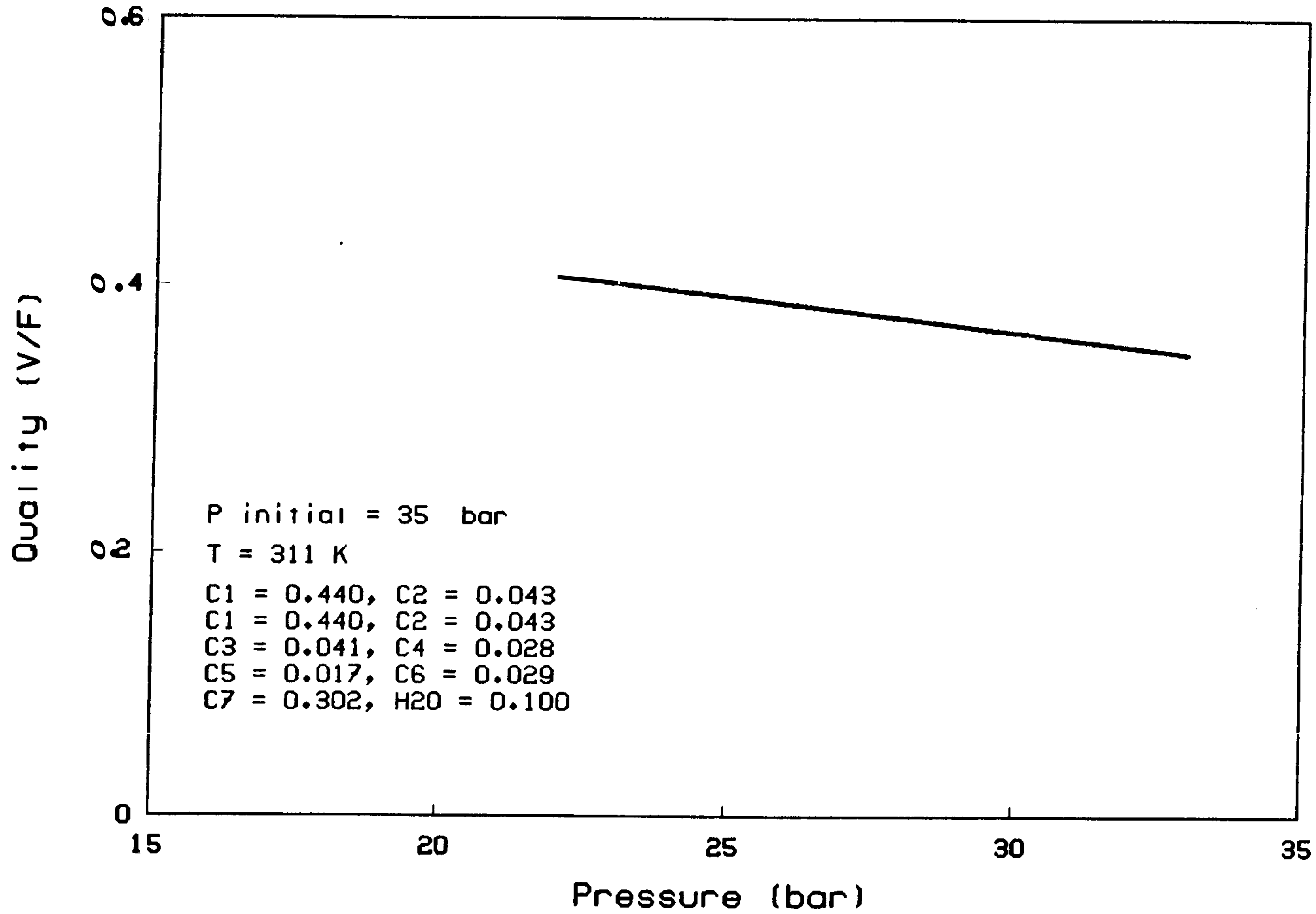


Fig. 4.43 Quality versus Pressure hydrocarbon System No.13

4.2.1. Gas Production

Production for this case is of only gas. After a pressure drop, some of the initial fluid vaporizes. The amount of gas remaining in the system fills the same volume that was occupied by the vaporized fluid. The rest of the gas is produced. Single-component water systems at different initial pressures were studied. These systems include a rock component evident through the enthalpy balance.

System No.14 -- Saturated water at an initial pressure of 40 bar in a 10 % porosity rock.

The computed compressibility due to production was graphed versus pressure (Fig. 4.44). As lhe system depleted, Lhe system compressibility increased. The value of compressibility at 40 bar was compared with that computed by Grant and Sorey (1978) for similar conditions of porosity and pressure. From this model, $C_{prod.}$ = 0.93 bar^{-1} and Grant and Sorey reported a $C_{prod.}$ = 0.9 bar–' This compressibility is thirty times larger than the compressibility of the gaseous phase at 40 bar. To see the effect of rock porosity for this kind of production. the value of porosity was changed to Φ = 25%.The system No.15 results for production compressibility against pressure are shown in Fig. 4.45. The results for this case resemble those for System No.14, except the two-phase compressibilities values for this case, System No.15, are lower than those for system No.14. That is, there is a lower mass of rock per unit mass of fluid for the high porosity case, thus less heat available to vaporize water.

For a low pressure, 9.3 bar, System No.16 (Fig. 4.46). System No.17 (Fig. 4.47). the same results were seen as for the higher pressure cases. A comparison of the production compressibility against two-phase compressibility and gas compressibility. Fig. 4.48. showed Lhat Lhe values of production compressibility are larger than the other compressibilities. These results emphasize the importance of the heat supplied by rock.

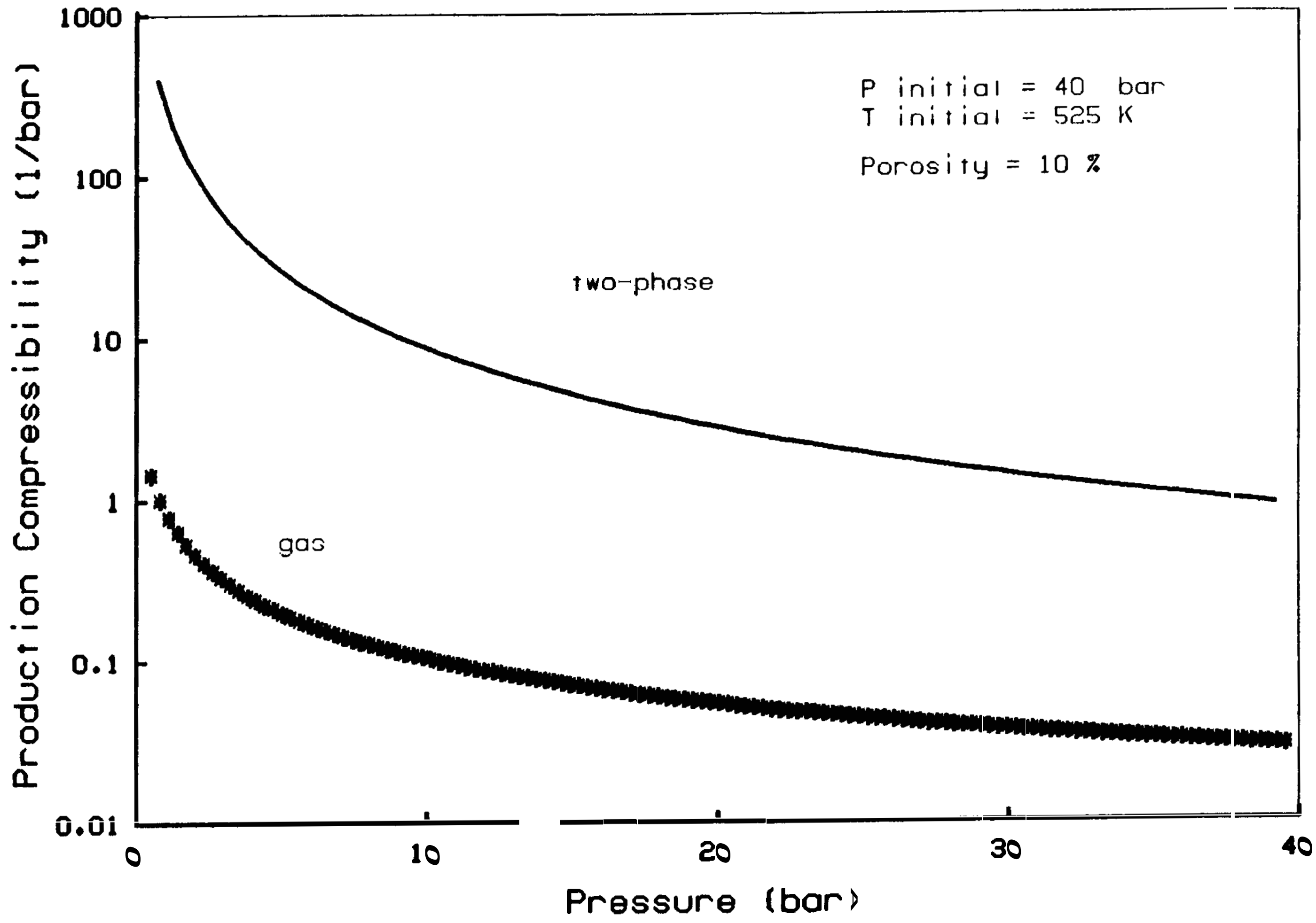


Fig. 4.44 Higher Enthalpy Fluid Production Compressiblity versus Pressure water System No. 14

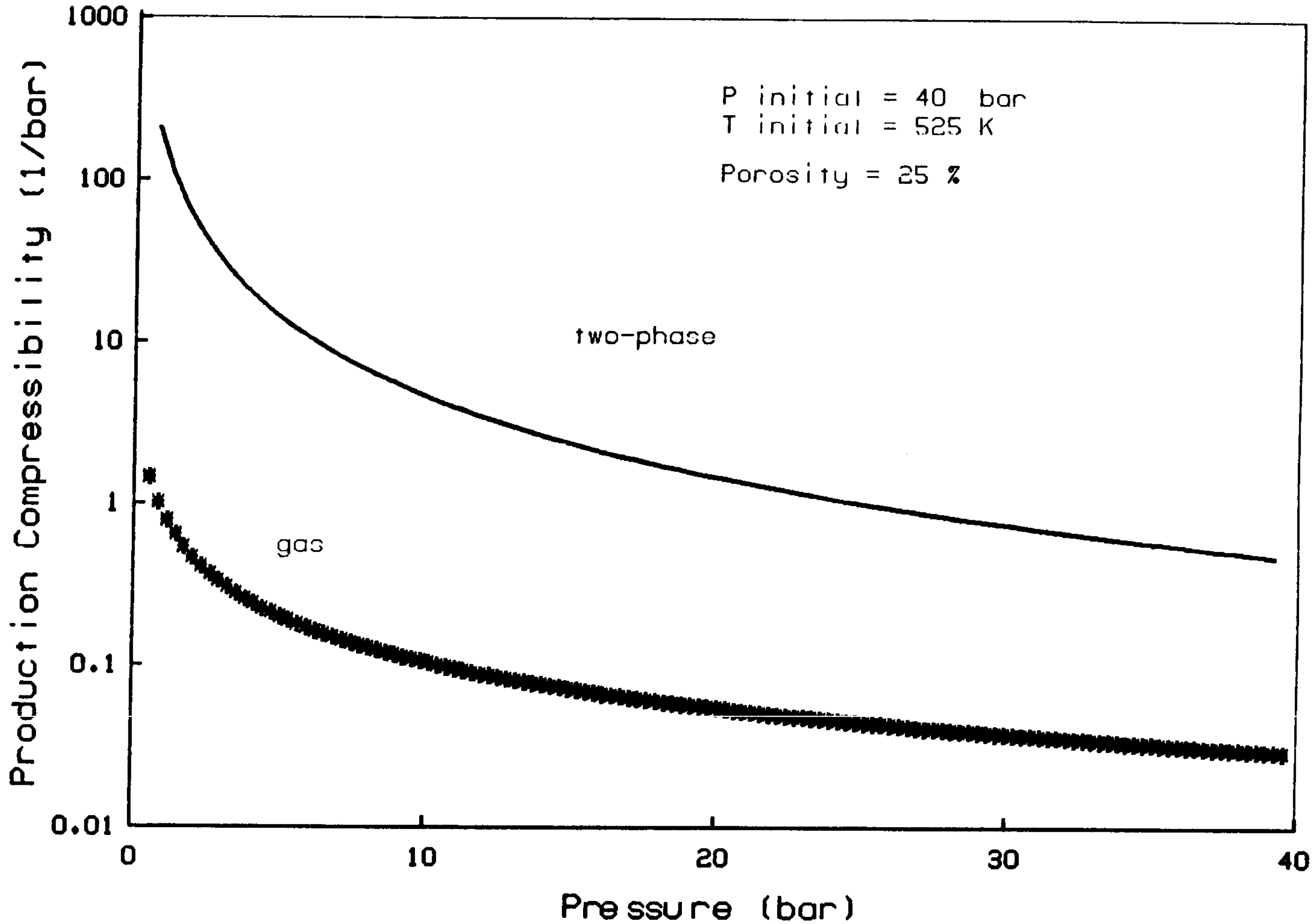


Fig. 4.45 Higher Enthalpy Fluid Production Compressibility versus Pressure, water System No. 15

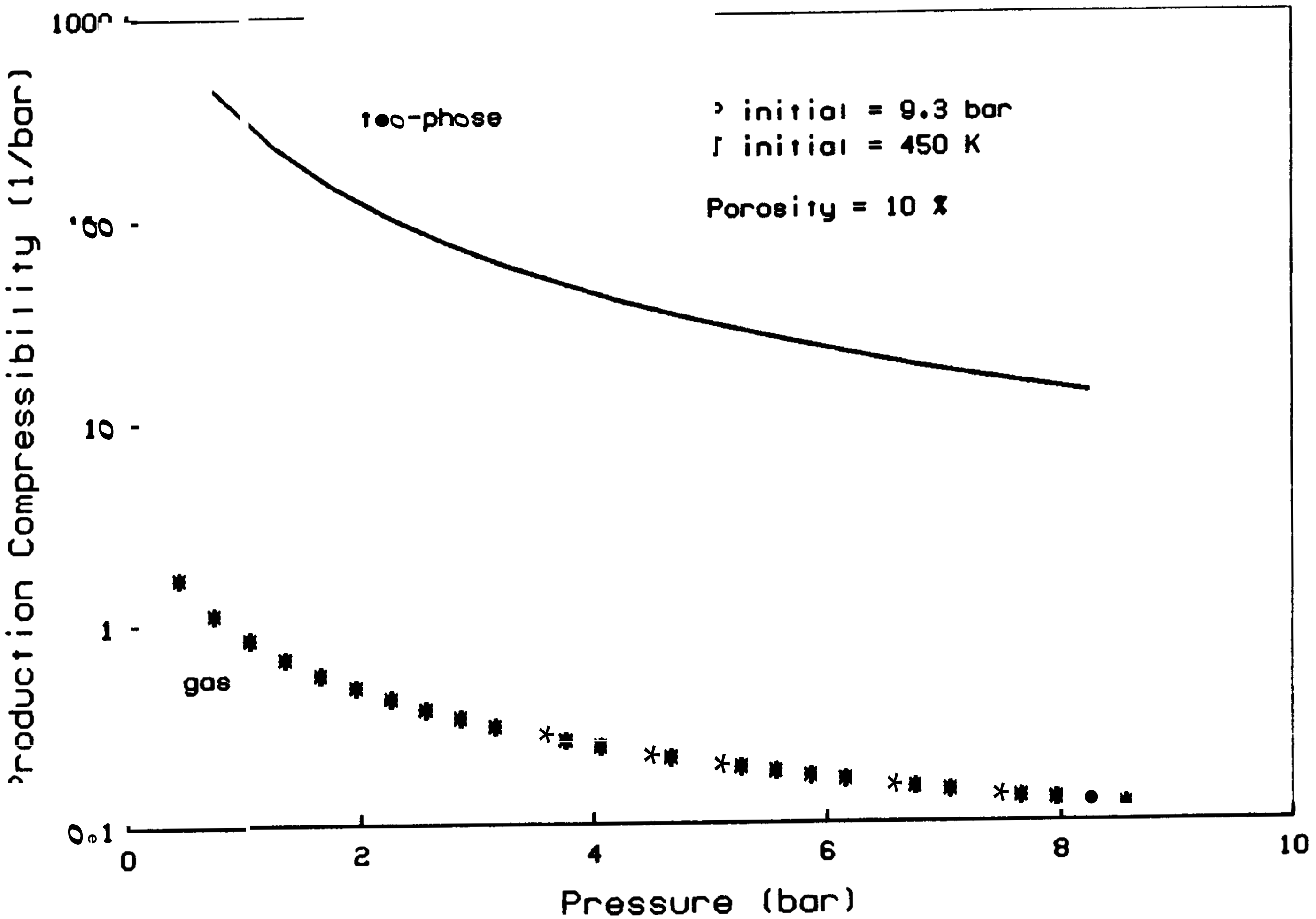


Fig. 4.46 Higher Enthalpy Fluid Production Compressibility versus Pressure water System No. 16

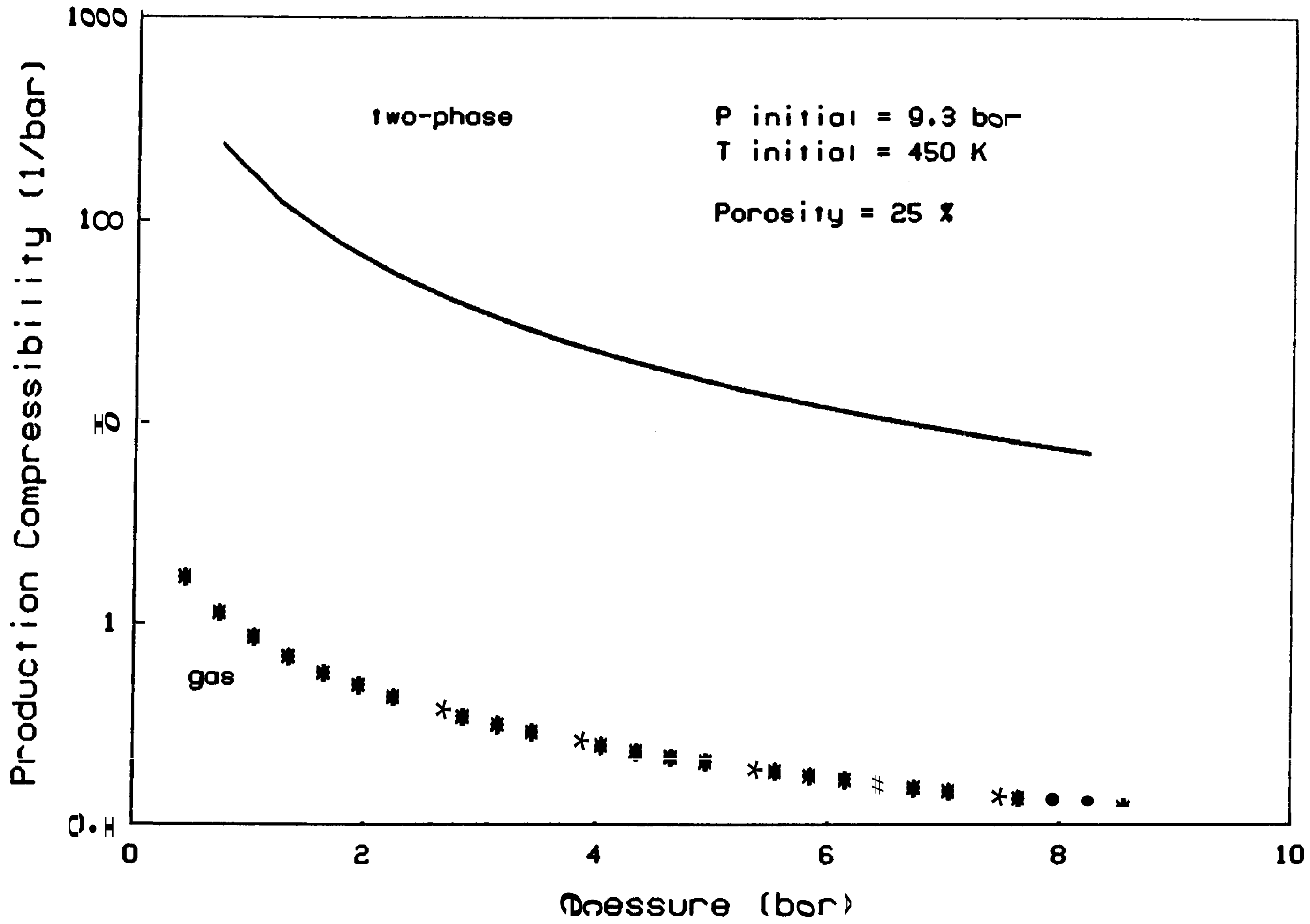


Fig. 4.47 Higher Enthalpy Fluid Production Compressibility versus Pressure water System No. 17

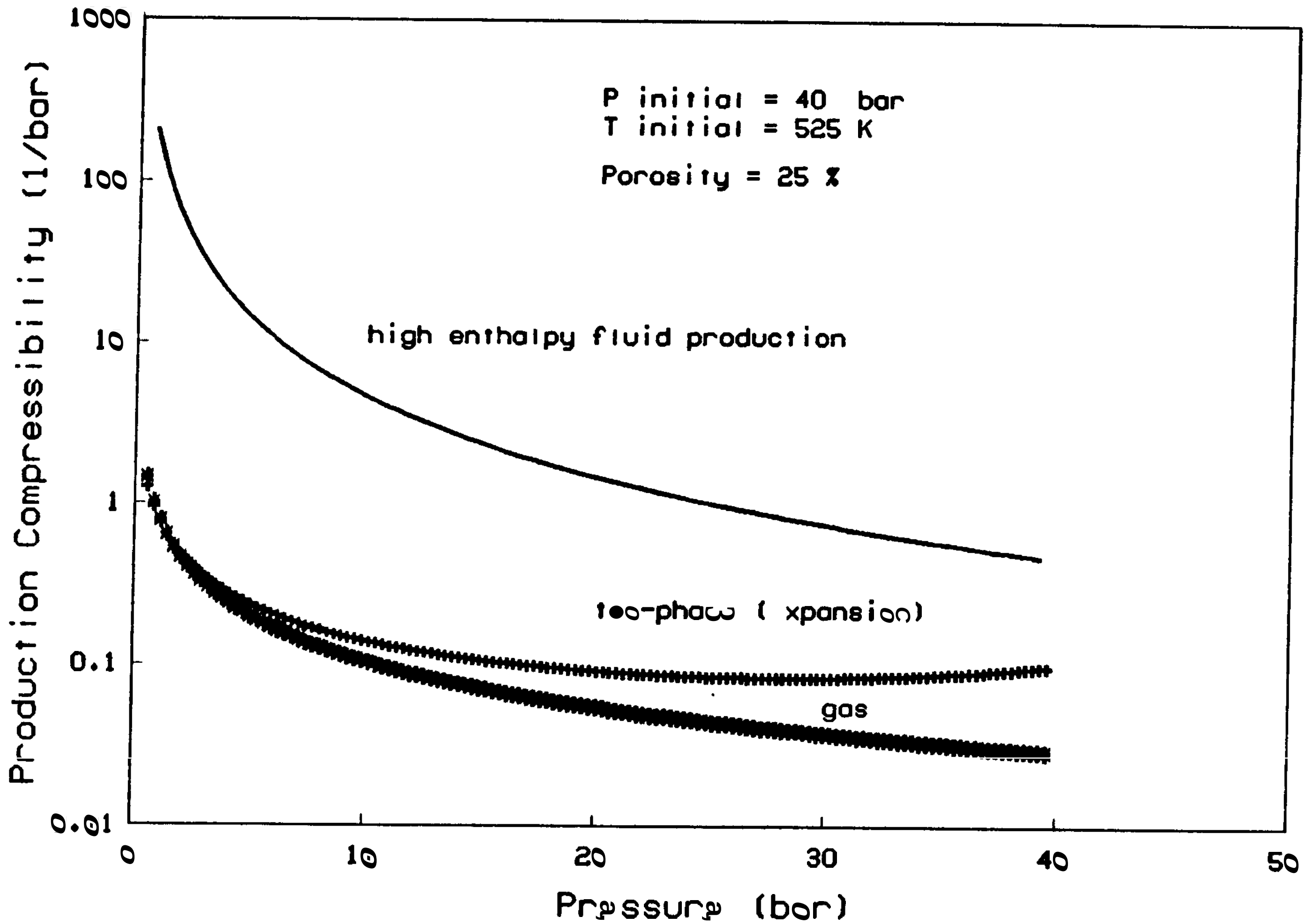


Fig. 4.48 Compressibility versus pressure a comparison between high enthalpy fluid production, expansion compressibility and gas(steam) compressibility for water systems

4.2.2. Multiphase Production (according to relative permeabilities)

For this production mode, liquid and gas were produced in proportion to relative permeabilities as determined from an average saturation between the higher and lower pressures of the pressure drop. As a validation run for this production pattern, the results from the study by Martin (1975) at a pressure of **9.3** bar were compared with the results of the flash routine. The same system properties as those of Martin's example were used. That. is, rock properties and relative permeabilities were taken from Martin's **work.** However fluid properties such as enthalpies, volume, pressure, and temperature were furnished by the flash routine. Viscosities were taken from published data, Keenan *et al.* (1969). and may be different from the values used by Martin. It is doubtful that fluid viscosity will influence the results to a significant degree.

