LBL-26048 c.2
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

RECEIVED
LAWRENCE
BERKELEY LABORATORY

MAR 13 1989

LIBRARY AND
DOCUMENTS SECTION

To be submitted for publication

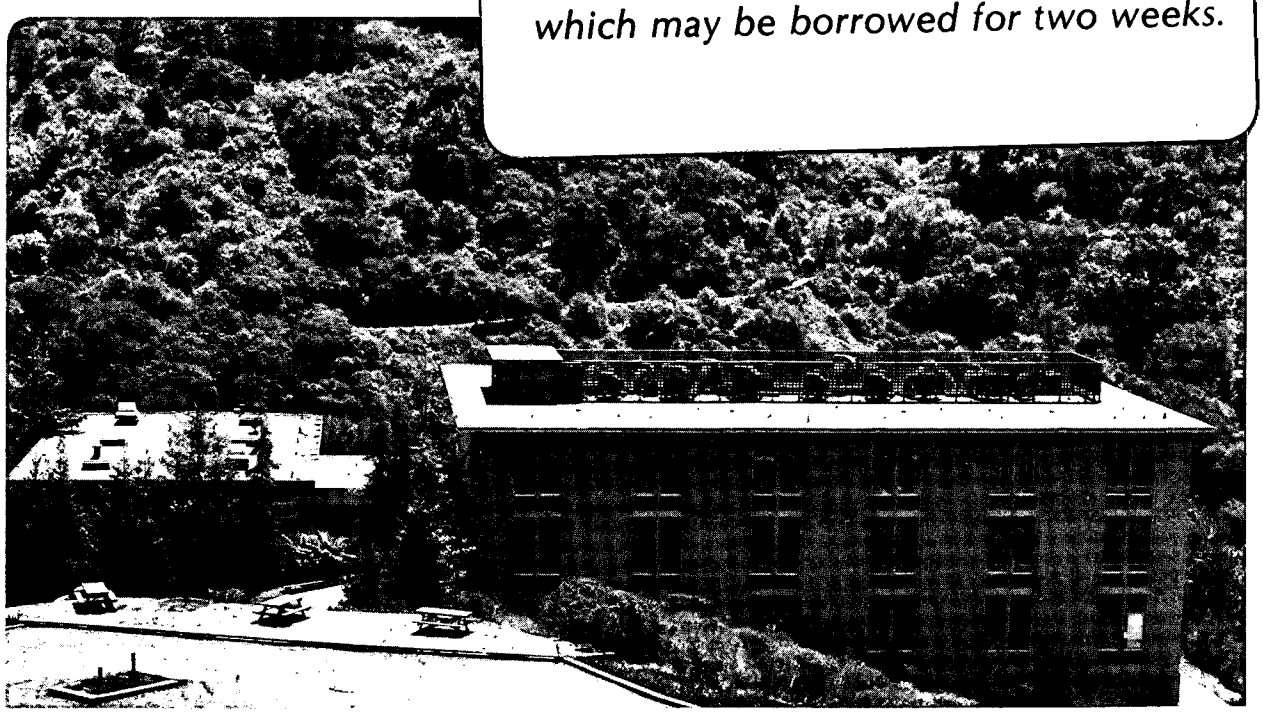
Condensation Behavior of Natural-Gas Mixtures in the Retrograde Dew-Point Region

G.F. Chou and J.M. Prausnitz

December 1988

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks.



LBL-26048 c.2

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

CONDENSATION BEHAVIOR OF NATURAL-GAS MIXTURES IN THE RETROGRADE DEW-POINT REGION

Grace F. Chou[†] *and John M. Prausnitz*[*]

Chemical Engineering Department
University of California

and

Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
1 Cyclotron Road
Berkeley, CA 94720

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

[†]Present address: Air Products and Chemicals, Inc., Allentown, PA 18195

[*]To whom correspondence should be addressed.