A temperature versus pressure graph for Martin's case and **for** an initial pressure of 9.3 bars for the flash routine are shown in Fig. **4.49. Also,** the pressure versus saturation is presented in **Fig.** 4.50 for both systems. An acceptable match was obtained between the two models. In addition to checking results of this study against the Martin's case, the production compressibility was also determined. The compressibility caused by production for the 9.3 bar saturated water System No.18 shows a large initial value followed **by** a decrease as shown in Fig. 4.51.

System No.19 is for the same saturated water system but started at an initial pressure of 40 bar. The results are presented in **Fig** 4.52. Production compressibility for both Systems 18 and 19 was larger than the gas (steam) compressibility at the same conditions. Discussion of the results for expansion compressibility and production compressibility are presented in the next section.

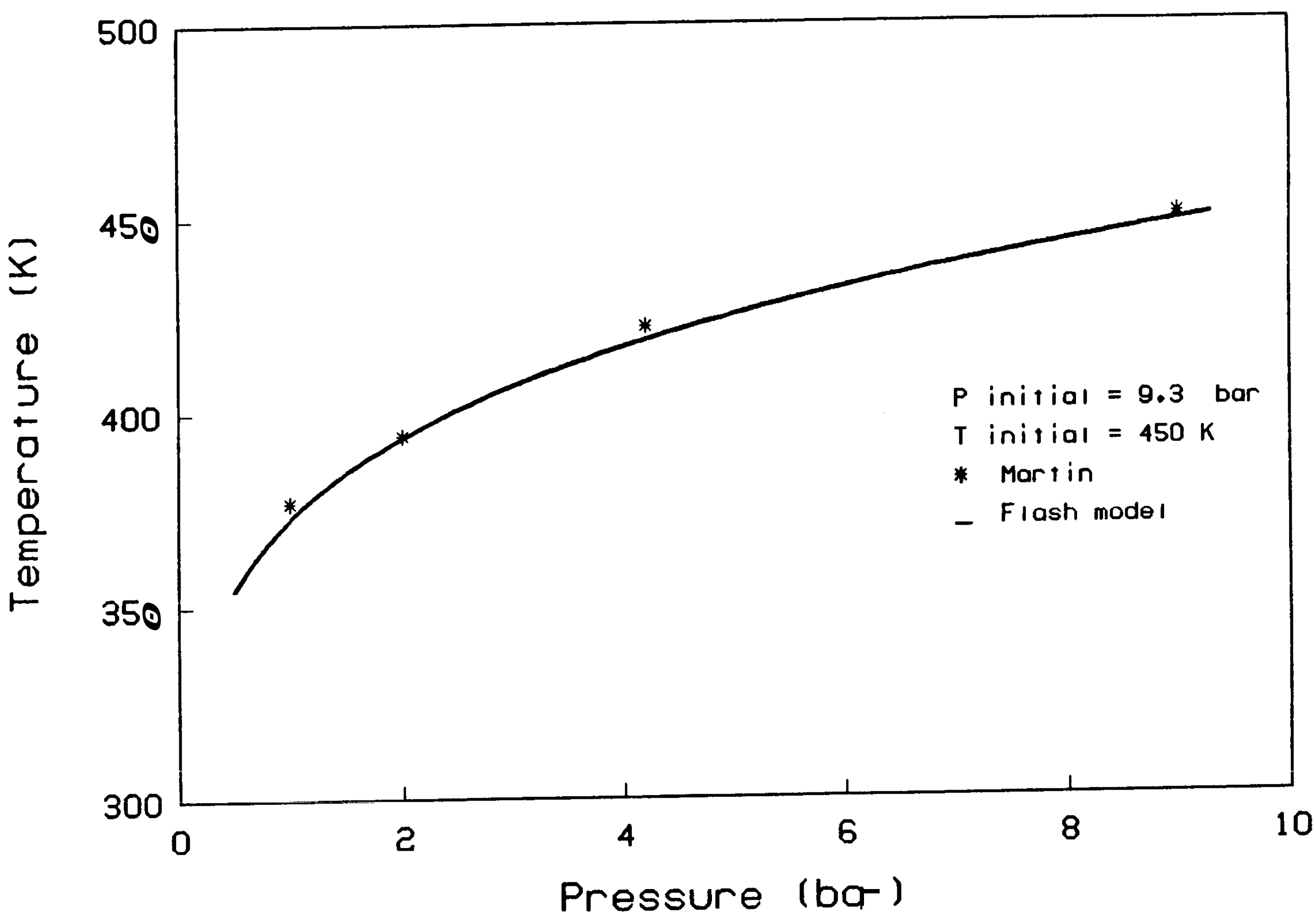


Fig. 4.49 Temperature versus Pressure water System No 18

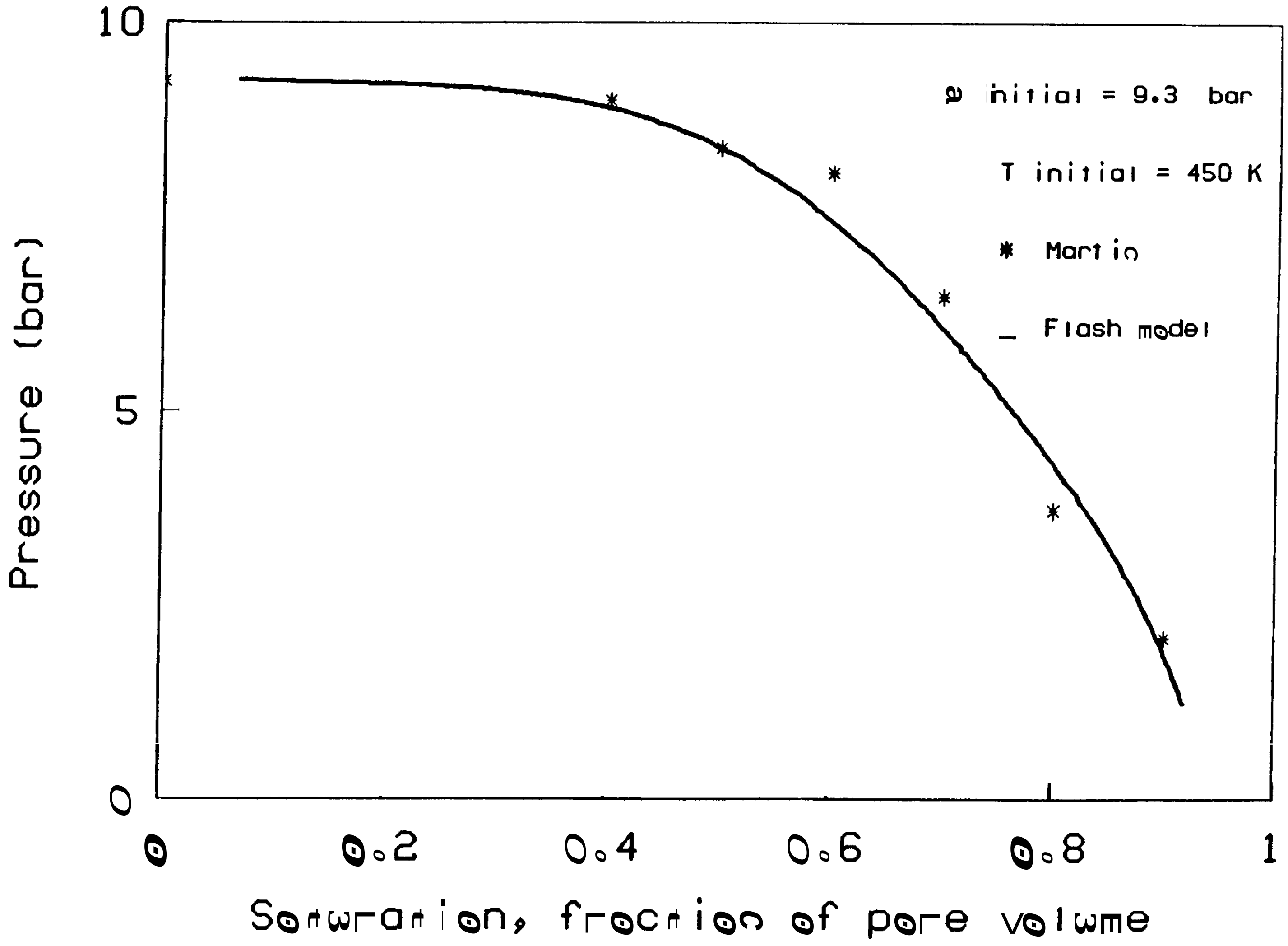


Fig. 4.50 Pressure versus Saturation, water System No. 18

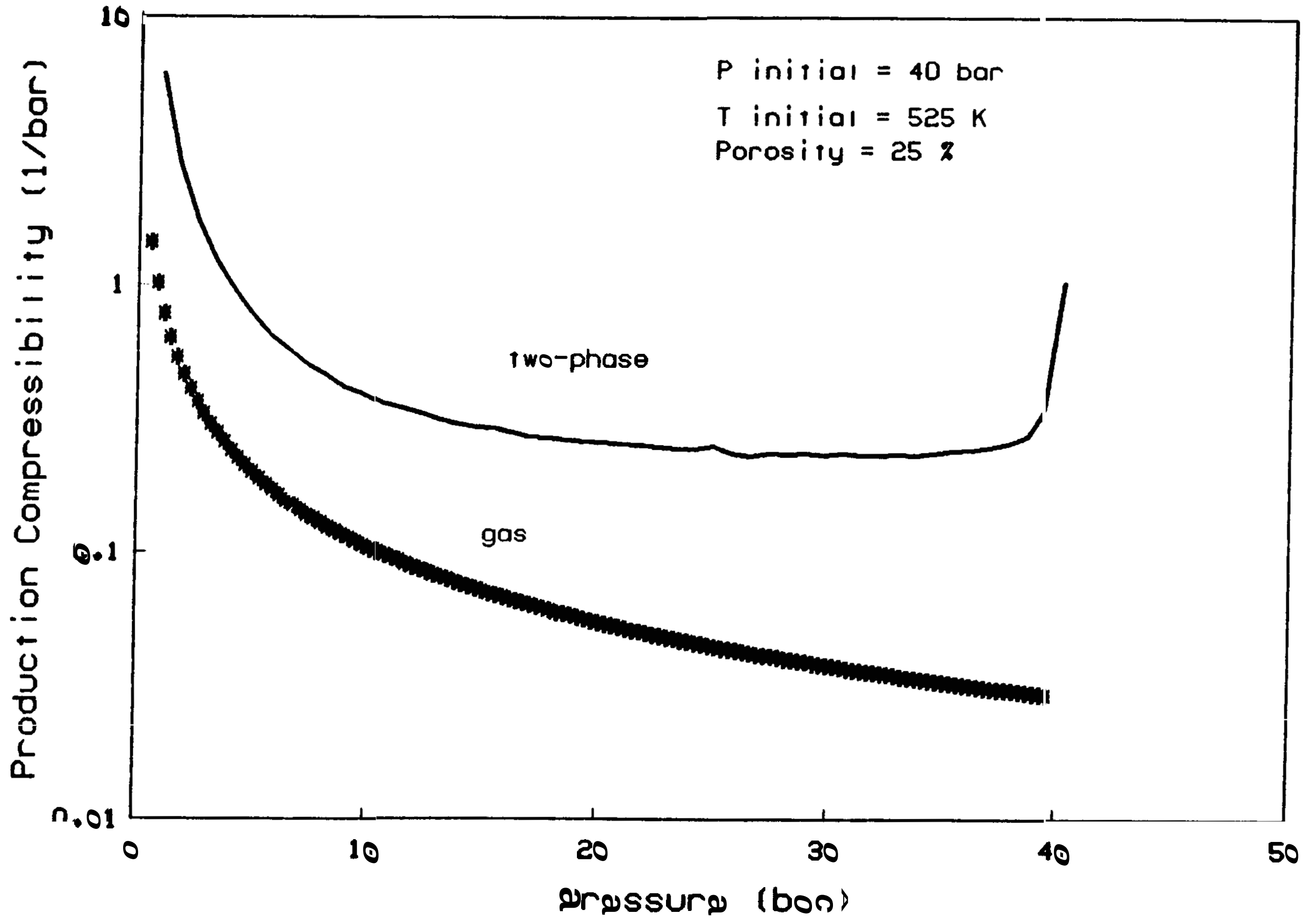


Fig. 4.51 Production Compressibility versus Pressure, production by relative permeability, System No. 18

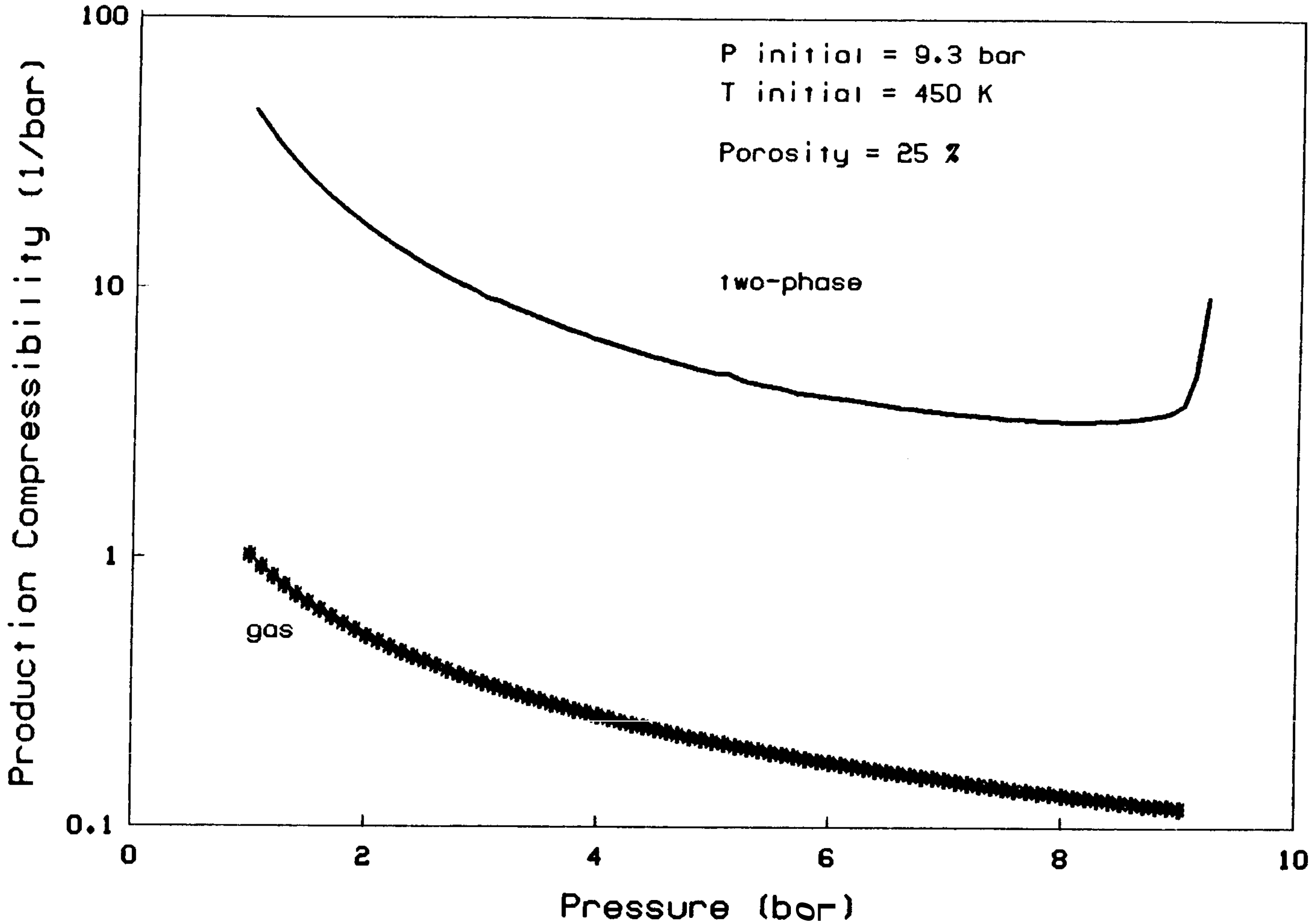


Fig. 4.52 Production Compressibility versus Pressure, production by relative permeability, System No. 19

5. DISCUSSION

The results of compressibility calculations for single-component systems are presented in Figs. 4.2, 4.6, and 4.10. The results for the three single-component water systems simulated (100 bar, 40 bar and 9.3 bar) appear to be in agreement with thermodynamic theory (p-V diagram) and with the calculations made by Kaiffer (1977) on adiabatic compressibility from sound velocity, Eq. 2.6, in liquid-gas mixtures (Fig. 5.1). Recall from Eq. 2.6 that adiabatic compressibility is reciprocally related to the velocity of sound in the medium. From this figure and Eq. 2.6 it can be seen that the lowest velocities (highest comprcssibilitics) can occur whcn a systcm has a low quality (low gas saturation), depending also on the pressure. The effect of quality is more noticeable at low pressures, as was shown in Fig. 4.6 for the 40 bar case, and more dramatically for the 9.3 bar case, Fig. 4.10. According to Keiffer, this behavior is caused by the fact that a two-phase system has nearly liquid density, but the compressibility of a gas. Also, the discontinuity in the speed of sound of a vapor with a small quantity of liquid is not as dramatic as that for a liquid with a small amount of gas.

Calculation of the two-phase compressibility for water can be performed from data given in steam tables, Keenan et al.(1969), if an estimate of the quality can be obtained from a flash calculation by using the quality to obtain the volume of the mixture. For example, see Table 5.1.

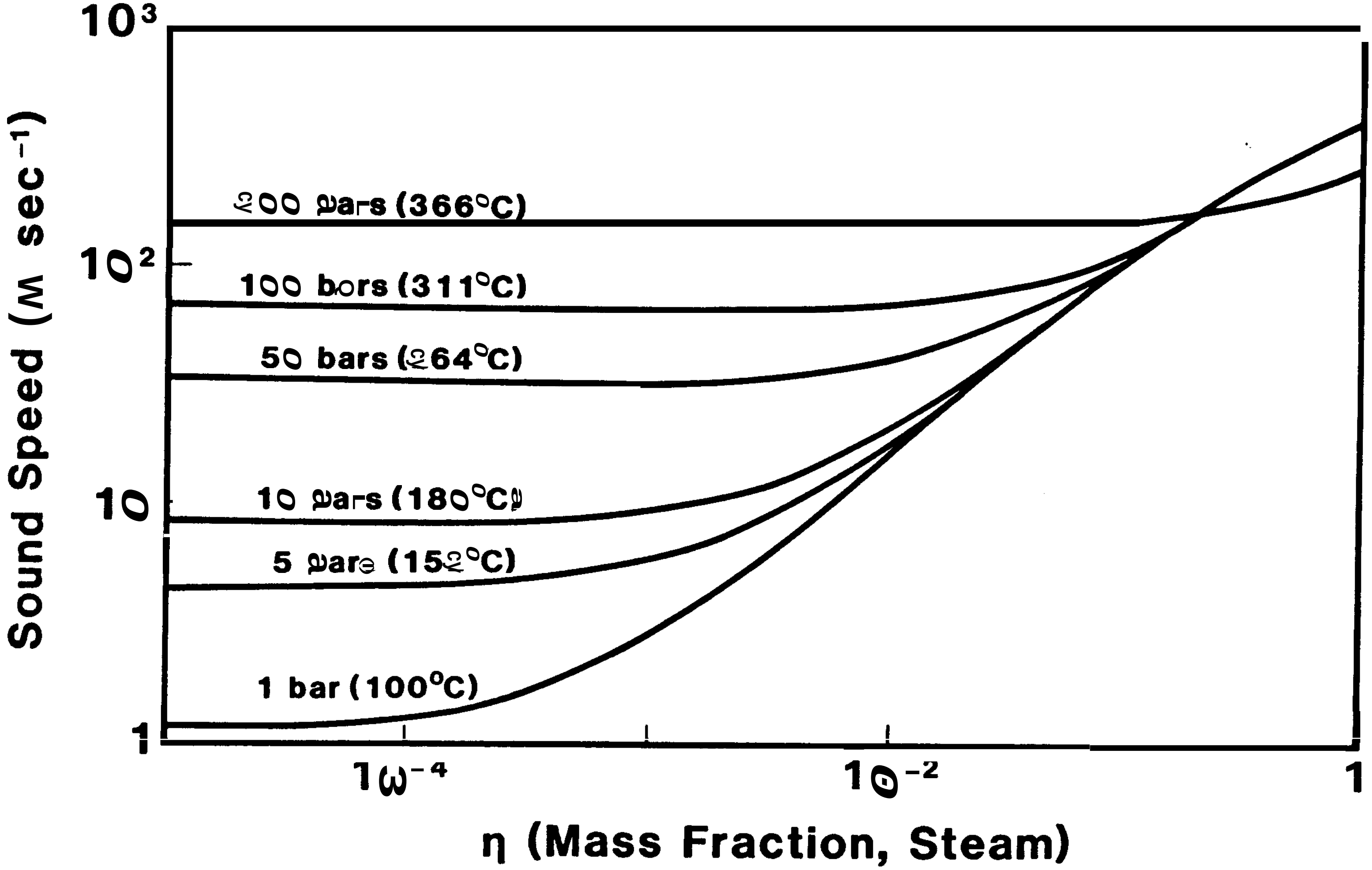


Fig. 5.1 Sound Speed in Liquid Gas Mixtures versus mass fraction of steam (Keiffer, 1977)

Table 5.1.- Specific Volume Calculations

	$v_l(cc/g)$ liquid volume	a	$v_g(cc/g)$ gas volume	$v_{mixture}$ (cc/g)
9.0	0,001121	0.0034	0.2174	0.001856
8.5	0.001118	0.0080	0.2289	0.00294

Data from table **5.1** can be used to compute a two-phase expansion compressibility similar to those obtained with the flash model for the same condition. For example:

$$C_{2\varphi} = \frac{0.00294 - 0.001856}{0.5(0.00294 + 0.001856)(9 - 8.5)} = 0.904 \text{ bar}^{-1}$$

$C_{2\varphi} = 0.899$ bar^{-1} from flash program

As can be seen, the two-phase Compressibility computed from the steam tables agrees well with that obtained from the flash program. We turn now to consideration of two-component systems.

In order to study a simple two-component system,,carbon dioxide was added to water in the liquid phase in proportion to published geothermal data (Ellis et al., **1977).** Contamination of a single-component system causes a reduction in the two-phase compressibility (isothermal and adiabatic). This can be observed from a **p-V** diagram for a pure substance and for a mixture. The isothermal compressibility diminishes in value with respect to the single-component. two-phase compressibility. The inverse slope of the isotherm for a single component system within the two-phase envelope is a much larger number than that corresponding to the multicomponent system.

For the adiabatic compressibility case, results for single-component water and the two-component case $(H_2O - CO_2)$ are presented on Figs. **4.6** and 4.13. Further increments in the amount of CO_2 (Fig. **4.17)** added to water produces **two-phase** compressibilities that are increasingly lower in value than those for the single-component case. Nevertheless, the compressibility of the two-phase region remained higher than the gas compressibility at the same conditions for the $H_2O - CO_2$ systems.

A comparison of one-component, two-phase compressibility and two-component, two-phase compressibility with gas compi-essibility, Fig. 5.2, shows that the compressibility of a single-component system. is larger than that for the two-component, Lwo-phase system, and also larger than the gas compressibility for the same conditions.