CONDENSATION BEHAVIOR OF NATURAL-GAS MIXTURES IN THE RETROGRADE DEW-POINT REGION

Introduction

Natural-gas mixtures often exhibit retrograde-condensation behavior at conditions encountered during production and processing. The observed retrograde behavior is of the *first kind* where condensation occurs at temperatures above the mixture's critical in the dew-point region of the phase diagram. For this region, multicomponent phase-equilibrium and density data are scarce. Existing molecular-thermodynamic correlations also tend to fail in this region; for example, the accuracy of predicted liquid drop-out (volume percent of liquid condensed) is often poor. Accurate determination of liquid drop-out is essential for proper sizing of the primary separator in gas processing.

Towards achieving better predictions, it is first necessary to isolate factors which affect the accuracy of the predicted liquid drop-out so that molecular-thermodynamic models may be modified to predict more accurate condensation behavior. We present here a critical discussion of the discrepancies which exist between experimental data and predictions from a commonly-used equation of state. To illuminate possible sources of these discrepancies, we consider the internal consistency of the experimental data.

Condensation Behavior in the Retrograde Dew Point Region

Fig. 1 shows the phase diagram in pressure-temperature coordinates for a typical natural-gas mixture. The retrograde dew point region extends from the critical point to the cricondentherm; this region is often large. Fig. 2 shows typical condensation curves (pressure vs. volume percent of liquid along isotherms) for a natural-gas condensate at temperatures both above and below the mixture critical point. For an isotherm above the critical point, there are two dew points, a lower(normal) dew point and an upper(retrograde) dew point. Near the retrograde dew point, the amount of liquid condensed decreases rapidly with rising pressure. As the system's temperature approaches its critical, the effect of

pressure on liquid drop-out becomes catastrophic; a few psi in pressure may change the liquid volume percent by more than an order of magnitude (Ng et al, 1986).

Because of the rapid changes in condensation behavior, this region is often called "critical" in the literature. Catastrophic condensation, however, should not be confused with "critical phenomena" arising from density fluctuations near a vapor-liquid critical point. The sharp curvature in the condensation curve near the upper dew point may be observed at temperatures as far as 20-30K from the mixture critical point; at this distance from a critical point, density fluctuations are unlikely to be significant.

Factors Affecting the Accuracy of Predicted Condensation Curve

To predict accurate condensation curves, an equation of state (or any other molecular-thermodynamic model) must predict accurate equilibrium K-values and accurate densities. We first consider the effect of K-values. For a given feed composition, the calculated molar liquid-to-feed ratio, L/F, is directly related to the K-values of all the components; that relation is determined by isothermal flash calculations.

The governing equations for isothermal flash calculations include those for phase equilibria

$$y_i = K_i\, x_i\,, \qquad (i=1, 2, \ldots n); \tag{1}$$

material balances

$$z_i = x_i\,(L/F) + y_i\,(1-L/F)\,, \qquad (i=1, 2, \ldots n); \tag{2}$$

and constraints on compositions for equilibrium phases

$$\sum_i x_i = \sum_i y_i = 1. \tag{3}$$

Here z_i, x_i and y_i are mole fractions of component i in the feed, liquid and vapor phases, respectively; K_i is the K-value of component i.

These governing equations may be solved iteratively using various convergence criteria. A reliable convergence criterion which allows bounded iterations is that of

Rachford-Rice (King, 1971):

$$\sum_i (y_i - x_i) = 0. \tag{4}$$

Combining Equations 1 to 4, an objective function for the flash calculation may be expressed in terms of feed composition, L/F, and K-values:

$$\sum_i \frac{z_i}{(1-L/F) + \left[\frac{1}{K_i - 1}\right]} = 0. \tag{5}$$

Eq. 5 indicates that the calculated L/F is most likely affected by the K-value of the most abundant component in the mixture and by the K-value which has the largest departure from unity. The accuracy of calculated L/F is also related to the accuracy of locating the mixture critical point; depending on the predicted critical temperature, flash calculation along an isotherm at high pressures may converge to either a bubble or a dew point, as discussed in the following section.

Once L/F is determined, the volume fraction of liquid condensed, χ, can be calculated from saturated vapor and liquid volumes, v^V and v^L:

$$\chi = \frac{(L/F)\, v^L}{(L/F)\, v^L + (1-L/F)\, v^V} \tag{6}$$

Rearranging Eq. 6, χ can be expressed in terms of the ratio of saturated vapor and liquid volumes:

$$\chi = \frac{L/F}{L/F + (1-L/F)\,(v^V / v^L)} \tag{7}$$

Eq. 7 shows that χ depends on L/F and v^V/v^L, while L/F depends on K-values. For an equation of state that gives good K-values but less accurate densities, a volume-translation method (Chou and Prausnitz, 1988) may be used to improve density predictions.