5.1. Two-Phase Compressibility from Published Data

Sage, Lacey and Schaafsma (1933), presented laboratory pVT measurements for several methane-propane systems. They reported pressure-specific volume measurements for different conditions of temperature, pressure, and composition. They indicated which measurements were made for two-phase conditions. Compressibility for two-phase conditions was calculated from their data. The results were two-phase compressibilities greater than the gas compressibility for all the conditions reported as two-phase conditions, even though the pressure decrements were large. Ap = 200 psi, specially for the shape of the isotherm as shown in Fig. 5.3.

A graph of compressibility versus Pressure calculated from the data of Sage, *et al.* for a C_1-C_3 system is given in Fig. 5.4. It. was reported from Sage's data that liquid volumes were measured at 1400 and 1200 psi, measurements for two-phase conditions were reported at 000 and 600 psi, and gas conditions at 400 psi. From fig. 5.4 it is shown that liquid compressibility goes to a larger value in the two-phase region, and within this region there is an increase of two-phase compressibility followed by a decrease towards the gas phase compressibility.

Field data from the Dominguez Field were presented by Sage et al. (1935), in which two-phase formation volume factors were reported versus pressure for

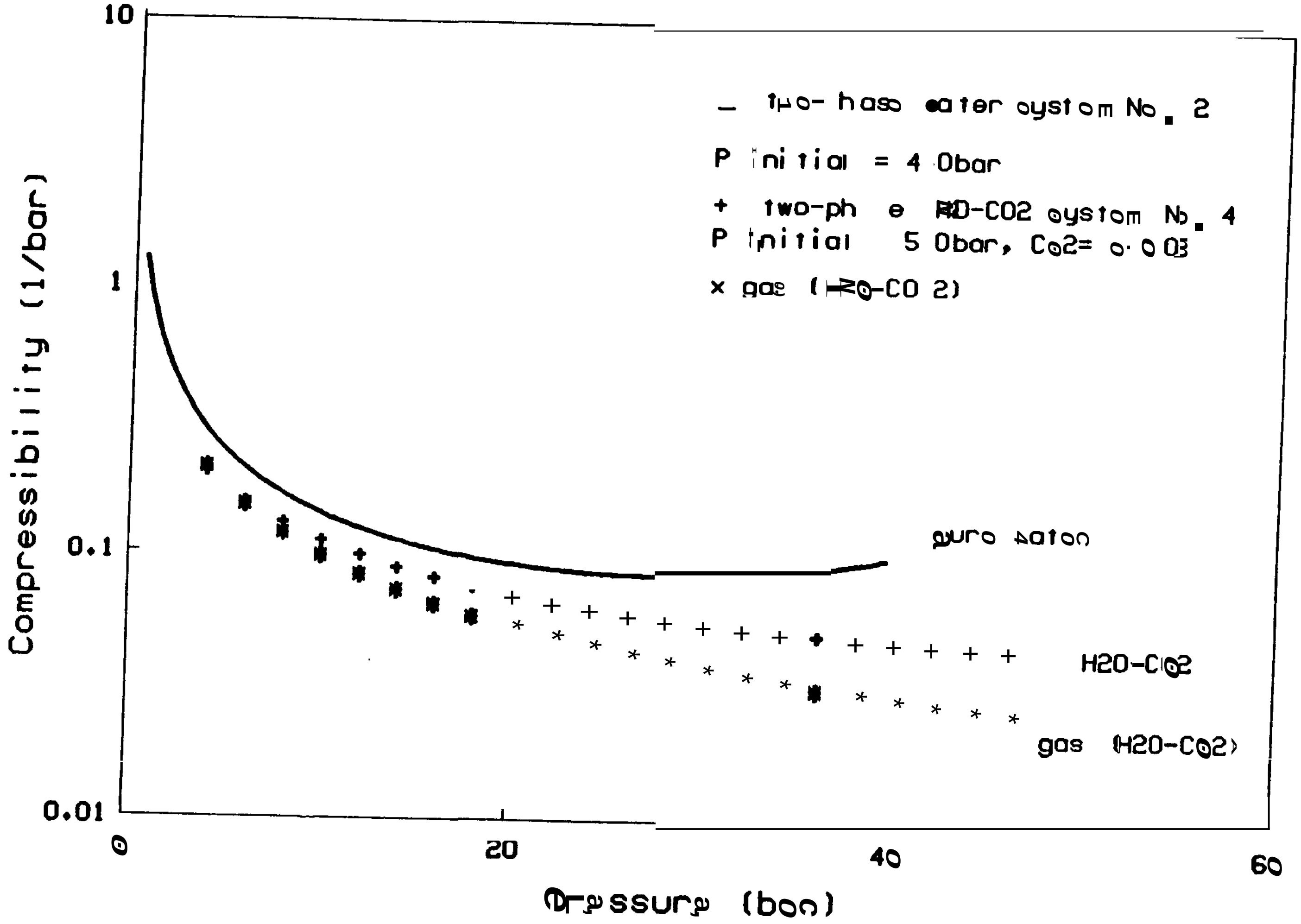


Fig. 5.2 Compressibility versus Pressure for single-component water system and multicomponent water-carbon dioxide systems

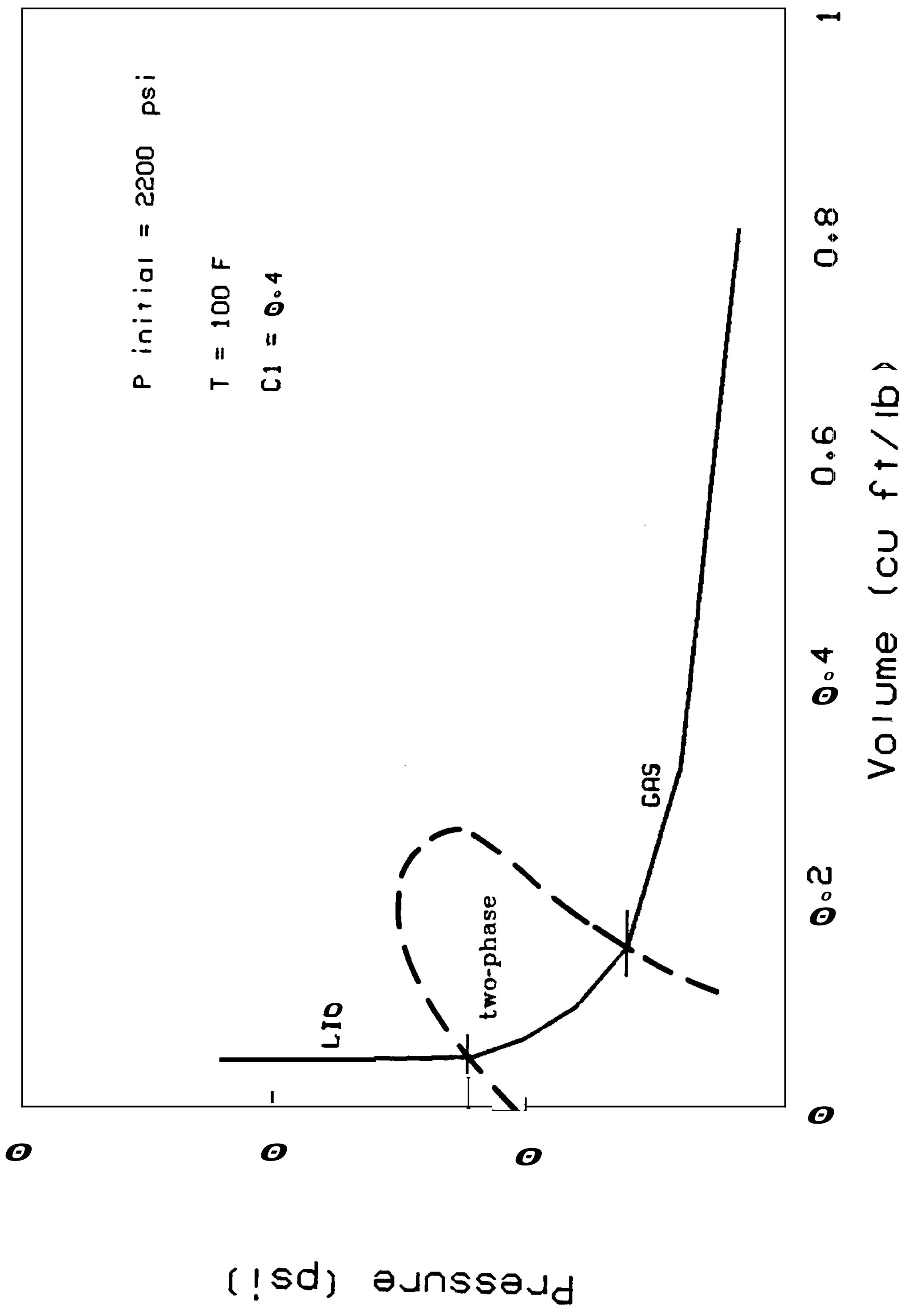


Fig. 5.3 Pressure versus Specific Volume from Sage at al.(1933) Data

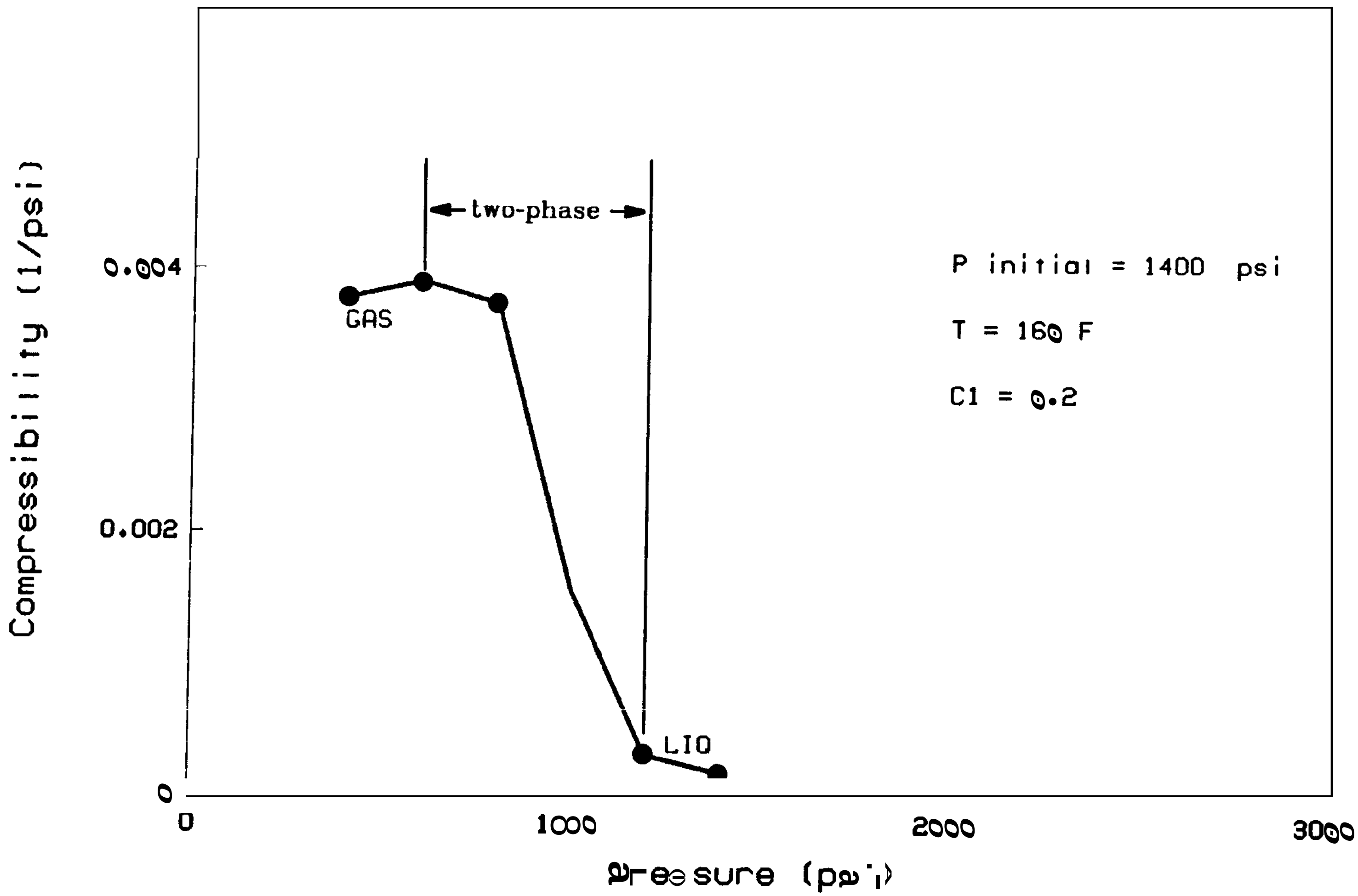


Fig. 5t Compressibility versus Pressure from Sage et. al (1933) data

large pressure decrements. Data were curve-fitted with a logarithmic expression and then compressibilities were calculated for small pressure decrements near the bubble point. Compressibilities of the two phases were greater than the gas compressibility, specially near the bubble point. For example, the formation volume factors **for** a system with a gas-oil ratio of ***728.2*** scf/B and temperature of 190°F with a bubble point pressure of 2974 psia was examined. The curve-fit obtained **was:**

$$B_t = 18.21 - 2.16 \ln p$$

At 2974 psia, the two-phase compressibility was 0.007 psi–', which compares with a gas compressibility at the same conditions **of** 0.0034 **psi–'.** This result produces a two-phase compressibility almost twice the compressibility of the gas phase at the same conditions.

Another example for different conditions of temperature 220°F, a gas-oil ratio of 352.5 scf/B, and a bubble point pressure of 1995 psi was examined. The result was:

$$B_t = 11.36 - 1.35 \ln p$$

The two-phase compressibility computed at 1900 psi was 0.00061 psi–'. The gas compressibility at the same conditions was 0.00053 psi^{-1}. This also shows a two-phase compressibility greater then the compressibility of gas at the same conditions.

From the data of Sage and Lacey (Phase Equilibrium in Hydrocarbon Systems, 1936) on properties of mixtures of natural gas and crude oil, the following examples were taken.

For a temperature of 220°F and a bubble point pressure of 1995 psia and with a mass % of gas of 5.611%:

$$v = 0.2 - 0.024 \ln p$$

At 1900 psia, the two-phase compressibility was 0.00087 psi–'. The corresponding gas compressibility for these conditions is 0.00053 psi–'. The compressibility of the two phases is greater than the Compressibility of the gaseous phase at the same conditions.

From Sage and Lacey (Formation Volume of Gas Cap Material from Kettleman Hills Field, 1936) other examples may be found to obtain formation volumes of mixtures of gas and oil. For a temperature of 220°F, and a bubble point pressure of 1986 psia, and a gas oil ratio of 1.992 scf/B:

$$B_t = 32.62 - 4.10 \ln p$$

At 1900 psia. the two-phase compressibility was 0.0013 psi'', and the c mpressibility of the gas at the same conditions was 0.00053 ps $^{-1}$,

For a temperature of 220°F, a weight per cent gas ***of*** 11.34%.and with **a** bubble point pressure of 1966 psia,

$$v = 0.491 - 0.617 \ln p$$

At 1900 psia, the two-phase compressibility was **found** to be 0.0013 psi $^{-1}$, and for the gas compressibility at the same conditions 0.0005 psi–'.

For another case at 220°F, a weight per **cent gas** of ***5.29*** %, and with a bubble point pressure of 1455 psi, the two-phase curve-fit was:

$$v = 0.424 - 0.055283 \ln p$$

At 1400 psi, the two-phase compressibility was 0.00017 psi–', and the **gas** compressibility for the same conditions was 0.0007 psi-''. Again it was observed that the two-phase compressibility was greater than the compressibility of the gas.

From these calculations and the results from the runs for the multicomponent hydrocarbon systems ($C_1 - C_7$, $C_1 - C_7 - H_2O$), it may be concluded that the compressibility below the bubble point can be greater than the gas compressibility, not only for systems at low pressures, but also for cases with higher pressures and a larger number of components. We now consider the effect of production mode on total system effective compressibility.

5.2. PRODUCTION COMPRESSIBILITY

The total compressibility for a reservoir (or a reservoir block) can be expressed as:

$$C_{TOTAL} = \text{fluid compressibility (expansion)} + \text{production compressibility}$$

Aziz and Settari (1979) showed the following expression for total compressibility for a block for the sequential solution method:

$$C_t = \left\{ \frac{V_p}{\Delta t} [S_w^n B_w^{n+1} b_w' + (1 - S_w^n) B_n^{n\ 1} b_n'] \right.$$

$$+ Q_{wp}' Bw^{n+1} + Q_{np}' B_n^{n+1} \qquad 5.1$$

which in a simplified form, becomes for a gas-oil system:

$$C_t = \frac{V_p}{\Delta t}(S_o C_o + Sg\ Cg) + \text{Change in production of oil and gas with respect pressure} \qquad 5.2$$

This agrees with **Eq. (3.4)** Aziz *et al.* (1979) indicated that the production terms can make the C_t negative for this isothermal case.

For nonisothermal systems, Grant, Atkinson, and Moench, among others, **also** found that combining an energy balance with a material balance can produce total compressibilities that may be larger than the compressibility of the gaseous phase at similar conditions.

Ramey (1981) proposed that compressibility can be computed from data generated from numerical simulations, such as that shown in Fig. 5.5 from J.C. Martin (1975). Figure 5.5 represents numerical simulation results for a water and or steam filled geothermal system. Total compressibility may be calculated from the inverse of the slope of the pressure vs. cumulative production curve presented in Fig. 5.5. That is:

$$C = \frac{1}{V_{pore}} \frac{\Delta V_{produced}}{\Delta p} \qquad 5.3$$

It can be seen from Fig. 5.5 that compressibility from a two-phase region should be greater than the compressibility for a single-phase gaseous region.

Runs made with a black oil simulator, BOSS, for an isothermal system can also be used for the calculation of production Compressibility. The results also show that compressibility below the bubble point is greater than the compressibility of the gas phase at the same conditions. See Fig. 5.6 for example.

From the results shown in Figs. 4.44 to 4.53 for different modes of production. it can be seen that production compressibility depends strongly on the manner in which a reservoir is produced, as suggested by Eqs. 3.51 and 3.61. Gas production compressibility follows a trend governed by Eqs. 3.49 and 3.50, in which the controlling effect is the amount of mass changing from liquid to gas. This depends on pressure drop, and for nonisothermal processes on the amount of energy (heat) scavenged from the porous medium. Therefore, the behavior encountered in Systems No. 14 to No.17 reflects mass changing to gas as pressure decreases, and also on the effect of increased heat available in the system from the rock.

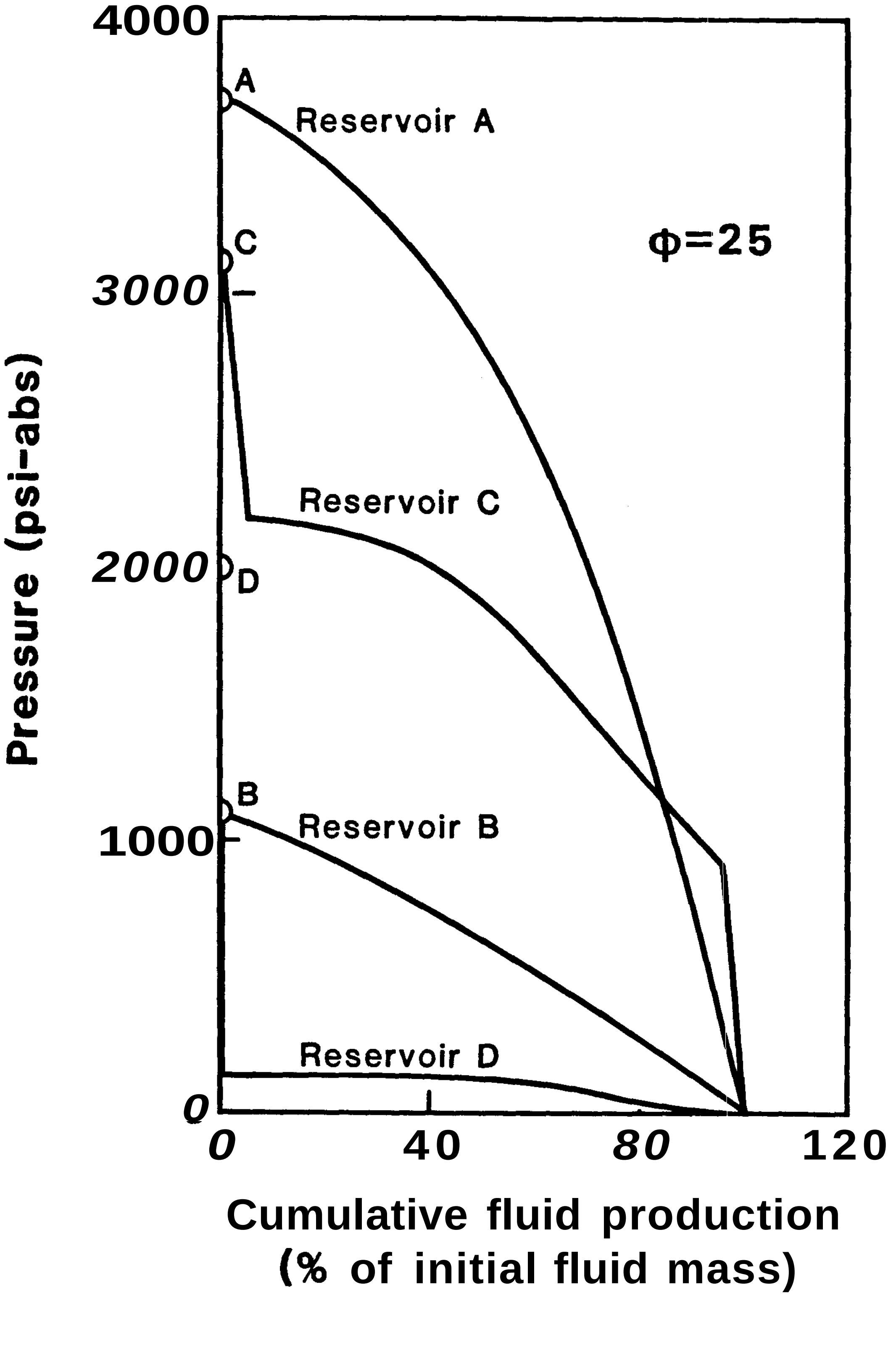


Fig. 5.5 Pressure versus Cumulative Production from Martin (1975)

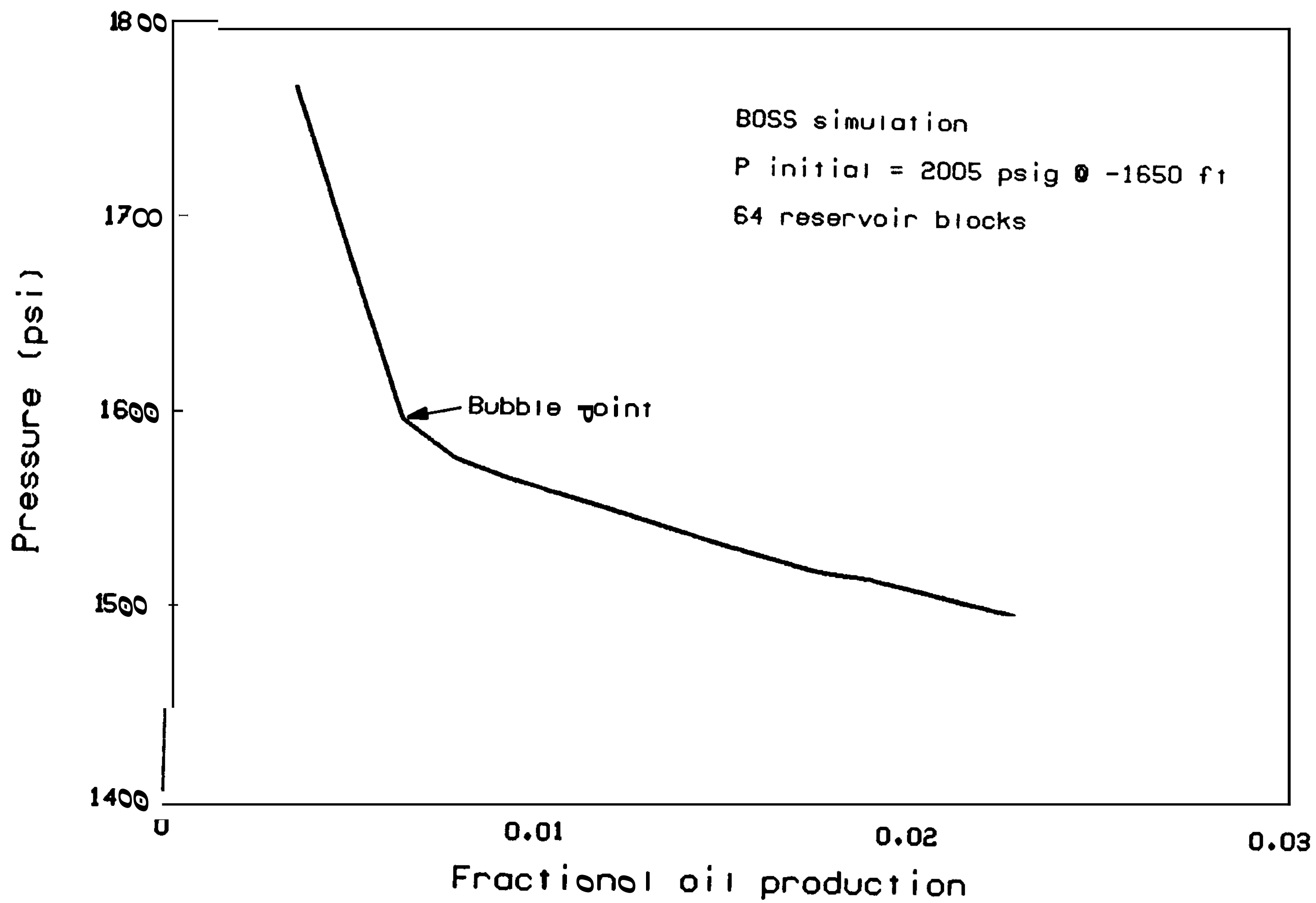


Fig. 5.6 Pressure versus Fractional oil production from a black oil simulation

Compressibility caused by rnultiphase production according to relative permeability relations for Systems No.18 and No.19 is initially high because there is a large change in mass due to liquid production and liquid changing to gas. Compressibility then decreases because gas saturation increases sufficiently to allow gas to be produced. At this time, ΔN_l in Eq. **3.59** is small causing the system to behave as if it were producing gas. Again. the compressibility is dependent on the pressure drop, and for nonisothermal processes, energy effects on the remaining fluid are dominated initially by the withdrawal liquid followed by the dominating effect of production of gas.