Condensation Curves from an Equation of State

We compare experimental condensation curves with those calculated using the Soave-Redlich-Kwong (SRK) equation of state for two different mixtures: a simulated natural-gas mixture (Oscarson, 1983) and a real gas-condensate system (Ng et al., 1986). The internal consistency of the experimental data is considered in all comparisons. To illustrate the effect of the predicted mixture critical temperature on calculated condensation curves, we also compare experimental and calculated critical temperature of the mixture.

Data Reported by Oscarson

Table 1 presents the measured composition of the simulated gas mixture. The experimental critical temperature for this mixture is 218.2K (Cunningham et al., 1980). Using conventional mixing rules and recommended binary parameters (Knapp et al., 1982) for the methane binaries, the SRK equation predicts a mixture critical temperature of 218.5K, nearly identical to the reported value.

Table 1. Composition of a Simulated Natural-Gas Mixture

Component	Mole%	Component	Mole%
Nitrogen	10.17	n-Pentane	0.60
Methane	70.14	n-Hexane	0.81
Ethane	14.33	n-Heptane	0.24
Propane	2.10	n-Octane	0.14
n-Butane	0.41	Carbon Dioxide	1.06

Since saturated volumes are not reported for this system, condensation curves are compared in terms of molar L/F rather than liquid volume percent. Fig. 3 presents the calculated and measured condensation curves for this system at 239K. For each pressure, there are two experimental data for L/F: one is obtained by direct measurement, and the other is calculated from experimental K-values and feed composition. The difference between these two values of L/F indicates a measure of internal inconsistency in the data. Depending on which data are trusted, the SRK equation may either overpredict or underpredict L/F.

Fig. 4 shows condensation curves for the same mixture at 255K. For this temperature, the data are more consistent than those at 239K. The SRK equation underpredicts molar L/F, especially near the upper dew point.

To show the effect of K-values on calculated L/F for this mixture, flash calculations are performed using input K-values that are displaced by a known amount from the experimental K-values. Figures 5 and 6 present, respectively, the effect of deviations in K-values for methane and nitrogen on calculated L/F. Since methane is the most abundant component in the mixture and has a large K-value compared to unity, a 10% negative deviation in its K-value results in a nearly 90% deviation in calculated L/F.

Data Reported by Ng et al.

For the real gas condensate, composition is given for 36 identified components (Ng and Robinson, 1985). We represent the composition by five normal paraffins, C_1, C_2, C_3, $n-C_4$, $n-C_5$, and a C_6^+ fraction. The critical properties for the C_6^+ fraction are estimated using its average molecular weight in correlations developed for normal paraffins (Cotterman, 1985). Using conventional mixing rules and recommended binary parameters for the methane binaries (knapp et al., 1982), the SRK equation predicts a critical temperature of 344K, which is much higher than the reported 252K (Ng et al., 1986). This large discrepancy in critical temperature is not sensitive to the representation of the C_6^+ fraction and the binary parameters used. Upon using different representations of the C_6^+ fraction and upon varying the binary parameters within reasonable limits, the calculated critical temperature remains much higher than the experimental value.

To check the consistency of the reported feed composition, component material balances are performed to calculate a feed composition for each of the five pressures at 311K where phase-equilibrium data are available:

$$z_i = x_i\,(L/F) + y_i\,(1-L/F) \tag{8}$$

where x_i and y_i are, respectively, experimental mole fraction of component i in liquid and vapor phases; L/F is the experimental molar liquid-to-feed ratio, and z_i is the calculated feed composition.

Table 2 shows that deviations between the reported composition (measured from gas-chromatographic analyses) and the average of the five calculated feed compositions are reasonably small. Using this average feed composition, the SRK equation predicts a critical temperature of 342K, similar to that calculated using the reported composition. The Peng-Robinson(PR) equation also predicts a much higher critical temperature than the reported one (Ng, 1988). Since both SRK and PR equations, in general, predict reasonably accurate critical temperatures for hydrocarbon mixtures, it is not clear why the calculated critical temperature is much higher than the experimental value for this particular system. Wax formation during the experiment may be the cause for this discrepancy in critical temperature (Ng, 1988).

Table 2. Deviations between measured and calculated feed composition

Component	z_i(measured)	z_i(calculated)*	%Deviation
Methane	0.7384	0.7403	-1.1
Ethane	0.0730	0.0739	1.2
Propane	0.0460	0.0448	-2.6
Butanes	0.0272	0.0258	-5.0
Pentanes	0.0183	0.0173	-5.4
Hexanes +	0.0971	0.0978	0.7

*z_i here is the average of the five calculated feed composition.

The large deviation between experimental and calculated critical temperatures causes qualitative discrepancies in calculated condensation curves. Fig. 7 compares calculated and experimental condensation curves for the gas condensate at 311K. Since 311K is below the predicted critical temperature, flash calculations at high pressures converge to a bubble point (100% liquid). However, since 311K is above the experimental critical temperature (252K), liquid drop-out at high pressures decreases to zero at an upper dew point. Fig. 7 demonstrates that accurate location of the mixture critical point is essential for predicting

correct condensation curves, especially for isotherms very near the mixture critical temperature.

Conclusions and Future Work

After examining some of the most recent experimental data on retrograde condensation in natural-gas mixtures, we conclude that a meaningful comparison between calculated and experimental condensation curves must take into account experimental inconsistency in measured liquid drop-outs. Experimental inconsistency is probably due to the inherent difficulty in measuring accurate liquid drop-outs near upper dew points which are extremely sensitive to pressure, and due to the difficulty in determining concentrations of components which exist in extreme dilution, as observed for real gas condensates. Some of these experimental difficulties are addressed by Oscarson (1983) and by Ng et al. (1986).

We also conclude that the deficiencies of an equation of state in the retrograde region are probably not related to "critical phenomena" arising from density fluctuations. The true critical region is restricted to a very small vicinity of the critical point where all fluids behave universally according to scaling laws and where intermolecular interactions become unimportant; this small vicinity includes, at most, a few degrees Celsius from a critical point.

To predict accurate condensation curves from an equation of state, the calculated K-values must be improved in the retrograde region. While simple cubic equations of state can correlate binary data fairly accurately, it is not clear that we can rely on their one-fluid extension to complex multicomponent systems, such as gas condensates. The computer-simulation studies of Shing and Gubbins (1982) indicate that the one-fluid theory of mixtures is not reliable, especially with respect to components present in small concentrations. We suspect that a better fundamental equation for mixtures, such as a perturbed Boublik-Mansoori equation (Boublik, 1970; Mansoori et al., 1971; Dimitrelis and Prausnitz, 1986), may resolve some of the discrepancies.

References

Boublik, T., "Hard-Sphere Equation of State," *J. Chem. Phys.*, **53**, 471 (1970).

Chou, G.F. and J.M. Prausnitz, "A Phenomenological Correction to an Equation of State for the Critical Region," submitted for publication, 1988.

Cotterman, R.L., *Ph.D. Dissertation*, University of California, Berkeley, 1985.

Cunningham, J.R., J.L. Oscarson and M.L. Jenson, Gas Processors Association Research Report RR-40, 1980.

Dimitrelis, D. and J.M. Prausnitz, "Comparison of Two Hard-Sphere Reference Systems for Perturbation Theories for Mixtures," *Fluid Phase Equil.*, **31**, 1 (1986).

King, C.J., *Separation Processes*, 2nd ed., McGraw-Hill, 1980.

Knapp, H., R. Döring, L. Oellrich, U. Plöcker and J.M. Prausnitz, *Vapor-Liquid Equilibria for Mixtures of Low Boiling Substances*, DECHEMA Chem. Data Ser., Vol. VI, 1982.

Mansoori, G.A., N.F. Carnahan, K.E. Starling and T.W. Leland, "Equilibrium Thermodynamic Properties of the Mixture of Hard Spheres," *J. Chem. Phys.*, **54**, 1523 (1971).

Ng, H.J., Personal Communication, August 1988.