5.3. Effect of the Change in Saturation with Presure on Two-Phase Compressibility

From the definition of total density:

$$\rho_t = \rho_g S_g + \rho_o S_o \tag{5.4}$$

and compressibility:

$$c = \frac{1}{\rho_t}\frac{\partial \rho_t}{\partial p} \tag{5.5}$$

We obtain:

$$c_{2\phi} = \frac{1}{\rho_g S_g + \rho_o S_o}\left\{\rho_g \frac{\partial S_g}{\partial p} + S_g \frac{\partial \rho_g}{\partial p}\right\} + \frac{1}{\rho_g S_g + \rho_o S_o}\left\{\rho_o \frac{\partial S_o}{\partial p} + S_o \frac{\partial \rho_o}{\partial p}\right\} \tag{5.6}$$

After a pressure drop in a two-phase system, there is a change in quality (increase in gas). Even though this change in quality with respect to pressure can be small for the pressure drop considered, the change of saturation with pressure can be greatly affected by $\left(\frac{\partial x}{\partial p}\right)$ as can be shown by the expression for saturation in quality terms given by:

$$S_g = \frac{v_g}{v_g + \frac{(1-x)}{x} v_f} \qquad 5.7$$

In Eq. 5.7 a small quality change yields a much larger saturation change. Therefore, a small $\left(\partial x / \partial p\right)$ can produce a significant $\left[\%\right]$.

It is believed that the inclusion of the change in saturation with respect to pressure in the classic definition of total compressibility should produce representative two-phase compressibilities, specially for conditions near the bubble point. For pressures that are removed from the bubble point, the quality associated with this condition will give gas saturations very close to 100%.because of volumetric effects between gas and liquid. This is a major finding of this study.

5.4. SUMMARY

As stated in Eq. 3.2, the total change in volume in a reservoir consists of two terms, both of which have to be considered when a reservoir is below the bubble point, either for reservoir simulation and/or well test analysis. Production compressibility can be the larger of the two. A thermodynamic model has been utilized for the individual computation of the components of total compressibility, for adiabatic and isothermal cases, using the virial equation of state. For the cases studied, it has been observed that the compressibility of a fluid under two-phase conditions is larger than the Compressibility of the gaseous phase at the same conditions. Other equations of state appropriate for different kinds of fluids and other pVT properties can be used. This model can yield information about expansion compressibility for well test analysis for reservoirs below the bubble point, and for reservoir simulation. Presently is no equation of state that represents the majority of reservoir fluid behavior below the bubble point satisfactorily. Therefore, no general correlations of pVT properties were generated in the present study to represent a variety of reservoir fluid conditions. Differences in production mode for particular cases also makes production of completely general information difficult. However present results prove that a new view of total compressibility is required for porous systems.

5.5. Non-Condensible Monitoring

The **flash** model is capable of yielding mole fractions of different components in the liquid and in the vapor phase, as well as the fractional vaporization ($\frac{\bar{V}}{F}$). With this information an approximation of the behavior of non-condensible gases in a given reservoir of interest may be computed. This is a significant problem in planning the long-term development of geothermal systems.

Runs were made to approximate the behavior of a vapor-dominated system with steam production. An initial pressure of 71 bar and a temperature of 513 °K with a porosity of 15% and an initial fractional vaporization ($\frac{\bar{V}}{F}$) of 0.65 were considered for a two-component $H_2O - CO_2$ system. Figure 5.7 presents CO_2 mole fractions of the discharged fluid versus pressure for three different initial liquid molar fractions of CO_2 of 0.10, 0.075 and 0.05, respectively.

After a pressure drop in the system, there is vaporization of the liquid phase causing the liquid-dissolved carbon dioxide to transfer to the gaseous phase. This causes an increase in the carbon dioxide concentration in the discharged fluid. After most of the CO_2 in the liquid phase is removed by the boiling process, the CO_2 concentration of the discharged fluid decreases sharply. This general trend of non-condensible behavior is similar t.o one observed in Larderello (Pruess et. al, 1985). CO_2 concentrations computed by the flash model

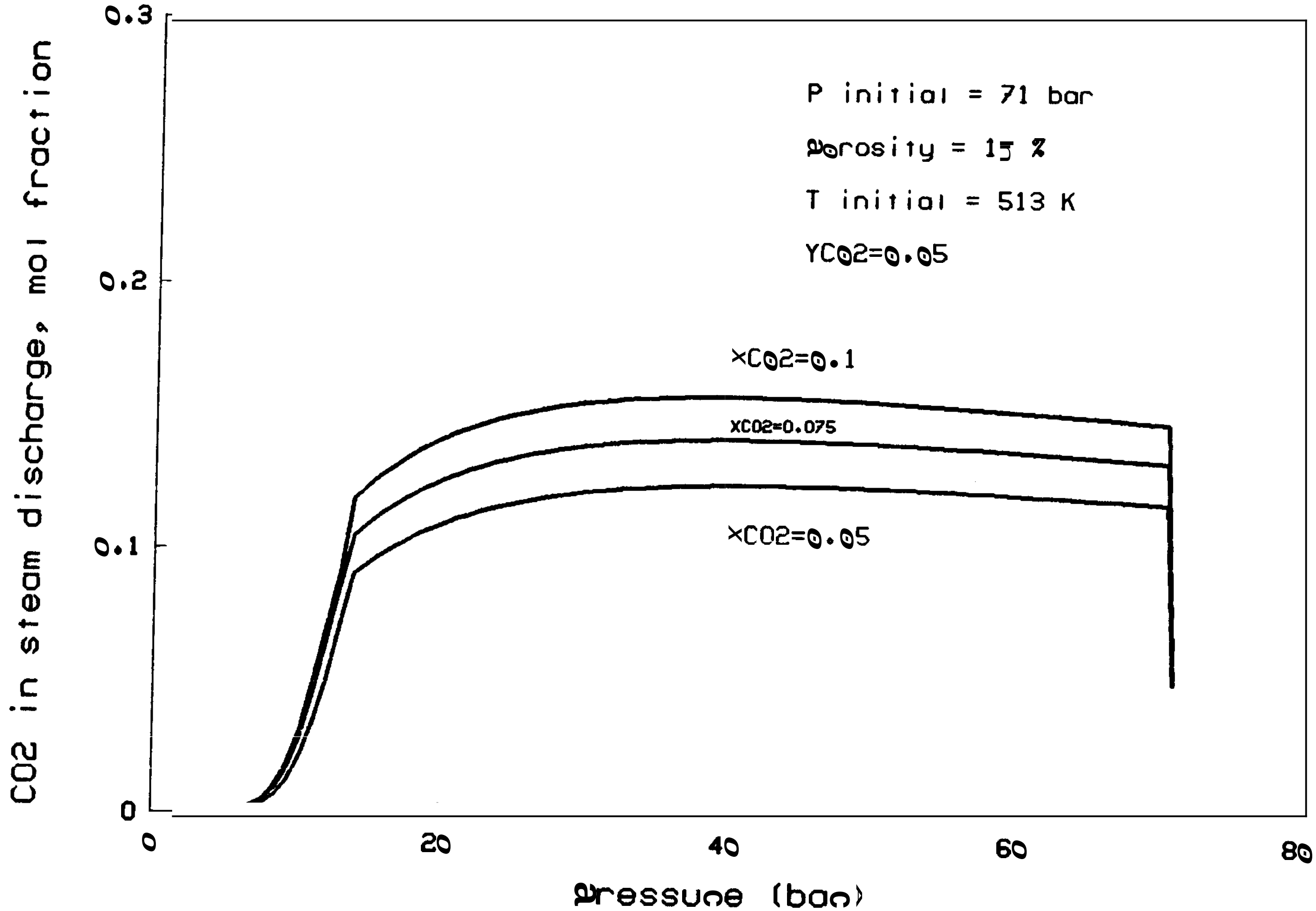


Fig. 5.7 *CO_2* discharge mol fraction versus pressure for a simulation of a vapor-dominated geothermal field with gas production.

are lower than the computed values reported by Pruess et al. which in turn were reported to be larger than the actual field data.

6. CONCLUSIONS

Total system compressibility as it is currently used in well test analysis can be underestimated because of oversimplification in its derivation. The major problem is that usual derivations neglect the change in fluid pore volume saturations with pressure. There are two different types of compressibility: one corresponding to the thermodynamic definition, and one due to production. The concept of total compressibility was revised showing that the compressibility of the fluid below the bubble point is greatly affected by a change of quality with respect to pressure, or a change of saturation with respect to pressure.

A thermodynamic model using the virial equation of state was utilized for the computation of the terms of total compressibility, for adiabatic and isothermal cases. For the cases studied, it was observed that the compressibility of a two-phase fluid was often larger than the compressibility of the gaseous phase at the same conditions. In addition, production compressibility could be larger then the compressibility of either the two-phase fluid, or the compressibility of the gaseous phase at the same conditions. Production compressibility is greatly affected by the way fluids are removed from a given reservoir.

Equations of state other than the virial equation which are appropriate for different kind of fluids and pressure-volume-temperature properties can be coupled with the present model to provide information about fluid (expansion) compressibility that can be used in well test analysis and reservoir simulation. Since there is *no* equation of state that represents a majority of reservoir fluids behavior, particularly below the bubble point, no general correlations of compressibility versus pressure were generated.

Non-condensible gas (CO_2) behavior in discharged geothermal fluids Follows a trend of increase in concentration, stabilization, and decline for one geothermal system studied. It appears that use of thermodynamic compositional models for non-condensible gas behavior forecasting may give more reasonable values of the future trend of non-condensibles gases in geothermal systems.

7. RECOMMENDATIONS

The following recommendations are made.

1. Other equations of state should be tested to study typical reservoir fluids and higher pressures.
2. Sonic velocity involvement in compressibility measurements should be studied.
3. The effects of relaxing thermodynamic equilibrium assumptions should be studied.
4. Study liquid compressibility, in particular the cases of adding compressible substances to water.
5. Use more sophisticated thermal-compositional models to study expansion compressibility and production compressibility.
6. Review old experimental data looking for pV measurements close to the bubble point for the computation of expansion compressibility. and laboratory pVT measurements should be carried out with smaller pressure decrements.

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9. NOMENCLATURE

A = flow area, cm^2
a_i = activity of pure component i
B = second virial coefficient
B_g = gas formation volume factor, $\frac{res.vol.}{std.vol.}$
B'_g = gas formation volume factor, $\frac{res.bbl}{scf}$
B_{ij} = second virial coefficient of binary mixture ij
B_{mix} = second virial coefficient of total mixture
B_o = oil formation volume factor, $\frac{res.vol.}{std.vol.}$
B_t = total formation volume factor, $\frac{res.vol.}{std.vol.}$
B_w = water formation volume factor, $\frac{res.vol.}{std.vol.}$
c = isothermal compressibility, 1/ bar
c_{oa} = apparent compressibility, 1/ bar
c_p = heat capacity of rock, $\frac{cal}{molC}$
c_s = adiabatic compressibility, 1/ bar
$c_{2\phi}$ = two phase compressibility, 1/ bar
C = third virial coefficient
F = initial moles of fluid in place
G = gas content, scf
f_i = fugacity of component i
f_i^{OL} = standard state fugacity
h = enthalpy, cal/mole
k = absolute permeability, darcies
k_{rel} = relative permeability
K_i = equilibrium ratio
L = moles of liquid after Δ p
N = Total number of moles present
N_o = oil content, STB
n = moles
p_s = saturation pressure, bar
p = pressure, bar
Q = External heat (enthalpy) addition from porous medium, cal
q_g = gas flow rate, $\frac{cm^3}{sec}$
q_w = liquid flow rate, $\frac{cm^3}{sec}$

R_s = gas solubility, scf/STB

R = universal gas constant, $\frac{cm^3}{g-molK}$

S = saturation, fraction of pore volume

T = temperature, K

V_T = Total Volume, cm^3

V_{pore} = pore volume. cm^3

V_{pv} = pore volume, cm^3

$\bar{V}$ =moles of vapor after Δ p

V = volume, cm^3

V_G = reservoir gas volume, $res.bbl$

V_o = reservoir oil volume, $res.bbl$

V_w = reservoir water volume, $res.bbl$

$\bar{v}$ = partial molar volume, $\frac{cm^3}{gm}$

v_g = gas specific volume, $\frac{cm^3}{gm}$

v_l = liquid specific volume, $\frac{cm^3}{gm}$

v_{mix} = specific volume of mixture, $\frac{cm^3}{gm}$

v = specific molar volume, $\frac{cm^3}{gm}$

v_s = speed of sound, $\frac{m}{sec}$

W = water content, STB

x_i = liquid mol fraction of component **i**

x = quality, moles of gas / moles total

y_i = **gas** mol fraction of component i

z = overall composition, mole fraction

Z = compressibility factor , actual volume / ideal gas volume

$\bar{z_i}$ = partial molar compressibility factor

Greek symbols

a = fractional vaporization, $\frac{\bar{V}}{F}$

β_t = two phase compressibility, 1/ bar

ΔN = change in liquid moles

Δm = Change in liquid mass

η = steam mass fraction

γ_i = activity coefficient of component i

κ = volume expansivity, see **Eq. 2.3**

λ = latent heat of vaporization, cal/mole

μ = viscocity, cp

φ_i = fugacity coefficient of component i

Φ = porosily, fraction of **bulk** volume

ρ_F = Auid density, $\frac{gm}{cm^3}$

ρ_f = formation density, $\frac{gm}{cm^3}$

ρ_r = **rock** density, $\frac{gm}{cm3}$

ρ_s = steam density, $\frac{gm}{cm^3}$

ρ_w = water density, $\frac{gm}{cm^3}$

ω_i = initial molar fraction

APPENDIX A

Total Isothermal System Compressibility

This follows an unpublished derivation by Ramey (1975), and is presented here in the same form as the original manuscript.

A unit V of bulk reservoir volume (bbl) is considered. The unit has a porosity Φ, and contains rock, oil, water, and gas:

$$V = V_o + V_w + V_G + V_r \quad \text{A.1}$$

The term V_G refers to free gas, and excludes gas in solution. If the volume originally contains N_o stb oil, W surface bbl of water, and G scf of gas:

$$V = N_o B_o + W B_w + \left(G - N_o R_s - W R_{sw}\right) \frac{B_g}{5.615} + V_r \quad \text{A.2}$$

We may define the total bulk volume compressibility as:

$$\Phi c_t = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \quad \text{A.3}$$

Substituting Eq. A.2 in Eq. A.3 :

$$\Phi c_t = -\frac{1}{V}\left\{N_o \frac{\partial B_o}{\partial p} + W \frac{\partial B_w}{\partial p} + \frac{G}{5.615}\frac{\partial B_g}{\partial p} - \frac{N_o R_s}{5.615}\frac{\partial B_g}{\partial p} - \right.$$

$$\left. \frac{N_o B_g}{5.615}\frac{\partial R_s}{\partial p} - \frac{W R_{sw}}{5.615}\frac{\partial B_g}{\partial p} - \frac{N_o B_g}{5.615}\frac{\partial R_{sw}}{\partial p} + \frac{\partial V_r}{\partial p}\right\} \quad \text{A.4}$$

$$\Phi = \frac{V_{pv}}{V} \quad \text{A.5}$$

$$S_o = \frac{N_o B_o}{V_{pv}} \quad \text{A.6}$$

$$S_w = \frac{WB_w}{V_{pv}} \qquad \text{A.?}$$

$$S_g = \frac{\left(G - N_o R_s - WR_{sw}\right) B_g}{5.615 V_{pv}} \qquad \text{A.8}$$

Substitution of Eqs. A.5 - A.8 in Eq. A.4 and insertion of ratios $\frac{B_o}{B_o}$, $\frac{B_w}{B_w}$ and $\frac{B_g}{B_g}$ in appropriate places yields:

$$\begin{aligned}
\Phi c_t = & -\Phi \frac{N_o B_o}{V_{pv}} \frac{1}{B_o} \frac{\partial B_o}{\partial p} - \Phi \frac{W B_w}{V_{pv}} \frac{1}{B_w} \frac{\partial B_w}{\partial p} \\
& - \Phi \frac{G B_g}{5.615 V_{pv}} \frac{1}{B_g} \frac{\partial B_g}{\partial p} + \Phi \frac{N_o R_s B_g}{5.615 V_{pv}} \frac{1}{B_g} \frac{\partial B_g}{\partial p} \\
& + \Phi \frac{N_o B_o}{5.615 V_{pv}} \frac{B_g}{B_o} \frac{\partial R_s}{\partial p} + \Phi \frac{WR_{sw} B_g}{5.615 V_{pv}} \frac{1}{B_g} \frac{\partial B_g}{\partial p} \\
& + \Phi \frac{W B_w}{5.615 V_{pv}} \frac{B_g}{B_w} \frac{\partial R_{sw}}{\partial p} - \Phi \frac{1}{V_{pv}} \frac{\partial V_r}{\partial p}
\end{aligned} \qquad \text{A.9}$$

Or:

$$\begin{aligned}
c_t = & S_o \left(-\frac{1}{B_o} \frac{\partial B_o}{\partial p} + \frac{1}{5.615} \frac{B_g}{B_o} \frac{\partial R_s}{\partial p} \right) + \\
& S_w \left(-\frac{1}{B_w} \frac{\partial B_w}{\partial p} + \frac{1}{5.615} \frac{B_g}{B_w} \frac{\partial R_{sw}}{\partial p} \right) + \\
& S_g \left(-\frac{1}{B_g} \frac{\partial B_g}{\partial p} \right) + \frac{1}{V_{pv}} \frac{\partial V_r}{\partial p}
\end{aligned} \qquad \text{A. 10}$$

Assuming no change in bulk volume, $dV_r = -dV_{pv}$, thus:

$$-\frac{1}{V_{pv}}\frac{\partial V_r}{\partial p}=\frac{1}{V_{pv}}\frac{\partial V_{pv}}{\partial p}=c_f \qquad \text{A.11}$$

the effective pore space compressibility. Thus the total system isothermal compressibility is:

$$c_t = S_o\left[-\frac{1}{Bo}\frac{\partial B_o}{\partial p}-\frac{B'_g}{Bo}\frac{\partial R_s}{\partial p}\right]-$$

$$S_w\left[-\frac{1}{B_w}\frac{\partial B_w}{\partial p}+\frac{B'_g}{B_w}\frac{\partial R_{sw}}{\partial p}\right]+$$

$$S_g\left[-\frac{1}{B_g}\frac{\partial B_g}{\partial p}\right]+c_f \qquad \text{A.12}$$

where B'_g has the units res. bbl/scf. This derivation does not include terms involving $\frac{\partial S}{\partial p}$. That **is,** it **is** assumed that saturations do not change with pressure change. Furthermore the production of fluid from the system is not considered. These assumptions are inherent in total system compressibilities in use in **well** test analysis today.

APPENDIX B

Computer Programs

This appendix contains computer programs to study multiphase-multicomponent compressibility. The main programs included are for compressibiiity calculations due to expansion for a single-component system, and for a multicomponent system, and for production compressibility for gas production and for multiphase production according to relative permeability-saturation relationships.

Input data are in metric units. The vapor-liquid equilibrium calculations were done using published routines by Prausnitz et al. (1980), and are presented here for the sake of completeness. The energy balance in the FLASH routine was modified to allow an energy contribution from a rock component.