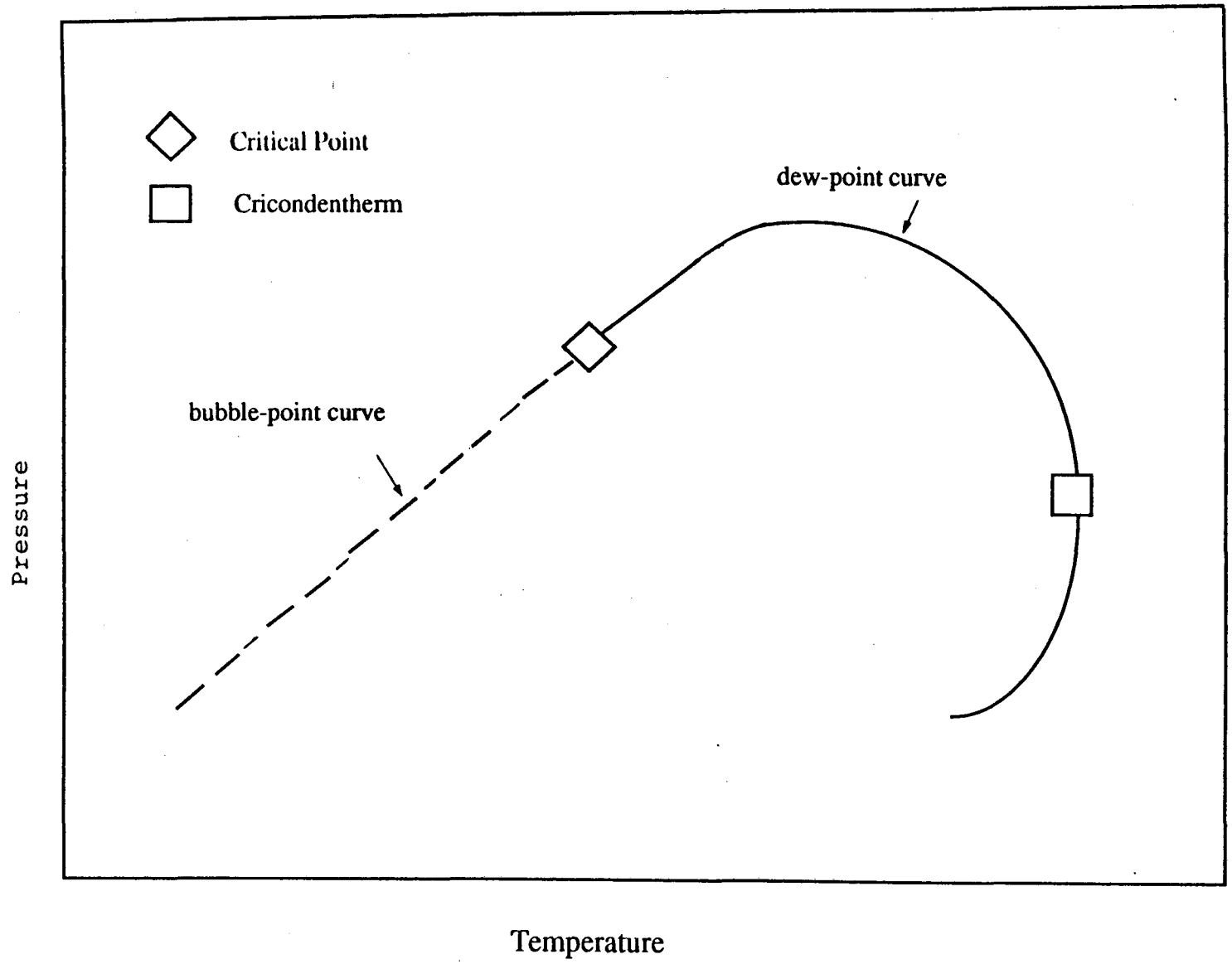
Ng, H.J., C.J. Chen and D.B. Robinson, Gas Processors Association Research Report RR-96, 1986.

Ng, H.J. and D.B. Robinson, Gas Processors Association Research Report RR-89, 1985.

Oscarson, J.L., Gas Processors Association Research Report RR-72, 1983.