Liquid densities for the water cases were calculated with published routines of Reynolds (1979), and for liquid hydrocarbon cases were calculated with Standing's (1977) method.

```
**********************************************************************
C MAIN PROGRAM FOR COMPRESSIBILITY CALCULATIONS DUE TO EXPANSION COUPLED
C WITH DRIVER PROGRAM FOR SUBROUTINES FLASH AND BUDET FOR SYSTEMS OF UP TO
C  10 COMPONENTS WITH VAPOR AND LIQUID FEED STREAMS (PRAUSNITZ ET AL. (1980))
C
**********************************************************************
C
      REAL Z(10),X(10),Y(10),K(10),V(10),BD(2),F(10)
      INTEGER ID(10),ER
      COMMON/PURE/NM1(100),NM2(100),TC(100),PC(100),RD(100),DM(100),
     1 A(100),C1(100),C2(100),C3(100),C4(100),C5(100),RU(100),QU(100),
     2 QP(100),D1(100),D2(100),D3(100),D4(100)
      COMMON/BINARY/ETA(5050),U(100,100)
      OPEN(UNIT=7,FILE='h2o',ACCESS='SEQUENTIAL',STATUS='OLD')
      OPEN(UNIT=8,FILE='c2o',ACCESS='SEQUENTIAL',STATUS='OLD')
      OPEN(UNIT=9,FILE='cgo',ACCESS='SEQUENTIAL',STATUS='OLD')
      OPEN(UNIT=10,FILE='qua',ACCESS='SEQUENTIAL',STATUS='OLD')
      AKK=0.
      VP1=0.
C ONE COMPONENT CASE, WATER
  100 CALL PARIN(1,ER)
      IF(ER.GT.0) GO TO 900
  200 READ(5,01) N
      NN=N
      READ(5,*)DELP
      WRITE(6,01)
   01 FORMAT(I3)
      IF(N.EQ.0) STOP
      READ(5.02) L,T,P,(ID(I),F(I),I=1,4)
      WRITE(6,02) L,T,P,(ID(I),F(I),I=1,4)
   02 FORMAT(I5,F10.2,F10.3,(5(I4,F6.3)))
      READ(5,03) TF,PF,VF,TV,(V(I),I=1,4)
      WRITE(6,03) TF,PF,VF,TV,(V(I),I=1.4)
   03 FORMAT(F10.2,F10.3,F10.4,F10.2,(5F8.3))
  206 CONTINUE
      DO 207 I=1,2
  207 BD(I)=0.
      DO 209 I=1,N
      Z(I)=(1.-VF)*F(I)+VF*V(I)
      X(I)=0.
  209 Y(I)=0.
  210 CALL BUDET(1,N,ID,1,Z,Y,BD(1),P,K,ER)
      CALL BUDET(2,N,ID,2,X,Z,BD(2),P,K,ER)
  220 DO 221 I=1,N
      X(I)=0.
  221 Y(I)=0.
      Q=0.0
      CALL FLASH(L,N,ID,2,VF,F,V,TF,TV,PF,Q,X,Y,T,P,K,ER)
      IF(ER.GT.0) WRITE(6,15) ER
   15 FORMAT(/' ERROR IN FLASH',I5/)
      IF(ER.GT.0) STOP
      II=ID(1)
      IF(L.EQ.1) WRITE(6,11)
      IF(L.EQ.2) WRITE(6,12)
```

```
 WRITE(6,13)
11 FORMAT(////48X,'FEED',26X,'TB/TD',15X,'ISOTHERMAL FLASH')
12 FORMAT(////48X,'FEED',26X,'TB/TD',15X,'ADIABATIC FLASH')
13 FORMAT(1X,'INDEX',3X,'COMPONENT',10X,'XF',4X,'TF(K) PF(BAR)',
 1 2X,'VFRACT  YF',4X,'TV(K)',6X,' (K)',5X,'P(BAR)  T(K)',
 2 4X,'V/F',6X,'X',5X,'Y'/)
 WRITE(6,16) II,NM1(II),NM2(II),F(1),TF,PF,VF,V(1),TV,BD(1),P,T,Q,
 1 X(1),Y(1)
 II=ID(2)
16 FORMAT(I2,2A10,F8.3,F8.1,F7.1,F9.3,F7.3,F8.1,F12.2,F9.1,F8.1,
 1 3F8.4)
 WRITE(6,17) II,NM1(II),NM2(II),F(2),V(2),BD(2),X(2),Y(2)
17 FORMAT(I2,2A10,F8.3,24X,F7.3,8X,F12.2,25X,2F8.4)
 WRITE(6,22)Q,T,P
22 FORMAT(////,'V/F=',E10.4,2X,'T=',E10.4,2X,'P=',E10.4,//)
 VF=Q
 IF(N.LT.3) GO TO 230
 DO 228 I=3,N
 II=ID(I)
 WRITE(6,18) II,NM1(II),NM2(II),F(I),V(I),X(I),Y(I)
18 FORMAT(I2,2A10,F8.3,24X,F7.3,45X,2F8.4)
228 COXTINUE
230 VF=Q
 TF=T
 DO 231 I=1,NN
 F(I)=X(I)
231 V(I)=Y(I)
 TV=T
 PF=P
 PRT=P/(83.1473*T)
 call vol(prt,t,vv,zz,dz)
 CG=(1/P)-(1/ZZ)*DZ
 WRITE(6,888)ZZ,VV,T,P,DZ,CG
888 FORMAT(2X,'Z=',E10.4,2X,'V=',E10.4,'cc/gm',2X,'T=',E10.4'K',2X,
 1'P=',E10.4,' bar',///,2x,'DZ=',E14.5,3x,'CG=',E10.5,' 1/bar'//)
 CALL RHOW(T,RF)
 VVL=18./RF
 VP2=VVL+Q*(VV-VVL)
 IF(AKK.EQ.0) GO TO 91
 DELV=VP2-VP1
 PPM=(P+(P-DELP))/2.
 VPM=(VP2+VP1)/2.
 CT=(1/VPM)*(DELV/DELP)
 write(8,*)ppm,ct
 write(9,*)ppm,cg
 write(10,*)ppm,q
 WRITE(6,89)VPM,P,CT
89 FORMAT(2X,'VT=',F10.4,'CC/GM',2X,'P=',F10.4,'BAR',/,2X,'CT
 1 =',F10.5,1'/BAR')
91 VP1=VP2
 P=P-DELP
 write(7,*) vpm,ppm
 write(6,*)p,t
 IF(P.LE.0.5)STOP
```

```
      AKK=1.
      VF=Q
      WRITE(6,*)VF,Q
      GO TO 206
  900 WRITE(6,19)
   19 FORMAT(/'  ERROR IN PARAMETER INPUT DECK'/)
      STOP
      END
      subroutine vol(prt,t,vv,zz,dz)
      COMMON/COEFF/BMM
      BM=BMM
      ZZ= 1+BM*PRT
      VV=ZZ/PRT
      DZ=BM/(83.1473*T)
      return
      end
```

```
***********************************************************************
***********************************************************************
C MAIN PROGRAM FOR COMPRESSIBILITY CALCUALTIONS DUE TO EXPANSION COUPLED
C WITH DRIVER PROGRAM FOR SUBROUTINES FLASH AND BUDET FOR SYSTEMS OF UP TO
C  10 COMPONENTS WITH VAPOR AND LIQUID FEED STREAMS (PRAUSNITZ ETAL. (1980)).
C LIQUID DENSITIES CALCULATED WITH STANDING'S (1977) METHOD>
C
***********************************************************************
***********************************************************************
C
C
      REAL Z(10),X(10),Y(10),K(10),V(10),BD(2),F(10),PD(2)
      INTEGER ID(10),ER
      COMMON/PURE/NM1(100),NM2(100),TC(100),PC(100),RD(100),DM(100),
     1 A(100),C1(100),C2(100),C3(100),C4(100),C5(100),RU(100),QU(100),
     2 QP(100),D1(100),D2(100),D3(100),D4(100)
      COMMON/BINARY/ETA(5050),U(100,100)
      COMMON/COEF/BMM
      OPEN(UNIT=7,FILE='hc7',ACCESS='SEQUENTIAL',STATUS='OLD')
      open(UNIT=3,FILE='rhhc',ACCESS='SEQUENTIAL',STATUS='OLD')
      open(UNIT=8,FILE='sthc',ACCESS='SEQUENTIAL',STATUS='OLD')
      open(UNIT=9,FILE='gasc',ACCESS='SEQUENTIAL',STATUS='OLD')
      open(UNIT=10,FILE='volt',ACCESS='SEQUENTIAL',STATUS='OLD')
      open(UNIT=11,FILE='quth',ACCESS='SEQUENTIAL',STATUS='OLD')
      open(UNIT=12,FILE='ct1h',ACCESS='SEQUENTIAL',STATUS='OLD')
      open(UNIT=13,FILE='ct2h',ACCESS='SEQUENTIAL',STATUS='OLD')
      rewind 7
      rewind 3
      VP1=0.
      FF=1.
      akk=0.
      READ(7,*)DELP,TOL,TCA
      READ(7,*)N
      NC=N
 100  CALL,PARIN(N,ER)
      IF(ER.GT.0) GO TO 900
 200  READ(7,01) N
 01   FORMAT(I3)
      IF(N.EQ.0) STOP
      READ(7,02) L,T,P,(ID(I),F(I),I=1,5)
      READ(7,201)(ID(I),F(I),I=6,NC)
 201  FORMAT(5(I4,F6.3))
      WRITE(6,02) L,T,P,(ID(I),F(I),I=1,5)
 02   FORMAT(I5,F10.2,F10.3,(5(I4,F6.3)))
      WRITE(6,201)(ID(I),F(I),I=6,NC)
      READ(7,03) TF,PF,VF,TV,(V(I),I=1,5)
      WRITE(6,03) TF,PF,VF,TV,(V(I),I=1,5)
 03   FORMAT(F10.2,2F10.3,F10.2,(5F8.3))
      READ(7,202)(V(I),I=6,NC)
      WRITE(6,202)(V(I),I=6,NC)
 202  FORMAT(5F8.3)
 206  CONTINUE
      DO 207 I=1,2
      pd(i)=0.
```

```
207 BD(I)=0.
    DO 209 I=1,N
    Z(I)=(1.-VF)*F(I)+VF*V(I)
    X(I)=0.
209 Y(I)=0.
    call budep(1,n,id,1,z,y,t,pd(1),k,er)
    call budep(2,n,id,2,x,z,t,pd(2),k,er)
210 CALL BUDET(1,N,ID,1,Z,Y,BD(1),P,K,ER)
    CALL BUDET(2,N,ID,2,X,Z,BD(2),P,K,ER)
220 DO 221 I=1,N
    X(I)=0.
221 Y(I)=0.
    Q=0.
    CALL FLASH(L,N,ID,2,VF,F,V,TF,TV,PF,Q,X,Y,T,P,K,ER)
    IF(ER.GT.0) WRITE(6,15) ER
 15 FORMAT(/' ERROR IN FLASH',I5/)
    II=ID(1)
    write(6,*)pd(1),pd(2)
    IF(L.EQ.1) WRITE(6,11)
    IF(L.EQ.2) WRITE(6,12)
    WRITE(6,13)
 11 FORMAT(////48X,'FEED',26X,'TB/TD',15X,'ISOTHERMAL FLASH')
 12 FORMAT(////48X,'FEED',26X,'TB/TD',15X,'ADIABATIC FLASH')
 13 FORMAT(1X,'INDEX',3X,'COMPONENT',10X,'XF',4X,'TF(K)  PF(BAR)',
   1 2X,'VFRACT   YF',4X,'TV(K)',6X,' (K) ',5X,'P(BAR)   T(K)',
   2 4X,'V/F',6X,'X',5X,'Y'/)
    WRITE(6,16) II,NM1(II),NM2(II),F(1),TF,PF,VF,V(1),TV,BD(1),P,T,Q,
   1 X(1),Y(1)
    II=ID(2)
 16 FORMAT(I2,2A10,F8.3,F8.1,F7.1,F9.3,F7.3,F8.1,F12.2,F9.1,F8.1,
   1 3F8.4)
    WRITE(6,17) II,NM1(II),NM2(II),F(2),V(2),BD(2),X(2),Y(2)
 17 FORMAT(I2,2A10,F8.3,24X,F7.3,8X,F12.2,25X,2F8.4)
    JF(N.LT.3) GO TO 230
    DO 228 I=3,N
    II=ID(I)
    WRITE(6,18) II,NM1(II),NM2(II),F(I),V(I),X(I),Y()
 18 FORMAT(I2,2A10,F8.3,24X,F7.3,45X,2F8.4)
228 CONTINUE
    IF(ER.GT.0) STOP
230 VF=Q
    TF=T
    TV=T
    BM=BMM
    PRT=P/(83.1473*T)
    ZZ= 1+BM*PRT
    VV=ZZ/PRT
    DZ=BM/(83.1473*T)
    CG=(1/P)-(1/ZZ)*DZ
    WRITE(6,888)ZZ,W,T,P,DZ,CG
888 FORMAT(2X,'Z=',E10.4,2X,'V=',E10.4,'cc/gm',2X,'T=',E10.4,'K',2X,
   1'P=',E10.4,' bar',///,2x,'DZ=',E14.5,3x,'CG=',E10.5,' 1/bar',//)
C  LIQUID SPECIFIC MOLAR VOLUME (cc/gmol)
    rrite(6,*)p,t,vf
```

```
      PR=P
      TE=T
      CALL RHOHC(X,P,T,NC,RHOME,PM1,API)
      P=PR
      T=TE
      VVL=RHOME
      write(6,*)rhome,pm1,api
      if(akk.eq.0) VPP=VVL
      if(akk.eq.0) VVI=VVL
C  MOLES OF LIQUID
      VFN=(1-VF)*FF
C  LIQUIDVOLUME (cc)
      VW=VVL*VFN
C  VOLUME OF GAS REMAINING IN BLOCK
      VGR=VVI-VW
C  TOTAL SPECIFIC MOLAR VOLUME OF MIXTURE
      VP2=VVL+Q*(VV-VVL)
      DELV=VP2-VP1
C  AVREAGE SPECIFIC MOLAR VOLUME
      PPM=(P+(P-DELP))/2.
      VPM=(VP2+VP1)/2.
C  ADIABATIC COMPRESSIBILITY OF MIXTURE (1/BAR)
      write(6,*)p,t,vf,vfn,vw
      if(akk.eq.0) go to 65
      if(tca.ne.1) go to 123
      CT=(1/VPM)*(DELV/DELP)
      CT1=(1/VP1)*(DELV/DELP)
      CT2=(1/VP2)*(DELV/DELP)
      call comp(delp,vp1,vp2,vpa,cta,ct1a,ct2a,ppma)
      write(8,*) ppm,ct,cta
      write(12,*) ppm,ct1,ct1a
      write(13,*) ppm,ct2,ct2a
      write(10,*)vpm,ppm,p,vp1,vp2
      write(9,*) ppm,cg
      write(11,*)ppm,q
      write(6,124)ct
  124 format(//,2x,'TWO PHASE CT=',f10.4,'1/bar')
      go to 65
C  APPARENT COMPRESSIBILITY (1/BAR)
  123 CAPP=(1/VPP)*(VF*(VV-VVL)/DELP)
C  GAS SATURATION REMAINIG IN BLOCK
      SAT=VGR/(VW+VGR)
      IF(SAT.GT.1.00) STOP
C  MOLES OF GAS IN BLOCK
      NS=VGR/VV
C  NEW FRACTIONAL VAPORIZATION
      VF=NS/(NS+VFN)
      FF=NS+VFN
      if(ff.gt.1.01)stop
      VPOR=VW+VGR
      WRITE(6,88) VW,VGR,VPOR
   88 FORMAT(2X,'VW=',F10.6,/,2X,'VGR=',F10.6,/,2X,'VPOR=',E10.6)
      WRITE(6,89)VP2,P,CT,CAPP,SAT
   89 FORMAT(2X,'VT=',F10.4,'CC/GM',2X,'P=',F10.4,'BAR',/,2X,'CT
```

```
    1=',F10.5,'1/BAR',/,2X,'CAPP=',F10.5,/,2X,'SAT=',F6.4)
 65 CONTINUE
    write(6,*)p,t,vf,ff
    DO 66 MM=1,8
    F(MM)=X(MM)
 66 V(MM)=Y(MM)
    VP1=VP2
C  DECREASE PRESSURE FOR NEXT CALCULATION
    PF=P
    P=P-DELP
    IF(P.LE.TOL) STOP
    akk=1.
    GO TO 206
900 WRITE(6,19)
 19 FORMAT(/' ERROR IN PARAMETER INPUT DECK/)
    STOP
    END
    SUBROUTINE PARIN(M,ERIN)
C PARIN READS PURE COMPONENT AND BINARY PARAMATERS FROM FORMATED CARDS
C OR OTHER FILES CONTAINING EQUIVALENT RECORDS, INTO COMMON STORAGE
C BLOCKS /PURE/ AND /BINARY/ FOR A LIBRARY OF M (LE.lOO)
C COMPONENTS. INPUT IS TAKEN FROM LOGICAL UNIT 3 PARIN RETURN ERIN=0
C UNLESS A DISCREPANCY IS DETECTED IN THE INPUT FILE, IN WHICH CASE IT
C RETURNS ERIN=5.
    INTEGER ERIN
    COMMON/PURE/NM1(100),NM2(100),TC(100),PC(100),RD(100),DM(100),
   1 A(100),C1(100),C2(100),C3(100),C4(100),C5(100),RU(100),QU(100),
   2 QP(100),D1(100),D2(100),D3(100),D4(100)
    COMMON/BINARY/ETA(5050),U(100,100)
    COMMON/INIP/PHI,PM1,RF1,NC
    OPEN(UNIT=7,FILE='hc7',ACCESS='SEQUENTIAL',STATUS='OLD')
100 ERIN=0
    IF(M.GT. 100) GO TO 900
    NC=M
C READ PURE COMPONENT PARAMETERS
    READ(7,*) PHI
    DO 109 I=1,M
C FIRST CARD FOR PURE COMPONENT PARAMETERS
    READ(7,07) J
 07 FORMAT(I3)
    READ(7,01) NM1(J),NM2(J),TC(J),PC(J),A(J),RD(J),DM(J),RU(J),
   1 QU(J),QP(J)
    WRITE(6,01) NM1(J),NM2(J),TC(J),PC(J),A(J),RD(J),DM(J),RU(J)
   1 ,QU(J),QP(J)
 01 FORMAT(2A10,2F7.2,F6.4,F6.4,4F5.2)
C CHECK CARD SEQUENCE
    IF(J.NE.I) GO TO 900
C SECOND CARD FOR PURE COMPONENT
    READ(7,02) C1(J),C2(J),C3(5),C4(J),C5(J)
    WRITE(6,02) C1(J),C2(J),C3(J),C4(J),C5(J)
 02 FORMAT(1X,5E14.7)
    IF(J.NE.I) GO TO 900
C THIRD CARD FOR PURE COMPONENT
    READ(7,03) D1(J),D2(J),D3(J),D4(J)
```

```
      WRITE(6,03) D1(J),D2(J),D3(J),D4(J)
   03 FORMAT(2X,4E14.7)
      IF(J.NE.I) GO TO 900
  109 CONTINUE
C CHECK REQUIRED BLANK CARD SEPARATOR
      READ(7,07) J
      IF(J.NE.0) GO TO 900
C READ IN BINARY ASSOCIATION PARAMETERS ETA
  110 DO 119 I=1,M
      I1=(I-1)*I/2+1
      I2=(I-1)*I/2+I
      READ(7,04) (ETA(IJ),IJ=I1,I2)
   04 FORMAT(7F4.2)
  119 CONTINUE
C CHECK FOR REQUIRED BLANK CARD SEPARATOR
      E=0.
      IF(ABS(E).GT.1.E-19) GO TO 900
C INITIALLY ZERO UNIQUAC BINARY INTERACTION PARAMETERS
  120 DO 121 I=1,M
      DO 121 J=1,M
  121 U(I,J)=0.
C READ IN UNIQUAC BINARY PARAMETERS
  125 READ(7,05)I,J,UIJ,UJI
   05 FORMAT(2I5,2F10.2)
      WRITE(06,05)I,J,UIJ,UJI
C TERMINATE READ IN BLANK FINAL CARD
      IF(I.EQ.0) GO TO 130
      U(I,J)=UIJ
      U(J,I)=UJI
      GO TO 125
  130 DO 139 I=1,M
C SET U(I,I) TO 1E+20 FOR NONCONDENSABLE I
      IF(A(I).LT.1.E-19) U(I,I)=1.E+20
  139 CONTINUE
      RETURN
C ERROR RETURN FOR DISCREPANCY IN INPUT DATA FILE
  900 ERIN=5
      RETURN
      END
```

```
C LIQUID HYDROCARBON DENSITY CALCULATIONS< STANDING''S METHOD
      subroutine rhohc (x,p,t,n,rhome,pm1,api)
      dimension x(10),pm(10),rho(10)
      open(UNIT=3,FILE='rhhc',ACCESS='SEQUENTIAL',STATUS:=' OLD')
      rewind 3
      n=?
      read(3,*) (pm(i),rho(i), i=1,n)
      rh3p=0.0
      pm3p=0.0
      do 1 i=3,n
      rh3p=rh3p+(pm(i)*x(i))/rho(i)
    1 pm3p=pm3p+(pm(i)*x(i))
      rho3p=pm3p/rh3p
      den=0.
      do 2 i=2,n
    2 den=den+pm(i)*x(i)
      w2=100.*(x(2)*pm(2))/den
      deno=0.
      do 3 i=1,n
    3 deno=deno+pm(i)*x(i)
      pm 1=deno
      w1=100.*(x(1)*pm(1))/deno
      rho2p=rho3p*( 1.0-001386*w2-0.000082*(w2**2.)
     1)+(0.379*w2)+0.0042*(w2**2.)
      rho1p=rho2p*(1-0.012*w1-0.000158*(w1**2.))+0.0133*w1
     1+0.00058*(w1**2.)
c pressure correction
      p=p*14.5
      deltap=(0.167+16.81*(10.**(-0.0425*rho1p)))*(p/1000.)
     1-0.01*(0.299+263.*(10.**(-0.0603*rho1p)))*(p/1000.)**2.
c temperature correction
      t=t*1.8-460.
      deltat=(0.0133+152.4*((rho1p+deltap)**(-2.45)))*(t-60.)
     1-((8.1*(10.**-6.))-0.0622*10.**(-0.0764*(rho1p+deltap)))
     2( (t-60.)**2.)
      rho1=rho1p+deltap-deltat
      p=p/14.5
      t=(t+460)/1.8
      call rhow (t,rf1)
      rf=rf1*62.42828
      sgo=rho1/rf
c hydrocarbon molar density in si units g mol / cc
      rhome=(rho1/pm1)*0.01604
c addition of water density using mol fraction as the wheighting parameter
      rhome=((rf1/18.)*x(8))+rhome
      api=(141.5/sgo)-131.5
      return
      end

C WATER LIQUID DENSITY CALCULATIONS
      SUBROUTINE DH2O(T,RF)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION G(8)
```

```
      DATA RHOC,G/317.0D0,0.36711257D1,-0.28512396D2,0.22265240D3,
     1 -0.88243852D3,0.20002765D4,-0.26122557D4,0.18297674D4,
     2 -0.53350520D3/
      DATA TCK/647.286D0/
      IF (T.EQ.TCK)  GO TO 30
      OT=1.0D0/3.0D0
      X=(1.D0-T/TCK)**OT
      IF (X.LT.1.0D-6)  X=0.D0
      CO=X
      SUM=1.0D0
      DO 20 I=1,8
      SUM=SUM+G(I)*CO
   20 CO=CO*X
      RHOF=RHOC*SUM
      GO TO 40
   30 RHOF=RHOC
      GO TO 40
   40 RF=RHOF*(1.E-03)
      RETURN
      END
      SUBROUTINE RHOW(T,RF)
      IMPLICIT REAL*8  (A-H,O-Z)
      EXTERNAL DH20
      CALL DH2O(T,RF)
      RETURN
      END
      subroutine comp(delp,vp1,vp2,vpm,ct,ct1,ct2,ppm)
      vpm=(vp1+vp2)/2.
      vpmi=1./vpm
      delv=vp2-vp1
      ct=vpmi*delv/delp
      ct1=(1./vp1)*(delv/delp)
      ct2=(1./vp2)*(delv/delp)
      ppm=(p+(p-delp))/2.
      return
      end
```

```
************************************************************************
C
C MAIN PROGRAM FOR COMPRESSIBILITY CALCULATIONS WITH  PRODUCTION
C OF THE HIGHER ENTHALPY FLUID, GAS PRODUCTION, COUPLED
C WITH DRIVER PROGRAM FOR SUBROUTINES FLASH AND BUDET FOR SYSTEMS OF UP TO
C  10 COMPONENTS WITH VAPOR AND LIQUID FEED STREAMS (PRAUSNITZ ET AL. (1980)
C
************************************************************************
      REAL Z(10),X(10),Y(10),K(10),V(10),BD(2),F(10)
      INTEGER ID(10),ER
      COMMON/PURE/NM1(100),NM2(100),TC(100),PC(100),RD(100),DM(100),
     1 A(100),C1(100),C2(100),C3(100),C4(100),C5(100),RU(100),QU(100),
     2 QP(100),D1(100),D2(100),D3(100),D4(100)
      COMMON/BINARY/ETA(5050),U(100,100)
      COMMON/COEFF/BMM
      open(UNIT=8,FILE='capd',ACCESS='SEQUENTIAL',STATUS='OLD')
      VP1=0.
      FF=1.
      akk=0.
C ONE COMPONENT CASE N=1, WATER
  100 CALL PARIN(1,ER)
      IF(ER.GT.0)  GO TO 900
  200 READ(5,01) N,DELP
   01 FORMAT(I3,F6.4)
      IF(N.EQ.0) STOP
      READ(5,02) L,T,P,(ID(I),F(I),I=1,4)
      WRITE(6,02) L,T,P,(ID(I),F(I),I=1,4)
   02 FORMAT(I5,F10.2,F10.3,(5(I4,F6.3)))
      READ(5.03)  TF,PF,VF,TV,(V(I),I=1,4)
      WRITE(6,03) TF,PF,VF,TV,(V(I),I=1,4)
   03 FORMAT(F10.2,F10.3,F10.4,F10.2,(5F8.3))
  206 CONTINUE
      DO 207 I=1,2
  207 BD(I)=0.
      DO 209 I=1,N
      Z(I)=(1.-VF)*F(I)+VF*V(I)
      X(I)=0.
  209 Y(I)=0.
  210 CALL BUDET(1,N,ID,1,Z,Y,BD(1),P,K,ER)
      CALL BUDET(2,N,ID,2,X,Z,BD(2),P,K,ER)
  220 DO 221 I=1,N
      X(I)=0.
  221 Y(I)=0.
      Q=0.0
      CALL FLASH(L,N,ID,2,VF,F,V,TF,TV,PF,Q,X,Y,T,P,K,ER)
      IF(ER.GT.0) WRITE(6,15) ER
   15 FORMAT(/'  ERROR IN FLASH',I5/)
      II=ID(1)
      IF(L.EQ.1) WRITE(6,11)
      IF(L.EQ.2) WRITE(6,12)
      WRITE(6,13)
   11 FORMAT(////48X,'FEED',26X,'TB/TD',15X,'ISOTHERMAL FLASH')
   12 FORMAT(////48X,'FEED',26X,'TB/TD',15X,'ADIABATIC FLASH')
   13 FORMAT(1X,'INDEX',3X,'COMPONENT',10X,'XF',4X,'TF(K)  PF(BAR)',
```

```
     1 2X,'VFRACT   YF',4X,'TV(K)',6X,' (K) ',5X,'P(BAR)   T(K)',
     2 4X,'V/F',6X,'X',5X,'Y'/)
      WRITE(6,16) II,NM1(II),NM2(II),F(1),TF,PF,VF,V(1),TV,BD(1),P,T,Q,
     1 X(1),Y(1)
      II=ID(2)
   16 FORMAT(I2,2A10,F8.3,F8.1,F7.1,F9.3,F7.3,F8.1,F12.2,F9.1,F8.1,
     1 3F8.4)
      WRITE(6,17) II,NM1(II),NM2(II),F(2),V(2),BD(2),X(2),Y(2)
   17 FORMAT(I2,2A10,F8.3,24X,F7.3,8X,F12.2,25X,2F8.4)
      WRITE(6,22)Q,T,P
   22 FORMAT(////,'V/F=',E10.4,2X,'T=',E10.4,2X,'P=',E10.4,//)
      IF(N.LT.3) GO TO 230
      DO 228 I=3,N
      II= ID(I)
      WRITE(6,18) II,NM1(II),NM2(II),F(I),V(I),X(I),Y(I)
   18 FORMAT(I2,2A10,F8.3,24X,F7.3,45X,2F8.4)
  228 CONTINUE
  230 VF1=Q
      TF=T
      TV=T
      PF=P
C SECOND VIRIAL COEFFICIENT
      BM=BMM
      PRT=P/(83.1473*T)
C GAS DEVIATION FACTOR
      ZZ=1+BM*PRT
C GAS SPECIFIC MOLAR VOLUME (cc/gmol)
      VV=ZZ/PRT
      DZ=BM/(83.1473*T)
C GAS COMPRESSIBILITY (EOS)
      CG=(1/P)-(1/ZZ)*DZ
      WRITE(6,888)ZZ,VV,T,P,DZ,CG
  888 FORMAT(2X,'Z=',E10.4,2X,'V=',E10.4,'cc/gm',2X,'T=',E10.4,'K',2X,
     1'P=',E10.4,' bar',///,2x,'DZ=',E14.5,3x,'CG=',E10.5,' 1/bar',//)
      PF1=P
C LIQUID SPECIFIC MOLAR VOLUME (cc/gmol)
      CALL RHOW(T,RF)
      VVL=18./RF
      if(akk.eq.0) VPP=VVL
      if(akk.eq.0) VVI=VVL
C MOLES OF WATER
      VFN=(1-VF1)*FF
C WATER VOLUME (cc)
      VW=VVL*VFN
C VOLUME OF GAS REMAINING IN BLOCK
      VGR=VVI-VW
C TOTAL SPECIFIC MOLAR VOLUME OF MIXTURE
      VP2=VVL+Q*(VV-VVL)
      DELV=VP2-VP1
C AVREAGE SPECIFIC MOLAR VOLUME
      VPM=(VP2+VP1)/2.
      PPM=(P+(P-DELP))/2.
      IF(DELP.EQ.0.) DELP=0.50
C ADIABATIC COMPRESSIBILITY OF MIXTURE (1/BAR)
```

```
      CT=(1/VPM)*(DELV/DELP)
C  APPARENT COMPRESSIBILITY (1/BAR)
      CAPP=(1/VPP)*(VF1*(VV-VVL)/DELP)
C  GAS SATURATION REMAINIG IN BLOCK
      sat=vv/(vv+((1-vf1)/vf1)*vvl)
      IF(SAT.GT.1.00) STOP
      if(vw.le.0.000) stop
C  MOLES OF GAS IN BLOCK
      NS=VGR/VV
C  NEW FRACTIONAL VAPORIZATION
      VF=NS/(NS+VFN)
      VPOR=VW+VGR
      FF=NS+VFN
      WRITE(6,88) VW,VGR,VPOR
   88 FORMAT(2X,'VW=',F10.6,/,2X,'VGR=',F10.6,/,2X,'VPOR=',F10.6)
      if(akk.eq.0) go to 90
      write(8,*)ppm,capp
      WRITE(6,89)VP2,P,CT,CAPP,SAT
   89 FORMAT(2X,'VT=',F10.4,'CC/GM',2X,'P=',F10.4,'BAR',/,2X,'CT
     1 =',F10.5,'1/BAR',/,2X,'CAPP=',F10.5,/,2X,'SAT=',F6.4)
   90 VP1=VP2
      PF=PF1
C  DECREASE PRESSURE FOR NEXT CALCULATION
      P=PF-0.5
      IF(P.LE.0.5)STOP
      IF(P.GT.100) P=PF1
      akk=1.
      GO TO 206
  900 WRITE(6,19)
   19 FORMAT(/' ERROR IN PARAMETER INPUT DECK'/)
      STOP
      END
```

```
*****************************************************************************
C
C MAIN PROGRAM FOR COMPRESSIBILTY CALCULATIONS WITH PRODUCTION ACCORDING
C TO RELATIVE PERMEABILITY-SATURATION HELATIONSHIPS COUPLED WITH
C DRIVER PROGRAM FOR SUBROUTINES FLASH AND BUDET FOR SYSTEMS OF U P TO
C 10 COMPONENTS WITH VAPOR AND LIQUID FEED STREAMS (PRAUSNITZ ET AL. (1980))
*****************************************************************************
C
C
      REAL Z(10),X(10),Y(10),K(10),V(10),BD(2),F(10)
      INTEGER ID(10),ER
      dimension sw(20),sg(20),rw(20),rg(20),pa(20),us(20),uw(20)
      COMMON/PURE/NM1(100),NM2(100),TC(100),PC(100),RD(100),DM(100),
     1 A(100),C1(100),C2(100),C3(100),C4(100),C5(100),RU(100),QU(100),
     2 QP(100),D1(100),D2(100),D3(100),D4(100)
      COMMON/BINARY/ETA(5050),U(100,100)
      COMMON/COEFF/BMM
      open(UNIT=9,FILE='fort.5',ACCESS='SEQUENTIAL',STATUS='OLD')
      open(UNIT=7,FILE='sat',ACCESS='SEQUENTIAL',STATUS='OLD')
      open(UNIT=8,FILE='cap',ACCESS='SEQUENTIAL',STATUS='OLD')
      open(UNIT=10,FILE='gcap',ACCESS='SEQUENTIAL',STATUS='OLD')
      rewind 9
C INITIAL MOL NUMBER
      FF=1.
      sat2=0.
      akk=0.
C ONE COMPONENT CASE, WATER.
  100 CALL PARIN(1,ER)
      IF(ER.GT.0) GO TO 900
  200 READ(9,01) N
   01 FORMAT(I3)
      IF(N.EQ.0) STOP
      READ(9,02) L,T,P,(ID(I),F(I),I=1,4)
      WRITE(6,02) L,T,P,(ID(I),F(I),I=1.4)
   02 FORMAT(I5,F10.2,F10.3,(5(I4,F6.3)))
      READ(9,03) TF,PF,VF,TV,(V(I),I=1.4)
      WRITE(6,03) TF,PF,VF,TV,(V(I),I=1,4)
   03 FORMAT(F10.2,F10.3,F10.4,F10.2,(5F8.3))
c delta p, time, permeability,viscosities, delx
      read(9,*)DELP,TIME,TOLL,AK,DELX
      write(6,*)delp,time,toll,ak,delx
c relative permeability data
      read(9,*)(SW(I),RW(I),I=1,13)
      read(9,*)(SG(I),RG(I),I=1,13)
      write(6,*)(SW(I),RW(I),I=1,13)
      write(6,*)(SG(I),RG(I),I=1,13)
c read viscocities gas (us) and liquid (ug)
      read(9,*)(pa(i),us(i),i=1,8)
      read(9,*)(pa(i),uw(i),i=1,8)
      read(9,*)tol,delt
  206 CONTINUE
      DO 207 I=1,2
  207 BD(I)=0.
      DO 209 I=1,N
```

```
      Z(I)=(1.-VF)*F(I)+VF*V(I)
      X(I)=0.
  209 Y(I)=0.
  210 CALL BUDET(1,N,ID,1,Z,Y,BD(1),P,K,ER)
      CALL, BUDET(2,N,ID,2,X,Z,BD(2),P,K,ER)
  220 DO 221 I=1,N
      X(I)=0.
  221 Y(I)=0.
      Q=0.0
      CALL FLASH(L,N,ID,2,VF,F,V,TF,TV,PF,Q,X,Y,T,P,K,ER)
      IF(ER.GT.0) WRITE(6.15)  ER
   15 FORMAT(/' ERROR IN FLASH',I5/)
      II=ID(1)
      IF(L.EQ. 1) WRITE(6,11)
      IF(L.EQ.2)  WRITE(6,12)
      WRITE(6,13)
   11 FORMAT(////48X,'FEED',26X,'TB/TD',15X,'ISOTHERMAL FLASH')
   12 FORMAT(////48X,'FEED',26X,'TB/TD',15X,'ADIABATIC FLASH')
   13 FORMAT( 1X,'INDEX ,3X,'COMPONENT', 10X,'XF',4X,'TF(K)  PF(BAR)',
     1 2X,'VFRACT   YF',4X,'TV(K)',6X,' (K) ',5X,'P(BAR)   T(K)',
     2  4X,'V/F',6X,'X',5X,'Y'/)
      WRITE(6, 16) II,NM1(II),NM2(II),F(1),TF,PF,VF,V(1),TV,BD(1),P,T,Q,
     1  X(1),Y(1)
      II=ID(2)
   16 FORMAT(I2,2A10,F8.3,F8.1,F7.1,F9.3,F7.3,F8.1,F12.2,F9.1,F8.1,
     1  3F8.4)
      WRITE(6,17) II,NM1(II),NM2(II),F(2),V(2),BD(2),X(2),Y(2)
   17 FORMAT(I2,2A10,F8.3,24X,F7.3,8X,F12.2,25X,2F8.4)
      WRITE(6,22)Q,T,P
   22 FORMAT(////,'V/F=',E10.4,2X,'T=',E10.4,2X,'P=',E10.4,//)
      IF(N.LT.3)  GO TO 230
      DO 228 I=3,N
      II=ID(I)
      WRITE(6,18) II,NM 1(11),NM2(II),F(I).V(I),X(I),Y(I)
   18 FORMAT(I2,2A10,F8.3,24X,F7.3,45X,2F8.4)
  228 CONTINUE
  230 VF1=Q
      TF=T
      TV=T
      PF=P
C SECOND VIRIAL COEFFICIENT
      BM=BMM
      PRT=P/(83.1473*T)
C  GAS DEVIATION FACTOR
      ZZ=1+BM*PRT
C  GAS SPECIFIC MOLAR VOLUME (cc/gmol)
      VV=ZZ/PRT
      DZ=BM/(83.1473*T)
C  GAS ISOTHERMAL COMPRESSIBILITY  (EOS)
      CG=(1/P)-(1/ZZ)*DZ
      WRITE(6,888)ZZ,VV,T,P,DZ,CG
  888 FORMAT(2X,'Z=',E10.4,2X,'V=',E10.4,'cc/gm',2X,'T=',E10.4,'K',2X,
     1'P=',E10.4,' bar',///,2x,'DZ=',E14.5,3x,'CG=',E10.5,' 1/bar',//)
      PF1=P
```

```
C  LIQUID SPECIFIC MOLAR VOLUME (cc/gmol)
      CALL RHOW(T,RF)
      VVL=18./RF
      if(akk.eq.0) VPP=VVL
      if(akk.eq.0) VVI=VVL
C  MOLES OF WATER (LIQUID)
      VFN=(1-VF1)*FF
C  WATERVOLUME (cc)
      vw1=vvl*vfn
C GAS VOLUME
      vg1=vf1*vv*ff
C  GAS  SATURATION (AFTER DELTA P)
      sat1=vv/(vv+((1-vf1)/vf1)*vvl)
      sat=(sat1+sat2)/2.
      if(akk.eq.0)sat=sat1
C LIQUID SATURATION
      satw=1-sat
C GET RELATIVE PERMEABILITIES ACCORDING TO SATURATION
      call tabseq(sw,rw,13,satw,rwk)
      call tabseq(sg,rg,13,sat,rgk)
C GET VISCOSITIES FOR GAS AND LIQUID ACCORDING TO PRESSURE
      call tabseq(pa,us,8,pf1,ug)
      call tabseq(pa,uw,8,pf1,ul)
C AREA TO FLOW
      ar=wi
C VOLUME WITHDRAWAL g GAS and w LIQUID
  788 qg=(ak*rgk*ar/(ug*delx))*delp*time
      qw=(ak*rwk*ar/(ul*delx))*delp*time
C VOLUME AFTER FLUID WITHDRAWAL
      vw=vw1-qw
      vg=vg1-qg
      vpor=vg+vw
      if(sat.gt.1.0)stop
C VOLUMETRIC BALANCE OF FLOW RATES WITHE TIME
      difn=abs(vpor-vvi)
      dif=(vpor-vvi)
      if(difn.le.toll) go to 92
      if(dif.gt.0) go to 71
      time=time-delt
      if(time.lt.O) write(6,70)
   70 format(///,'increase  delta P, time.lt.0')
      if(time.lt.0) stop
      go to 788
   71 time=time+delt
      go to 788
   92 vf=(vg/vv)/((vg/vv)+(vw/vvl))
      write(6,789)qg,qw
  789 format(/,2x,'QG=',e10.3,2x,'QW=',f10.6)
      write(6,905)difn,vvi,vpor
  905 format(2x,'difn=',f7.4,2x,'vvi=',f7.4,2x,'vpor=',f7.4)
      write(6,91)time,toll,delp
   91 format(/,2x,'time=',f6.3,2x,'toll=',f7.4,2x,'delp=',f7.4)
      WRITE(6,88) VW,VG,VPOR
   88 FORMAT(2X,'VW=',F10.6,/,2X,'VG=',F10.6,2x,'VPOR=',F10.6)
```

```
C  GAS SATURATION REMAINIG IN BLOCK
     sat2=vv/(vv+((1-vf)/vf)*vvl)
C  APPARENT COMPRESSIBILITY (1/BAR)  AND NEW V/F
     ctwo=(1/vpor)*(qg+qw)/delp
     CAPP2=(1/VPP)*(VFN-(VW/VVL))*(VV-VVL)/DELP
C  MOLES OF GAS IN BLOCK
     NS=VG/VV
C MOLES OF LIQUID IN BLOCK
     VFN=VW/VVL
C TOTAL NUMBER OF MOLES PRESENT IN BLOCK (F)
     FF=NS+VFN
     WRITE(6,90)VFN,P,CAPP2,SAT2,VF,FF
   90 FORMAT(2X,'VFN=',F10.4,'CC/GM',2X,'P=',F10.4  B  R',/,2X,
    1 /,2X,'CAPP2=',F10 5,/,2X,'SAT2=',F6.4,2x,'vf=',f10.6,
    2 2x,'F=',f10.6)
     write(7,+)pf,sat2
     write(8,*)pf,ctwo
     write(10,*)pf,cg
     write(6,901)ctwo
  901 format(2x,/,'CTWO=',f10.4)
     PF=PF 1
C  DECREASE PRESSURE FOR NEXT CALCULATION
     P=PF-delp
     IF(P.LE.tol) STOP
     IF(P.GT. 100) P=PF 1
     if(sat1.gt.1) stop
     if(sat2.gt.1) stop
     akk=1.
c
     DO 66 MM=1,N
     F(MM)=X(MM)
   66 V(MM)=Y(MM)
c
     GO TO 206
  900 WRITE(6,19)
   19 FORMAT(/' ERROR IN PARAMETER INPUT DECK /)
     STOP
     END
```

VAPOR-LIQUID EQUILIBRIUM ROUTINES

(PRAUSNITZ ET AL. 1980)

```
      SUBROUTINE FLASH(TYPE,N,ID,KEY,VF,XF,YF,TL,TV,PF,A,X,Y,T,P,K,ERF)
C FLASH CONDUCTS ISOTHERMAL (TYPE=1) OR ADIABATIC (TYPE=2) EQUILIBRIUM
C FLASH VAPORIZATION CALCULATIONS AT A GIVEN PRESSURE P (BAR) FOR THE
C
C THE SUBROUTINE ACCEPTS BOTH A LIQUID FEED OF COMPOSITION XF AT
C TEMPERATURE TL(K) AND A VAPOR FEED OF COMPOSITION YF AT TV(K) AND
C PRESSURE PF (BAR), WITH THE VAPOR FRACTION OF THE FEED BEING VF
C (MOL BASIS). FOR AN ISOTHERMAL FLASH THE TEMPERATURE T(K) MUST
C ALSO BE SUPPLIED. THE SUBROUTINE DETERMINES THE V/F RATIO A, THE
C THE LIQUID AND VAPOR PHASE COMPOSITIONS X AND Y .AND. FOR AN ADIABATIC
C FLASH, THE TEMPERATURE T(K). THE EQUILIBRIUM RATIOS K ARE ALSO P
C VIDED.IT NORMALLY RETURNS ERF=0, BUT IF COMPONENT COMBINATIONS
C LACKING DATA ARE INVOLVED IT RETURNS ERF=1, AND IF NO SOL
C FOUND IT RETURNS ERF=2. FOR FLASH T .LT. TB OR T .GT. TD FLASH RETURNS
C ERF=3 OR 4 RESPECTIVELY , AND FOR BAD INPUT DATA IT RETURNS ERF=5.
C IF ESTIMATES ARE AVAILABLE FOR A,X,Y,(AND T) T H N CAN BE ENTERED
C IN THESE VARIABLES - OTHERWISE THESE VARIABLES SHOULD BE SET TO
C ZERO.
C KEY SHOULD BE 1 ON INITIAL CALL FOR A NEW SYSTEM AND 2 OTHERWISE.
      REAL XF(N),YF(N),X(N),Y(N),K(N),Z(20),U(20),W(20),K1
      INTEGER ID(10),TYPE,ERF,ER,EB
      DATA EPS/0.001/
  100 ERF=0
      KEE=KEY
      Kv= 1
C CHECK IF FEED IS LIQUID (KV=1), AND VAPOR (KV=3), OR BOTH (KV=2).
      IF(VF.GT.0.001) KV=2
      IF(VF.GT.0.999) KV=3
      SX=0.
      SY=0.
      SXF=0.
      SYF=0.
C SUM FEED AND PHASE MOLE FRACTIONS
      DO 109 I=1,N
      SX=SX+X(I)
      SY=SY+Y(I)
      SXF=SXF+XF(I)
  109 SYF=SYF+YF(I)
C CHECK THAT SUM OF FEED MOL FRACMONS IS UNITY
      IF(KV.LE.2.AND.ABS(SXF-1.).GT.0.01) GO TO 903
      IF(KV.GE.2.AND.ABS(SYF-1.).GT.0.01) GO TO 903
C CHECK THAT FLASH PRESSURE IS WITHTIN LIMITS
      IF(P.LT.1.E-6.OR.P.GT.100.)GO TO 903
```

```
  110 GO TO (112,114,116),KV
C FOR LIQUID FEED USE XF AS ESTIMATE FOR X AND Y IF NOT GIVEN AND SET
C TOTAL FEED Z TO XF.
  112 DO 113 I=1,N
    IF(ABS(SX-1.).GT.0.01) X(I)=XF(I)
    IF(ABS(SY-1.).GT.0.01) Y(I)=XF(I)
  113 Z(I)=XF(I)
    GO TO 120
C FOR MIXED FEED USE XF AS ESTIMATE FOR X AND YF FOR Y IF NOT GIVEN
C AND FIND TOTALFEED Z
  114 DO 115 I=1,N
    IF(ABS(SX-1.).GT.0.01) X(I)=XF(I)
    IF(ABS(SY-1.).GT.0.01) Y(I)=YF(I)
  115 Z(I)=(1.-VF)*XF(I)+VF*YF(I)
    GO TO 120
C FOR VAPOR FEED USE YF AS ESTIMATE FOR X AND Y IF NOT GIVEN AND
C SET TOTAL FEED Z TO W
  116 DO 117 I=1,N
    IF(ABS(SX-1.).GT.0.01) X(I)=YF(I)
    IF(ABS(SY-1.).GT.0.01) Y(I)=YF(I)
  117 Z(I)=YF(I)
C INITIALIZE LIQUID AND VAPOR PRODUCT COMPOSITIONS
  120 DO 121 I=1,N
    U(I)=W(I)
  121 W(I)=YF(I)
C FIND INITIAL ESTIMATE FOR A (IF NOT GIVE) FOR ISOTHERMAL FLASH
    TB=TL
    IF(T.GT.200..AND.T.LT.600) TB=T
    TD=TB
    CALL BUDET(1,N,ID,KEE,Z,W,TB,P,K,EB)
    IF(EB.GT.1) GO TO 900
    CALL BUDET(2,N,ID,2,U,Z,TD,P,K,ER)
    IF(ER.GT.1) GO TO 900
    IF(TYPE.EQ.2) GO TO 125
    IF(EB.LT.-2) TB=(T-TD*VF)/(1.1-VF)
    IF(T.LT.TB) GO TO 901
    IF(T.GT.TD) GO TO 902
    IF(A.LT.0.001.OR.A.GT.0.999) A=(T-TB)/(TD-TB)
    GO TO 150
C FIND FEED ENTHALPY FOR ADIABATIC FLASH
  125 HLF=0.
    HVF=0.
    IF(PF.LT.1.E-6.OR.PF.GT.100.) GO TO 903
    IF(KV.GT.2) GO TO 126
    IF(TL.LT.200..OR.TL.GT.600.) GO TO 903
    CALL ENTH(N,ID,10,0,XF,TL,PF,HLF,ER)
    IF(ER.GT.1) GO TO 900
  126 IF(KV.LT.2) GO TO 127
    IF(TV.LT.200..OR.TV.GT.600.) GO TO 903
    CALL ENTH(N,ID,10,2,YF,TV,PF,HVF,ER)
    IF(ER.GT.1) GO TO 900
  127 HF=(1.-VF)*HLF+VF*HVF
C FIND INITIAL ESTIMATES FOR A AND T (IF NOT GIVEN) FOR ADIABATIC FLASH
    IF(EB.LT.-2) TB=200.
```

```
      IF(A.GT.0.001.AND.A.LT.0.999) GO TO 128
      CALL ENTH(N,ID,10,0,Z,TB,P,HL,ER)
      IF(ER.GT. 1) GO TO 900
      CALL ENTH(N,ID,10,2,Z,TD,P,HV,ER)
      IF(ER.GT.l)  GO TO 900
      IF(HF.LT.HL) GO TO 901
      IF(HF.GT.HV) GO TO 902
      A=(HF-HL)/(HV-HL)
  128 IF(T.GT.TB.AND.T.LT.TD) GO TO 150
      T=TB+A*(TD-TB)
C INITIALIZE ITERATIVE SOLUTION
  150 IT=0
      SL= 1.
      KEE=2
      IF(TYPE.EQ.2)  KEE=6
      KD=0
      TN=T
      AN=A
      GO TO 250
C CONDUCT NEWTON RAPHSON ITERATION (200 STATEMENTS)
  200 IT=IT+1
      IF(IT.EQ. 1) GO TO 205
      IF(TYPE.EQ.2)   GO TO 203
      IF(ABS(DFA).GE.0. 1) GO TO 203
      EPF=EPS* 10.*ABS(DFA)
      IF(ABS(F).LE.EPF) GO TO 300
      GO TO 204
C CHECK CONVERGENCE OF OBJECTIVE FUNCTION
  203 IF(FV.LE.EPS) GO TO 300
C EXIT WITHOUT SOLUTION AFTER 60 ITERATIONS
  204 IF(IT.GT.100)   GO TO 900
  205 FO=FV
      KD=0
      IF(TYPE.NE.2)   GO TO 280
C DETERMINES KS AND ENTHLPIES AT 0.2 K  T INCREASE FOR T DERIVATIVES
C (ADIABATIC)
  210 CALL VALIK(N,ID,7,X,Y,T+0.2,P,K,ER)
      IF(ER.GT. 1) GO TO 900
      CALL ENTH(N,ID,7,0,X,T+0.2,P,HL,ER)
      IF(ER.GT.1)GO TO 900
      CALL ENTH(N,ID,7,2,Y,T+0.2,P,HV,ER)
      IF(ER.GT. 1) GO TO 900
      FP=0.
C UPDATE PHASE COMPOSITION
  211 DO 214 I=1,N
      X(I)=U(I)/SX
      Y(I)=W(I)/SY
      K1=K(I)-1.
  214 FP=FP+K1*Z(I)/(K1*A+1.)
      DELT=TL-T
      QF=0.000
      GP=(A*(HV-HL)+HL-QF)/HF-1.
C FIND TEMPERATURE DERIVATIVES BY FINITE DIFFERENCES (ADIABATIC)
      DFT=(FP-F)*5.
```

```
      DGT=(GP-G)*5.
C SOLVE 2 DIMENSIONAL NEWTON-RAPHSON ITERATION FOR A AN T CORRECTIONS
C(ADIABATIC)
  220 DET=DFA*DGT-DFT*DGA
      DA=(F*DGT-G*DFT)/DET
      DT=(G*DFA-F*DGA)/DET
  230 AN=A-SL*DA
C LIMIT A TO RANGE 0 - 1
      IF(AN.LT.0.) AN=0.01
      IF(AN.GT. 1.) AN=0.99
      IF(TYPE.NE.2)   GO TO 239
      TN=T-SL*DT
C LIMIT T TO RANGE TB - TD (ADIABATIC)
      IF(TN.LT.TB) GO TO 235
      IF(TN.GT.TD) GO TO 237
      GO TO 250
C CORRECTY FOR T SET TO TB
  235 IF(EB.LT.-2) GO TO 903
      CALL BUDET(1,N,ID,2,Z,Y,TB,P,K,EB)
      IF(EB.GT. 1) GO TO 900
      TN=TB
      GO TO 251
C CORRECT X FOR T SET TO TD
  237 CALL BUDET(2,N,ID,2,X,Z,TD,P,K,ER)
      IF(ER.GT. 1) GO TO 900
      TN=TD
      GO TO 251
  239 IF(KD.EQ.l)   GO TO 25 1
C GET NEW K VALUES
  250 CALL VALIK(N,ID,KEE,X,Y,TN,P,K,ER)
      IF(ER.GT. 1) GO TO 900
  251 SX=0.
      SY=0.
      DFA=0.
C FIND EQUILIBRIUM OBJECTIVE FUNCTION F AND UNNORMALIZE COMPOSITIONS
  252 DO 254 I=1,N
      K1=K(I)-1.
      U(I)=Z(I)/(K1*AN+1.)
      W(I)=K(I)*U(I)
      SX=SX+U(I)
      SY=SY+W(I)
C FIND DERIVATIVE OF F WRT A
      DFA=DFA-(W(I)-U(I))**2/Z(1)
  254 CONTINUE
      F=SY-SX
      IF(TYPE.NE.2)   GO TO 260
  255 CALL ENTH(N,ID,KEE,0,X,TN,P,HL,ER)
      IF(ER.GT. 1) GO TO 900
      CALL ENTH(N,ID,KEE,2,Y,TN,P,HV,ER)
      IF(ER.GT. 1) GO TO 900
      DELT=TL-T
      QF=0.000
      G=(AN*(HV-HL)+HL-QF)/HF-1.
C FIND DERIVATIVE OF G WRT A (ADIABATIC)
```

```
      DGA=(HV-HL)/HF
C FIND NORM OF OBJECTIVE FUNCTION AND CHECK FOR DECREASE
  260 FV=ABS(F)
      IF(TYPE.EQ.2) FV=SQRT((F*F+G*G)/2.)
      IF(IT.EQ.0) GO TO 200
      IF(IT.LE.2) GO TO 270
      IF(KD.EQ.2) GO TO 270
      IF(FV.LE.FO) GO TO 270
C APPLY STEP LIMITING PROCEDURE TO DECREASE OBJECTIVE FUNCTION
  265 KD=1
      SL=0.7*SL
C CHECK FOR FAILURE OF STEP LIMITING
      IF(SL.LT.0.20) GO TO 268
      GO TO 230
C ABANDON STEP-LIMITING AND PROCEED
  268 AN=A
      TN=T
      KD=2
      GO TO 250
C PROCEED TO NEXT ITERATION
  270 A=AN
      T=TN
      SL=1.
      GO TO 200
C FIND NEWTON-RAPHSON CORRECTION TO A (ISOTHERMAL)
  280 DA=F/DFA
C UPDATE PHASE COMPSITIONS (ISOTHERMAL)
  281 DO 284 I=1,N
      X(I)=U(I)/SX
  284 Y(I)=W(I)/SY
      GO TO 230
C FOR CONVERGED ITERATION GET FINAL NORMALIZED PHASE COMPOSITIONS
  300 DO 304 I=1,N
      X(I)=U(I)/SX
  304 Y(I)=W(I)/SY
      ERF=ER
      RETURN
C ON FAILURE TO CONVERGE ITERATION SET A TO 0 (T TO 0 ADIABATIC AND
C ERF TO 2
  900 ERF=2
      GO TO 905
C FOR T LESS THAN TB SET ERF TO 3 (A TO 0)
  901 ERF=3
      GO TO 905
C FOR T GREATER THAN TD SET ERF TO 4 (A TO 1)
  902 ERF=4
      A=1.
      GO TO 906
C FOR BAD DATA INPUT SET ERF TO 5 (A TO 0)
  903 ERF=5
  905 CONTINUE
  906 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE VALIK(N,ID,KEY,X,Y,T,P,K,ERR)
C VALIK CALCULATES VAPORIZATION EQULIBRIUM COEFICIENTS , K, FOR ALL N
C COMPONENTS (N.LE.20) WHOSE INDICES APPEAR IN VECTOR ID,GIVEN
C TEMPERATURE T(K), PRESSURE P(BAR), AND ESTIMATES OF PHASE COMPOSITION
C X AND Y (USED WITHOUT CORRECTION IN EVALUATION OF ACTIVITIES,ETC).
C CALCULATIONS ARE AN IMPLEMANTATION OF THE UNIQUAC MODEL.
C VALIK NORMALLY RETURNS ERR'0,BUT IF COMPONENT COMBINATIONS LACKING
C DATA ARE INVOLVED IT RETURNS ERb o AND IF NO SOLUTION IS FOUND
C IT RETURNS ERR=2. KEY SHOULD BE 1 ON INITIAL CALL FOR A SYSTEM,2 ON
C SUBSEQUENT CALL WHEN ALL VARIABLES ARE CHANGED, 3 IF ONLY COMPOSITION
C IS CHANGED, AND 4 IF ONLY T (AND P)IS CHANGED. KEY IS 6 OR 7,
C INSTEAD OF 2 OR 4, IF ENTH CALLS ARE TO BE MADE FOR SAME CONDITIONS.
      REAL X(N),Y(N).K(N),PHI(20),GAM(20),XF(20),YF(20)
      INTEGER ID(10),ERR,ER,ERG,IDF(20)
      COMMON/VAL/FIP(20)
  100 ERR=0
      T1=T
C CONVERT VECTORS TO DIMENSION 20 TO MATCH LOWER LEVEL SUBROUTINES
  101 DO 102 I=1,N
      XF(I)=X(I)
      YF(I)=Y(I)
  102 IDF(I)=ID(I)
C GET VAPOR PHASE FUGACITY COEvce8rq'TS, PHI
  110 CALL PHIS(N,IDF,KEY,YF,T,P,PHI,ER)
      IF(ER.GT.I) GO TO 900
      GO TO(120,120,130,120,120,120,120,120,120,120),KEY
C GET PURE COMPONENT LIQUID FUGACITIES, FIP
  120 CALL PURF(N,IDF,T,P,FIP)
C GET LIQUID PHASE ACTIVITY COEFFICIENTS, GAM
  130 CALL GAMMA(N,IDF,KEY,XF,T,GAM,ERG)
C CALCULATE VAPORIZATION EQUILIBRIUM RATIOS
  140 DO 149 I=1,N
      K(I)=GAM(I)*FIP(I)/(PHI( I)*P)
      IF(K(I).LE.0..OR.K(I).GT.1.E19) GO TO 900
  149 CONTINUE
      ERR=ERG
      RETURN
C ON FAILURE TO FIND PHI SET K TO ZERO, ERR TO 2
  900 ERR=ER
  905 DO 906 I=1,N
  906 K(I)=0.
      RETURN
      END
```

```
      SUBROUTINE ENTH(N,ID,KEY,LEV,ZF,T,P,H,ERE)
C ENTH CALCULATES VAPOR OR LIQUID ENTHALPIES (REF IDEAL GAS AT 300 K) H
C IN JOULES/GMOL FOR MIXTURES OF N COMPONENTS (N.LE.20) WHOSE INDICES
C APPEAR IN VECTOR ID, GIVEN TEMPERATURE, PRESSURE P, AND LIQUID OR
C VAPOR COMPOSITION Z. ENTH RETURNS ERE=0 UNLESS BINARY DAT ARE
C MISSING FOR THE SYSTEM, IN WHICH CASE IT RETURNS ERE=1, OR NO
C SOLUTION IS FOUND IN PHIS, WHEN IT RETURNS ERE=2. FOR LEV = 0
C THE LIQUID ENTHALPY IS CALCULATED WITH EXCESS ENTHALPY OF MIXING
C TAKEN AS 0, FOR LEV=1 EXCESS ENTHALPY IS CALCULATED FROM THE
C TEMPERATURE DEPENDENCE OF ACTMTY COEFFICIENTS, AND FOR LEV=2
C VAPOR ENTHALPY IS CALCULATED. IF VALIK HAS BEEN CALLED FOR THE SAME
C CONDITIONS, KEY SHOULD BE AS IN VALIK. IF VALIK HAS NOT'BEING
C CALLED , KEY MUST BE 9.FOR A NEW SYSTEM, 10 OTHERWISE.
      REAL Z(20),PHI(20),ZF(N)
      INTEGER ID(10),ERE,ERB
      COMMON/PURE/NMI(100),NM2(100),TC(100),PC(100),RD(100),DM(100),
     1 A(100),C1(100),C2(100),C3(100),C4(100),C5(100),RU(100),QU(100),
     2 QP(100),D1(100),D2(100),D3(100),D4(100)
      COMMON/BINARY/ETA(5050),U(100,100)
      COMMON/GS/IER,RL(20),TH(20),TP(20),GCL(20),TAU(20,20)
      COMMON/VIRIAL/KV,B(210),BD(210),DB(210),DBD(210),BM
      COMMON/PS/PHL(20),ZI(20),C(210),VNT,TL,PL
      DATA R,CJ/8.31439,0.098808/,TR,TR2,TRF/300.,90000.,1411./
      ERE=0
C LACKING T DEPENDENT UNIQUAC INTERACTION PARAMETER SET THEIR T
C DERIVATIVE TERM TO,0
      BU=0.
  100 DO 104 I=1,N
C CONVERT COMPOSITION VECTOR TO DIMENSIONS 20 TO MATCH LOWER LEVEL
C SUBROUTINES
  104 Z(I)=ZF(I)
C SKIP FUGACITY CALCULATIONS IF VALIK CALLED AT SAME CONDITIONS
      IF(I(EY.LT.9)  GO TO 120
C SKIP VAPOR CALCULATIONS FOR LIQUID
      IF(LEV.LT.2)  GO TO 110
C GET VTRIAL COEFFICIENTS IF NOT PREVIOUSLY CALCUALETED
      CALL BIJS(N,ID,KEY,T,ERB)
      IF(ERB.GT. 1) GO TO 900
      IF(KV.EQ.0) GO TO 110
C GET TRUE COMPOSITION FROM ASSOCIATING VAPORS
      CALL PHIS(N,ID,8,Z,T,P,PHI,ERR)
      IF(ERR.GT. 1) GO TO 900
      GO TO 120
  110 IF(LEV.EQ.0) GO TO 120
C GET UNIQUAC INTERACTION TERMS IF EXCESS ENTHALPY IS CALCULATED FOR
C LIQUID
      CALL TAUS(N,ID,T,TAU,IER)
C SET ERE=1 FOR BINARY DATA MISSING
      IF(IABS(IER).EQ.1) ERE=1
      ST=0.
      STP=0.
C CALCULATION OF TERMS FOR EXCESS ENTHALPY EVALUATION
  111 DO 115 I=1,N
      II=ID(I)
```

```
      TH(I)=Z(I)*QU(II)
      TP(I)=Z(I)*QP(11)
      STP=STP+TP(I)
  115 ST=ST+TH(I)
  116 DO 119 I=1,N
      TH(I)=TH(I)/ST
  119 TP(I)=TP(I)/STP
C CALCULATION OF IDEAL GAS ENTHALPY
  120 TM1=T-TR
      TM2=ALOG(T/TR)
      TM3=(T**2.-TR2)/2.
      TLT=T*ALOG(T)-T-TRF
      HIG=0.
  125 DO 129 I=1,N
      II=ID(I)
  129 HIG=HIG+Z(I)*(D1(II)*TM1+D2(II)*TM2+D3(II)*TM3+D4(II)*TLT)
      IF(LEV.LT.2) GO TO 150
C CALCULATION OF ENTHALPY FOR NONASSOCATING VAPOR
  130 IF(KV.EQ. 1) GO TO 140
      HV=0.
  131 DO 135 I=1,N
      LI=(I-1)*I/2
      DO 135 J=1,I
      CMT=2.
      IF(J.EQ.I) CMT=1.
  135 HV=HV+CMT*Z(I)*Z(J)*(B(LI+J)-DB(LI+J))
  139 HV=HIG+CJ*P*HV
      H=HV
      RETURN
C CALCULATION OF ENTHALPY FOR ASSOCIATING VAPOR
  140 SD=0.
      S0=0.
      S1=0.
  141 DO 145 I=1,N
      LI=(I-1)*I/2
      S0=S0+ZI(I)*(B(LI+I)-DB(LI+I))
      DO 143 J=1,I
      ZIJ=ZI(I)*ZI(J)*C(LI+J)
      SD=SD+ZIJ*(1.-DBD(LI+J)/BD(LI+J))
  143 S1=S1+ZIJ*(B(LI+J)-DB(LI+J))
  145 CONTINUE
      HV=HIG+VNT*(CJ*P*(S0+S1)-R*T*SD)
      H=HV
      RETURN
C CALCULATION OF LIQUID ENTHALPY
  150 TMR=T**2
      TMS=2.*T*TMR
      HL=0.
  151 DO 155 I=1,N
      II=ID(I)
  155 HL=HL+Z(I)*(-C2(II)+C3(II)*TMR+C4(II)*T+C5(II)*TMS)
      H=HIG-R*HL
C FOR LEV = 0 SKIP EXCESS ENTHALPY CALCULATION
  160 IF(LEV.EQ.0) RETURN
```

```
C CALCULATION OF EXCESS ENTHALPY CONTRIBUTION FOR LIQUID
      HE=0.
      HC=0.
  161 DO 169 I=1,N
      II=ID(I)
      TM1=0.
      TM2=0.
      IF(U(II,II).GT.1.E+19) GO TO 166
      DO 165 J=1,N
      JJ=ID(J)
      TM3=TP(J)*TAU(J,I)
      TM1=TM1+TM3
  165 TM2=TM2+TM3*(U(JJ,II)-2.*BU/T)
      HE=HE+QP(II)*Z(I)*TM2/TM1
      GO TO 169
  166 DO 168 J=1,N
      JJ=ID(J)
  168 TM1=TM1+TH(J)*U(JJ,II)
      HC=HC+Z(I)*TM1
  169 CONTINUE
      H=H+R*(HE+HC)
      RETURN
C FOR FAILURE TO FIND SOLUTION IN PHIS SET ERE = 2.(H=0)
  900 ERE=2
      H=0.
      RETURN
      END
```

```
      SUBROUTINE PHIS(N,ID,KEY,Y,T,P,PHI,ERR)
C PHIS CALCULATES VAPOR PHASE FUGACITY COEFFICIENTS, PHI,FOR ALL N
C COMPONENTS (N.LE.20) WHOSE INDICES APPEAR IN VECTOR ID, GIVEN
C TEMPERATURE T(K), PRESSURE P(BAR), AND VAPOR PHASE COMPOSITION Y.PHIS
C RETURNS ERR=0 UNLESS NO SOLUTIONS ARE FOUND IN WHICH CASE IT RETURNS
C ERR=2. KEY SHOULD BE 1 FOR A NEW SYSTEM, 2 FOR ALL CONDITIONS CHANGED
C SINCE LAST CALL FOR SAME SYSTEM, 3 IF TEMPERATURE IS UNCHANGED FROM
C LAST CALL FOR SAME SYSTEM, 4 (7) IF ONLY TEMPERATURE HAS CHANGED, AND
C 8 IF BIJS HAS ALREADY BEING CALLED AT SAME CONDITIONS.
      REAL Y(20),SI(20),ZO(20),PHI(20),SS(20)
      INTEGER ID(10),ERR,ERB
      COMMON/VIRIAL/KV,B(210),BD(210),DB(210),DBD(210),BM
      COMMON/PS /PHL(20),ZI(20),C(210),VNT,TL,PL
      COMMON/COEFF/BMM
      DATA R /83.1473/
  100 ERR=0
      PRT=P/(R*T)
      GO TO(110,101,120,101,101,101,101,120,110,101),KEY
C CHECK FOR SIGNIFICANT CHANGE IN T OR P SINCE LAST CALL FOR SYSTEM
  101 IF(ABS(T-TL).LT.0.02) GO TO 103
      GO TO 110
  103 IF(ABS(P-PL).LT.0.01) GO TO 105
      GO TO 110
C RETURN IF NO CHANGE IN T,P,OR Y SINCE LAST CALL
  105 IF(KEY.EQ.4.OR.KEY.EQ.7) RETURN
      GO TO 120
C GET SECOND VIRIAL COEFFICIENT IN /VIRIAL/
  110 CALL BIJS(N,ID,KEY,T,ERB)
      IF(ERB.GT.1)  GO TO 900
C GO TO SPECIAL CALCULATION FOR ASSOCIATING GAS MIXTURES
  120 IF(KV.EQ.1) GO TO 200
C CALCULATE SECOND VIRIAL COEFFICIENT FOR GAS MIXTURE
      BM=0.
  130 DO 139 I=1,N
C CALCULATE EFF SECOND VIRIAL COEFFICIENT FOR COMP I IN MIXTURE, SS(I)
      SS(I)=0.
      LI=(I-1)*I/2
      DO 133 J=1,I
  133 SS(I)=SS(I)+Y(J)*B(LI+J)
      I1=I+1
      IF(I1.GT.N)  GO TO 136
      DO 135 J=I1,N
      LJ=(J-1)*J/2
  135 SS(I)=SS(I)+Y(J)*B(LJ+I)
  136 BM=BM+Y(I)*SS(I)
      BMM=BM
  139 CONTINUE
C CALCUALTE VAPOR PHASE FUGACITY COEFFICIENTS, PHI(I)
  140 DO 149 I=1,N
      PHI(I)=EXP(PRT*(2.*SS(I)-BM))
C SAVE FUGACITY COEFFICIENTS FOR USE AT SIMILAR CONDITIONS
      PHL(I)=PHI(I)
  149 CONTINUE
C SAVE CONDITIONS AT WHICH PHIS CALCULATED
```

```
      TL=T
      PL=P
      RETURN
C SPECIAL CALCULATION FOR ASSOCIATING GAS MIXTURES
  200 KO=0
      GO TO(203,201,201,201,201,201,201,203,203,201),KEY
C IF PREVIOUS PHI VALUES AVAILABLE USE TO GET FIRST ESTIMATE OF ACTUAL
C VAPOR COMPOSITION
  201 DO 202 I=1,N
      LI=(I-1)*I/2
  202 ZI(I)=PHL(I)*Y(I)*EXP(-PRT*B(LI+I))
      IF(KEY.EQ.3) GO TO 208
      KO= 1
C FOR NO PREVIOUS PHI VALUES AVAILABLE (KO=0) MAKE FIRST ESTIMATES OF
C ACTUAL VAPOR COMPOSITION
C FOR ALL CASES (EXCEPT KEY=3 )FIND VALUES OF ASSOCAITING EQUILIBRIUM
C CONSTANTS C.
  203 DO 207 I=1,N
      IF(KO.EQ.0) ZI(I)=Y(I)
      LI=(I-1)*I/2
      DO 206 J=1,I
      LJ=(J-1)*J/2
      C(LI+J)=-2.*PRT*BD(LI+J)*EXP(PRT*(B(LI+I)+B(LJ+J)-B(LI+J)))
      IF(C(LI+J).LT.0.) GO TO 900
      IF(J.EQ.I) GO TO 205
      IF(KO.EQ.l) GO TO 206
C INITIAL ESTIMATES OF ZI(I)
      IF(C(LI+J).LE.0.5) GO TO 206
      IF(Y(J).LT.Y(I)) GO TO 204
      ZT=Y(I)/(C(LI+J)*Y(J)+1.)
      ZJ=Y(J)/(C(LI+J)*ZT+ 1.)
      IF(ZT.LT.ZI(I)) ZI(I)=ZT
      IF(ZJ.LT.ZI(J)) ZI(J)=ZJ
      GO TO 206
  204 ZJ=Y(J)/(C(LI+J)*Y(I)+ 1.)
      ZT=Y(I)/(C(LI+J)*ZJ+1.)
      IF(ZT.LT.ZI(I)) ZI(I)=ZT
      IF(ZJ.LT.ZI(J)) ZI(J)=ZJ
      GO TO 206
  205 C(LI+J)=C(LI+J)/2.
      IF(KO.EQ.1) GO TO 206
      IF(C(LI+J).LE.0.5) GO TO 206
      ZT=(SQRT(1.+8.*C(LI+J)*Y(I))-1.)/(4.*C(LI+J))
      IF(ZT.LT.ZI(I)) ZI(I)=ZT
  206 CONTINUE
  207 CONTINUE
C START ITERATIVE CALCULATION OF ACTUAL VAPOR COMPOSITION, ZI(I)
C STORE FIRST ITERATION VALUES
  208 DO 209 I=1,N
  209 ZO(I)=ZI(I)
      IT=0
  210 IT=IT+1
      IF(IT.GT.20) GO TO 900
      RM=1.
```

```
 220 DO 229 I=1,N
     SI(I)=0.
C DAMP ITERATION 20 %
     ZI(I)=.2*ZO(I)+.8*ZI(I)
     ZO(I)=ZI(I)
     LI=(I-1)*I/2
     DO 221 J=1,I
 221 SI(I)=SI(I)+C(LI+J)*ZI(J)
     DO 223 J=I,N
     LJ=(J-1)*J/2
 223 SI(I)=SI(I)+C(LJ+I)*ZI(J)
     RM=RM+ZI(I)*SI(I)/2.
 229 CONTINUE
 230 DO 235 I=1,N
 235 ZI(I)=RM*Y(I)/(1.+SI(I))
     DO 239 I=1,N
     IF(Y(I).LT. 1.E-09) GO TO 239
C CHECK CONVERGENCE FOR EACH ZI(I)
     IF(ABS((ZI(I)-ZO(I))/Y(I)).GT.0.005) GO TO 210
 239 CONTINUE
C CALCULATE VAPOR PHASE FUGACITY COEFFICIENTS FOR ACTUAL COMPOSITION OF
C ASSOCIATING VAPOR
 240 DO 249 I=1,N
     LI=(I-1)*I/2
     PHI(I)=RM*EXP(PRT*B(LI+I))/(1.+SI(I))
     IF(KEY.EQ.8) GO TO 249
C SAVE FUGACITY COEFFICIENTS FOR USE AT SIMILAR CONDITIONS
     PHL(I)=PHI(I)
 249 CONTINUE
C CALCULATE TOTAL MOLS OF ASSOCIATING VAPOR PER MOL STOICHIOMETRIC VAOR
 250 VNT=1./RM
     TL=T
     PL=P
     RETURN
C ERROR RETURN FOR FAILURE OF ITERATION FOR ZI(I) TO CONVERGE
 900 ERR=2
     DO 901 I=1,N
     PHL(I)=1.
 901 PHI(I)=1.
     RETURN
     END
```

```
      SUBROUTINE BIJS(N,ID,KEY,T,ERB)
C BIJS CALCULATES SECOND VIRIAL COEFFICIENTS, BIJ, FOR ALL PAIRS OF N
C COMPONENTS (N.LE.20) WHOSE INDICES APPEAR IN VECTOR ID, FOR
C TEMPERATURE T(K). COEFFICIENTS ARE RETURNED IN COMMON STORAGE M R I A
C WITH B(I,J)=B(L), L=(I-1)*I/2+J. IF CARBOXILIC ACIDS ARE PRESENT
C KV (IN COMMON/VIRIAL) IS SET TO 1 (OTHERWISE 0), AND BO IS RETURNED
C IN B, BT IN BD. IF ANY ANOMALIES ARE DETECTED IN CALCULATION ERB IS
C SET TO 2 (OTHERWISE 0). TEMPERATURE INDEPENDENT PARAMETERS ARE
C EVALUATED ONLY IF KEY = 1 OR 9, TEMPERATURE DERIVATIVES OF
C COEFFICIENTS (MULTIPLIED BY TEMPERATURE) ARE FOUND AND RETURNED IN
C DB(L) (AND DBD(L)) IN COMMON/VIRIAL IF KEY IS 6 OR LARGER.
      INTEGER ID(10),ERB
      COMMON/PURE/NM1(100),NM2(100),TC(100),PC(100),RD(100),DM(100),
     1 A(100),C1(100),C2(100),C3(100),C4(100),C5(100),RU(100),QU(100),
     2 QP(100),D1(100),D2(100),D3(100),D4(100)
      COMMON/BINARY/ETA(5050),U(100,100)
      COMMON/VIRIAL/KV,B(210),BD(210),DB(210),DBD(210),BM
      COMMON/BS/G(210),TS(210),S(210),Z(210),H(210),E(210),W(210),
     1 ET(210)
      DATA B1,B2,B3/1.2618,7243.8,1.7941E07/,CN1,CN2,CN3,CN4/0.94,-1.47,
     1-.085,1.015/,CP1,CP2,CP3,CP4/-0.75,3.,-2.1,-2.1/,CA1,CA2,CH1,CH2/
     2 -0.3,-0.05,1.99,0.2/,CW1,CW2,CW3/0.006026,0.02096,-.001366/,
     3 CS1,CK1,CK2,CE1,CE2,CE3,CE4,CE5/2.4507,0.7,0.6,650.,300.,4.27,
     4 42800.,22400./,CO1,CO2,CO3/0.748,0.91,0.4/,E3/0.33333/
  100 ERB=0
C CALCULATE TEMPERATURE-INDEPENDENT PARAMETERS ONLY FOR NEW SYSTEM
      GO TO (109,200,200,200,200,200,200,200,109,200),KEY
C RESET ASSOCIATING VAPOR FLAG
  109 KV=0
C CALCULATE TEMPERATURE-INDEPENDENT PARAMETERS FOR PURE COMPONENTS
  110 DO 119 I=1,N
C IDENTIFY COMPONENT
      II=ID(I)
      L=(I+1)*I/2
C NONPOLAR ACENTRIC PARAMETER
      W(L)=CW1*RD(II)+CW2*RD(II)**2+CW3*RD(II)**3
C MOLECULAR SIZE PARAMETER (CUBED)
      S(L)=(CS1-W(L))**3*TC(II)/PC(II)
      IF(S(L).LT.0.) GO TO 900
      III=(II+1)*II/2
      ET(L)=ETA(III)
      IF(ET(L).GE.4.4999) KV=1
CENERGYPARAMETER
      TS(L)=TC(II)*(CO1+CO2*W(L)-CO3*ET(L)/(2.+20.*W(L)))
      IF(TS(L).LT.0.) GO TO 900
      IF(DM(II).LT.1.45) GO TO 117
C MODIFICATION OF PARAMETERS FOR LARGE DIPOLE MOMENTS
      H(L)=16.+400.*W(L)
      T1=H(L)/(H(L)-6.)
      T2=3./(H(L)-6.)
      TK=2.882-(1.882*W(L)/(0.03+W(L)))
      Z(L)=B3*DM(11)**4/(TS(L)*S(L)**2*TC(II)*TK)
      IF(Z(L).LT.-1.) GO TO 900
C MODIFIED MOLECULAR SIZE PARAMETER (CUBED)
```

```
      S(L)=S(L)*(1.+T2*Z(L))
C MODIFIED ENERGY PARAMETER
      TS(L)=TS(L)*(1.-T1*Z(L)+T1*(T1+1.)*Z(L)**2/2.)
C REDUCE DIPOLE MOMENT
  117 G(L)=B2*DM(II)**2/(TS(L)*S(L))
  119 CONTINUE
      IF(N.EQ.1) GO TO 130
C CALCULATE TEMPERATURE -INDEPENDENT PARAMETERS FOR COMPONENT PAIRS
  120 DO 129 I=2,N
      II=ID(I)
      LI=(I+1)*I/2
      I1=I-1
      DO 129 J=1,I1
      JJ=ID(J)
      LJ=(J+1)*J/2
      L=(I-1)*I/2+J
C CROSS NONPOLAR ACENTRIC PARAMETER
      W(L)=(W(LI)+W(LJ))/2.
C CROSS MOLECULAR SIZE PARAMETER
      S(L)=SQRT(S(LI)*S(LJ))
C CROSS ENERGY PARAMETER
      TS(L)=CK1*SQRT(TS(LI)*TS(LJ))+CK2/(1./TS(LI)+1./TS(LJ))
      IF(DM(II).LT.1.E-19) GO TO 123
      IF(DM(JJ).GT.1.E-19) GO TO 124
      IF(DM(II).LT.2.5) GO TO 124
      Z(L)=DM(II)**2*(TS(LJ)**2*S(LJ))**E3/(TS(L)*S(LI))
      GO TO 125
  123 IF(DM(JJ).LT.2.5) GO TO 124
C MODIFICATION OF PARAMETERS IN POLAR-NONPOLAR PAIRS
      Z(L)=DM(JJ)**2*(TS(LI)**2*S(LI))**E3/(TS(L)*S(LJ))
      GO TO 125
  124 Z(L)=0.
      GO TO 126
  125 H(L)=16.+400.*W(L)
      T1=H(L)/(H(L)-6.)
      T2=3./(H(L)-6.)
C MODIFY CROSS MOLECULAR SIZE, PARAMETER
      S(L)=S(L)*(1.-T2*Z(L))
C MODIFIED CROSS ENERGY PARAMETER
      TS(L)=TS(L)*(1.+T1*Z(L))
C CROSS REDUCED DIPOLE MOMENT
  126 G(L)=B2*DM(II)*DM(JJ)/(TS(L)*S(L))
C DETERMINE EFFECTIVE ASSOCIATION/SOLVATION PARAMETER
      IJ=(II-1)*II/2+JJ
      IF(JJ.GT.II) IJ=(JJ-1)*JJ/2+II
      IF(ABS(ETA(IJ)).LT.1.E-19) GO TO 127
      ET(L)=ETA(IJ)
      IF (ET(L).GE.4.4999) KV=1
      GO TO 129
  127 ET(L)=0.
      IF(ABS(ET(LI)-ET(LJ)).LT.1.E-19) ET(L)=ET(LI)
  129 CONTINUE
C CALCULATE TEMPERATURE INDEPENDENT TERMS IN VIRIAL COEFFICIENTS FOR
C PURE COMPONENTS AND PAIRS
```

```
  130 DO 139 I=1,N
      DO 139 J=1,I
      L=(I-1)*I/2+J
      S(L)=B1*S(L)
      H(L)=CH1+CH2*G(L)**2
      Z(L)=CA1+CA2*G(L)
C DETERMINE MODIFIED REDUCED DIPOLE PARAMETER
      IF(G(L).LT.0.04) GO TO 135
      IF(G(L).GE.0.25) GO TO 134
      G(L)=0.
      GO TO 135
  134 G(L)=G(L)-0.25
  135 IF(ET(L).GE.4.5) GO TO 137
      IF(ET(L).LT.1.E-19) GO TO 139
C ENERGY TERM FOR NONASSOCIATING TERM
      E(L)=CE1/(TS(L)+CE2)-CE3
      GO TO 139
C ENERGY TERM FOR ASSOCIATING TERM
  137 E(L)=CE4/(TS(L)+CE5)-CE3
  139 CONTINUE
C CALCULATE TEMPERATURE DEPENDENT TERMS AND VIRIAL COEFFICIENTS
  200 DO 209 I=1,N
      DO 209 J=1,I
      L=(I-1)*I/2+J
      TA=T/TS(L)
      T1=1./(1./TA-1.6*W(L))
      T2=T1*T1
      T3=T2*T1
C NONPOLAR FREE CONTRIBUTION
      BN=CN1+CN2/T1+CN3/T2+CN4/T3
      IF(G(L).GT.1.E-19) GO TO 201
      BP=0.
      GO TO 202
C POLAR FREE CONTRIBUTION
  201 BP=(CP1+CP2/T1+CP3/T2+CP4/T3)*G(L)
C TOTAL FREE CONTRIBUTION TO VIRIL COEFFICIENT
  202 B(L)=S(L)*(BN+BP)
C METASTABLE PLUS BOUND CONTRIBUTIONS
      BN=Z(L)*EXP(H(L)/TA)
      IF(ET(L).LT.1.E-19) GO TO 204
C CHEMICAL CONTRIBUTION
      BP=EXP(ET(L)*E(L))-EXP(ET(L)*(1500./T+E(L)))
      GO TO 205
  204 BP=0.
C METASTABLE, BOUND, AND CHEMICAL CONTRIBUTIONS TO VIRIAL COEFFICIENT
  205 BD(L)=S(L)*(BN+BP)
      IF(KEY.GT.1.AND.KEY.LE.5) GO TO 208
C CALCULATION OF T DERIVATIVES OF VIRIAL COEFFICIENTS (ALL MULTIPLIED
C BY T)
      DBN=-CN2-2.*CN3/T1-3.*CN4/T2
      DBP=(-CP2-2.*CP3/T1-3.*CP4/T2)*G(L)
C DERIVATIVE OF THE TOTAL FREE CONTRIBUTION TO VIRIAL COEFFICIENT
      DB(L)=S(L)*(DBN+DBP)/TA
      DBN=-H(L)*BN/TA
```

```
      IF(ET(L).LT.1.E-19) GO TO 206
      DBP=1500.*ET(L)*EXP(ET(L)*(1500./T+E(L)))/T
      GO TO 207
  206 DBP=0.
C DERIVATIVE OF METASTABLE, BOUND, AND CHEMICAL CONTRIBUTIONS TO VIRIAL
C COEFFICIENT
  207 DBD(L)=S(L)*(DBN+DBP)
C CALCULATION OF TOTAL VIRIAL COEFFICIENT FOR CASES WITHOUT ASSOCIATING
C VAPORS
      IF(KV.EQ.0) DB(L)=DB(L)+DBD(L)
  208 IF(KV.EQ.0) B(L)=B(L)+BD(L)
  2C9 CONTINUE
      RETURN
C ERROR FOR FAILURE TO FIND VALID VIRIAL COEFFICIENTS.
  900 ERB=2
      NL=(N+1)*N/2
      DO 902 L=1,NL
      B(L)=0.
  902 BD(L)=0.
      RETURN
      END
```

```
      SUBROUTINE PURF(N,ID,T,P,FIP)
C PURF CALCULATES PURE COMPONENT LIQUID FUGACITIES, FIP, AT SYSTEM
C TEMPERATURE T(K) AND PRESSURE P(BAR) FOR ALL N COMPONENTS (N.LE.20)
C WHOSE INDICES APPEAR IN VECTOR ID. FUGACITIES OF HYPOTHETICAL LIQUID
C PHASES ARE CALCULATED FOR NONCONDENSABLE COMPONENTS.
      REAL FIP(20),FO(20),VIP(20)
      INTEGER ID(10)
      COMMON/PURE/NM1(100),NM2(100),TC(100),PC(100),RD(100),DM(100),
     1 A(100),C1(100),C2(100),C3(100),C4(100),C5(100),RU(100),QU(100),
     2 QP(100),D1(100),D2(100),D3(100),D4(100)
      DATA R,CA,CB,CC,E/83.1473,1.60,0.655,0.006930,0.285714/
  100 RT=R*T
      AT=ALOG(T)
      T2=T*T
  101 DO 109 I=1,N
C IDENTIFY COMPONENT
      II=ID(I)
C GET PURE COMPONENT 0-PRESSURE FUGACITIES,FO.
      FO(I)=EXP(C1(II)+C2(II)/T+C3(II)*T+C4(II)*AT+C5(II)*T2)
C GET PURE COMPONENT LIQUID MOLAR VOLUMES,VIP
      TR=T/TC(II)
      IF(TR.GT.0.75) GO TO 105
      TAU=1.+(1.-TR)**E
      GO TO 107
  105 TAU=CA+CC/(TR-CB)
  107 VIP(I)=R*TC(II)*A(II)**TAU/PC(II)
  109 CONTINUE
C CALCULATE PURE COMPONENT LIQUID FUGACITIES AT P
  110 DO 119 I=1,N
      FIP(I)=FO(I)*EXP(VIP(I)*P/RT)
  119 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE GAMMA(N,ID,KEY,X,T,GAM,ERG)
C GAMMA CALCULATES LIQUID PHASE ACTMTY COEFFICIENTS, GAM, FOR ALL N
C COMPONENTS (N.LE.20) WHOSE INDICES APPEAR IN VECTOR ID, GIVEN
C TEMPERATURE T(K) AND LIQUID COMPOSITION X, USING THE UNIQUAC MODEL.
C FOR NONCONDENSABLE COMPONENTS (U(I,I) SET TO 1.E+20) AND UNSYMMETRIC
C CONVENTION IS USED TO DERIVE EFFECTIVE ACTIVITY COEFFICIENTS. GAMMA
C RETURNS ERG=0 UNLESS BINARY DATA ARE MISSING FOR THE SYSTEM, IN WHICH
C CASE IT RETURNS ERG=1. KEY SHOULD BE 1 FOR A NEW SYSTEM, 3 FOR T
C UNCHANGED, AND 4 OR 5 FOR X UNCHANGED.
      REAL X(20),GAM(20),PT(20),PTS(20)
      INTEGER ID(10),ERG
      COMMON/PURE/NM1(100),NM2(100),TC(100),PC(100),RD(100),DM(100),
     1 A(100),C1(100),C2(100),C3(100),C4(100),C5(100),RU(100),QU(100),
     2 QP(100),D1(100),D2(100),D3(100),D4(100)
      COMMON/BINARY/ETA(5050),U(100,100)
      COMMON/GS/IER,RL(20),TH(20),TP(20),GCL(20),TAU(20,20)
      DATA Z/10./
C SKIP SYSTEM INITIALIZATION ON SUBSEQUENT CALCULATIONS
  100 GO TO(110,120,120,130,130,120,130,120,110,120),KEY
  110 ERG=0
C CALCULATE COMPOSITION INDEPENDENT TERMS
  111 DO 119 I=1,N
      II=ID(I)
  119 RL(I)=Z*(RU(II)-QU(II))/2.-RU(II)+1.
C CALCULATE SEGMENT AND AREA FRACTIONS FOR COMPONETS IN MIXTURE
  120 SP=1.E-30
      ST=1.E-30
      STP=1.E-30
      SS=0.
      SL=0.
  121 DO 125 I=1,N
      II=ID(I)
      TH(I)=X(I)*QU(II)
      TP(I)=X(I)*QP(II)
      SP=SP+X(I)*RU(II)
      ST=ST+TH(I)
      STP=STP+TP(I)
C SKIP FOR NONCONDENSABLE COMPONENTS
      IF(U(II,II).GT.1.E+19) GO TO 125
      SS=SS+X(I)
      SL=SL+X(I)*RL(I)
  125 CONTINUE
  126 DO 129 I=1,N
      II=ID(I)
      TH(I)=TH(I)/ST
      TP(I)=TP(I)/STP
      IF(U(II,II).GT.1.E+19) GO TO 128
C CALCULATE COMBINATORIAL CONTRIBUTION TO EXCESS FREE ENERGY
  127 GCL(I)=RL(I)-RU(II)*SL/SP+ALOG(RU(II)*SS/SP)+Z*QU(II)*ALOG(QU(II)
     1 *SP/(RU(II)*ST))/2.
      GO TO 129
  128 GCL(I)=0.
  129 CONTINUE
      IF(KEY.EQ.3) GO TO 140
```

```
C GET UNIQUAC BINARY INTERACTION PARAMETER TERMS
  130 CALL TAUS(N,ID,T,TAU,IER)
C CALCULATE RESIDUAL CONTRIBUTION TO EXCESS FREE ENERGY
  140 DO 141 I=1,N
  141 PTS(I)=0.
  142 DO 149 I=1,N
      PT(I)=1.E-30
      DO 143 J=1,N
  143 PT(I)=PT(I)+TP(J)*TAU(J,I)
      DO 145 J=1,N
  145 PTS(J)=PTS(J)+TP(I)*TAU(J,I)/PT(I)
  149 CONTINUE
  150 DO 159 I=1,N
      II=ID(I)
      IF(U(II,II).GT.1.E+19) GO TO 155
C RESIDUAL FREE ENERGY FOR CONDENSABLE COMPONENTS
      GRL=QP(II)*(1.-ALOG(PT(I))-PTS(I))
      GO TO 158
  155 GRL=0.
      DO 156 J=1,N
      JJ=ID(J)
C RESIDUAL FREE ENERGY FOR NONCONDENSABLE COMPONENTS
  156 GRL=GRL+TH(J)*(U(II,JJ)+U(JJ,II)/T)
C CALCULATE ACTIVITY COEFFICIENT
  158 GAM(I)=EXP(GCL(I)+GRL)
  159 CONTINUE
      IF(IABS(IER).EQ.1) ERG=1
      RETURN
      END
```

```
      SUBROUTINE TAUS(N,ID,T,TAU,IER)
C TAUS CALCULATES TEMPERATURE DEPENDENT INTERACTION COEFFICIENTS TAU FOR
C USE IN SUBROUTINE GAMMA. IF SYSTEM DATA ARE MISSING (SOME REQUIRED
C ENTRY IN MATRIX U IN COMMON/BINARY IS ZERO) CORRESPONDING TAU IS
C SET TO 1 AND IER IS RETURNED AS +/- 1. FOR NONCONDENSABLES PRESENT
C IER IS -2 OR -1 (OTHERWISE 0).
      REAL TAU(20,20)
      INTEGER ID(10)
      COMMON/BINARY/ETA(5050),U(100.100)
  100 IER=0
  110 DO 119 I=1,N
      II=ID(I)
C CHECK IF ANY COMPONENT IS A NONCONDENSABLE AND FLAG IER
      IF(U(II,II).GT.1.E+19) IER=ISIGN(IER**2-2,-1)
      DO 119 J=1,N
      IF(J.EQ.I) GO TO 115
      JJ=ID(J)
C CHECK IF BINARY PAIR ARE BOTH NONCONDENSABLES.
      IF(U(II,II).GT.1.E+19.AND.U(JJ,JJ).GT.1.E+19) GO TO 115
C CHECK IF BINARY DATA ARE MISSING
      IF(ABS(U(II,JJ)).LT.1.E-19) GO TO 112
C CHECK IF EITHER COMPONENT IN BINARY PAIR IS A NONCONDENSABLE
      IF((U(II,II)+U(JJ,JJ)).GT.1.E+19) GO TO 115
C CALCULATE INTERACTION TERM
      TAU(I,J)=EXP(-U(II,JJ)/T)
      GO TO 119
  112 IER=ISIGN(1,IER)
C SET INTERACTION TERM EQUAL TO UNITY FOR PAIR WITH MISSING DATA
  115 TAU(I,J)=1.
  119 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE BUDET(TYPE,N,ID,KEY,X,Y,T,P,K,ERR)
C BUDET CALCULATES BUBBLE (TYPE= 1) OR DEW (TYPE=2) POINT TEMPERATURE
C T(K) FOR GIVEN PRESSURE P(BAR) AND FEED COMPOSITION X (OR Y) FOR THE
C SYSTEM OF N COMPONENTS (N.LE.20) WHOSE INDICES APPEAR IN ID.
C IT RETURNS T AND INCIPIENT PHASE COMPOSITION Y (OR X), UTILIZING AN
C INITIAL ESTIMATE OF T AND Y (OR X) IF SUPPLIED (NE.0). THE EQUILIBRIUM
C RATIOS K ARE ALSO PROVIDED BY THE SUBROUTINE. THE PROGRAM NORMALLY
C RETURNS ERR=0, BUT IF COMPONENT COMBINATIONS LACKING DATA ARE INVOLVED
C IT RETURNS ERR=1, AND IF NO SOLUTION IS FOUND IT RETURNS ERR=2.
C FOR BAD OR OUT OF RANGE INPUT DATA THE PROGRAM RETURNS ERR=5, AND FOR
C SYSTEMS WITH BP BELOW 200 K (WITH NONCONDENSABLES) ERR=-5.KEY
C SHOULD BE 1 ON INITIAL CALL FOR A NEW SYSTEM AND 2 OTHERWISE.
      REAL X(N),Y(N),K(N),CN(20)
      INTEGER ID(10),TYPE,ERR,ER
      DATA EPS/0.001/
  100 ERR=0
C CHECK FOR VALID PRESSURE
      IF(P.LT.1.E-6.OR.P.GT.100.)GO TO 903
      KEE=KEY
      S=0.
      SS=0.
C CHECK FOR VALID FEED COMPOSITIONS AND FOR ESTIMATE OF INCIPIENT PHASE
C COMPOSITION
  101 DO 109 I=1,N
      S=S+X(I)
  109 SS=SS+Y(I)
      IF(TYPE.EQ. 1.AND.ABS(S-1.).GT.0.01) GO TO 903
      IF(TYPE.EQ.2.AND.ABS(SS-1.).GT.0.01) GO TO 903
  110 IF(TYPE.EQ.1.AND.ABS(SS-1.).GT.0.01) GO TO 114
      IF(TYPE.EQ.2.AND.ABS(S-1.).GT.0.01) GO TO 118
      GO TO 120
C FOR NO ESTIMATE OF INCIPIENT VAPOR COMPOSITION SET EQUAL TO FEED
  114 DO 115 I=1,N
  115 Y(I)=X(I)
      GO TO 120
C FOR NO ESTIMATE OF INCIPIENT LIQUID COMPOSITION SET EQUAL TO FEED
  118 DO 119 I=1,N
  119 X(I)=Y(I)
  120 IT=0
C FOR NO ESTIMATE OF TEMPERATURE SET TO 400 K
  200 IF(T.LT.200..OR.T.GT.600.) T=400.
C CONDUCT ITERATION STEP
  210 IT=IT+1
      LF(IT.GT.10)  GO TO 900
C GET KVALUES
  220 CALL VALIK(N,ID,KEE,X,Y,T,P,K,ER)
      IF(ER.GT. 1) GO TO 900
      S=0.
C CALCULATE SUM OF KX (BP) OR Y/X (DP)
  221 DO 229 I=1,N
      IF(I" " E.EQ.2) GO TO 225
      CN(I)=K(I)*X(I)
      GO TO 229
  225 CN(I)=Y(I)/K(I)
```

```
 229 S=S+CN(I)
 230 F0=ALOG(S)
C CHECK CONVERGENCE
     IF(ABS(F0).LE.EPS) GO TO 290
C GET K VALUES AT T+1 FOR FINITE DIFFERENCE DERIVATIVE
     CALL VALIK(N,ID,4,X,Y,T+1.,P,K,ER)
     IF(ER.GT.l) GO TO 900
     SS=0.
     IF(TYPE.EQ.2) GO TO 235
C CALCULATE NEW VAPOR COMPOSITION FOR BP
 231 DO 234 I=1,N
     Y(I)=CN(I)/S
 234 SS=SSiK(I)*X(I)
     GO TO 240
C CALCULATE NEW LIQUID COMPOSITION FOR DP
 235 DO 239 I=1,N
     X(I)=CN(I)/S
 239 SS=SS+Y(I)/K(I)
 240 F1=ALOG(SS)
C DETERMINE NEW NEWTON-RAPHSON TEMPERATURE ITERATE
     T=(F1-F0)*T/(F1-T*F0/(T+1.))
C CHECK FOR T Iii RANGE FOR POSSIBLE CONVERGENCE
     IF(T.GT.700) GO TO 900
     IF(T.GT.100) GO TO 245
     IF(ER.LT.0) GO TO 901
     GO TO 900
 245 KEE=2
     IF(TYPE.EQ. 1)KEE=5
      GO TO 210
C GET NORMALIZED INCIPIENT PHASE COMPOSITION
 290 DO 299 I=1,N
     IF(TYPE.EQ.2) GO TO 295
     Y(I)=CN(I)/S
     GO TO 299
 295 X(I)=CN(I)/S
 299 CONTINUE
C CHECK FOR T IN RANGE FOR THERMO SUBROUTINES
     IF(T.GT.600.) GO TO 903
     IF(T.GT.200.) GO TO 199
     IF(ER.LT.0) GO TO 901
     GO TO 903
C SET ERR RETURN FOR MISSING BINARY DATA
 199 IF(IABS(ER).EQ. 1)ERR=1
     RETURN
C ON FAILURE TO CONVERGE SET T TO 0 AND ERR TO 2
 900 ERR=2
     GO TO 905
C ON TB LESS THAN 200 K SET TO 0 AND ERR TO -5
 901 ERR=-5
     GO TO 905
C FOR BAD INPUT DATA (OR TB/TD OUT OF RANGE ) SET T TO 0 AND ERR TO 5
 903 ERR=5
 905 T=0.
     RETURN
```