Shing, K.S. and K.E. Gubbins, "The Chemical Potential in Dense Fluids and Fluid Mixtures via Computer Simulation," *Molecular Phys.*, **46**, 1109 (1982).

Fig. 1 Phase Boundary of a Typical Natural Gas Mixture



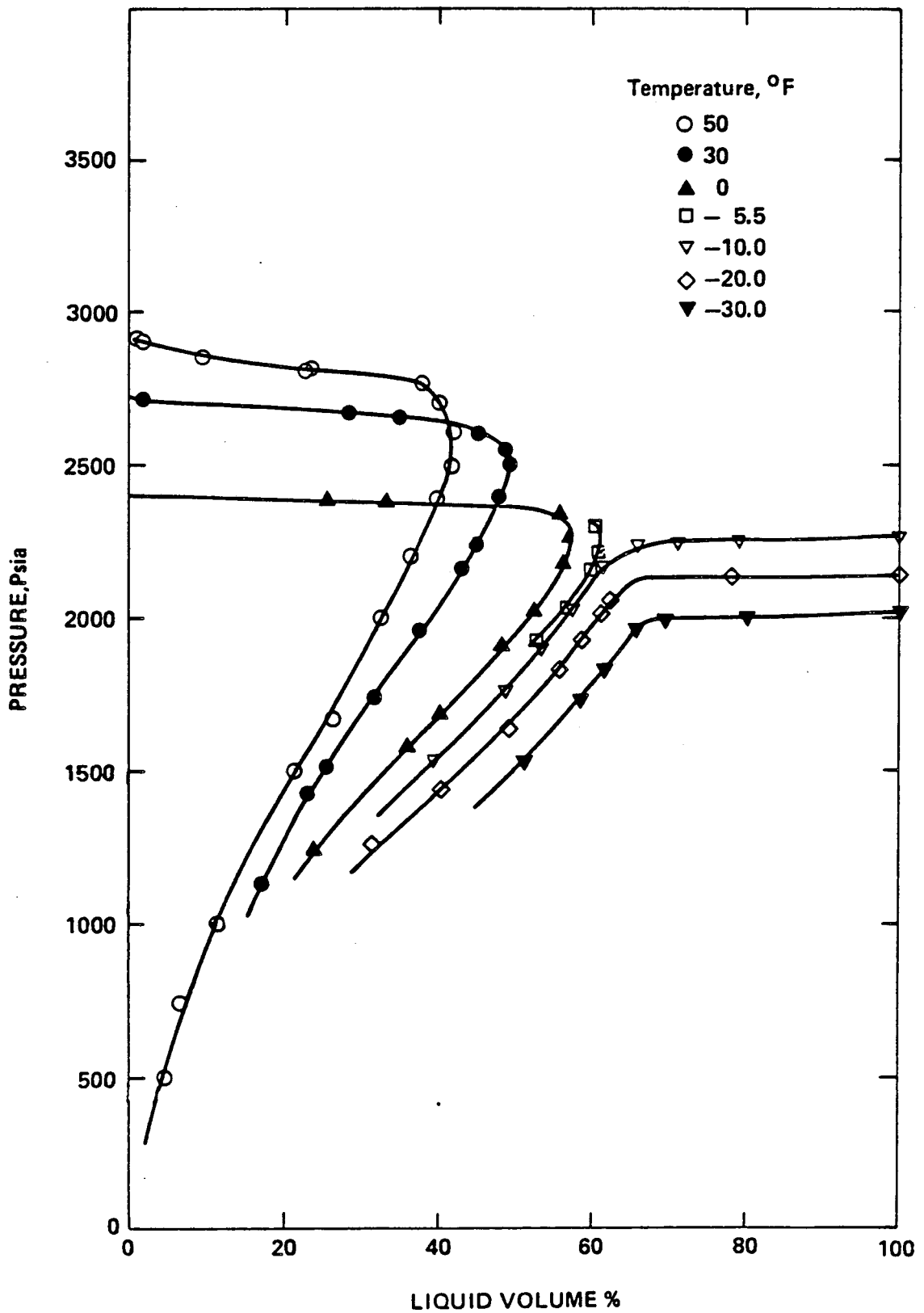


Fig. 2. Condensation curves for a real natural-gas condensate (taken from Ng et al., 1986).

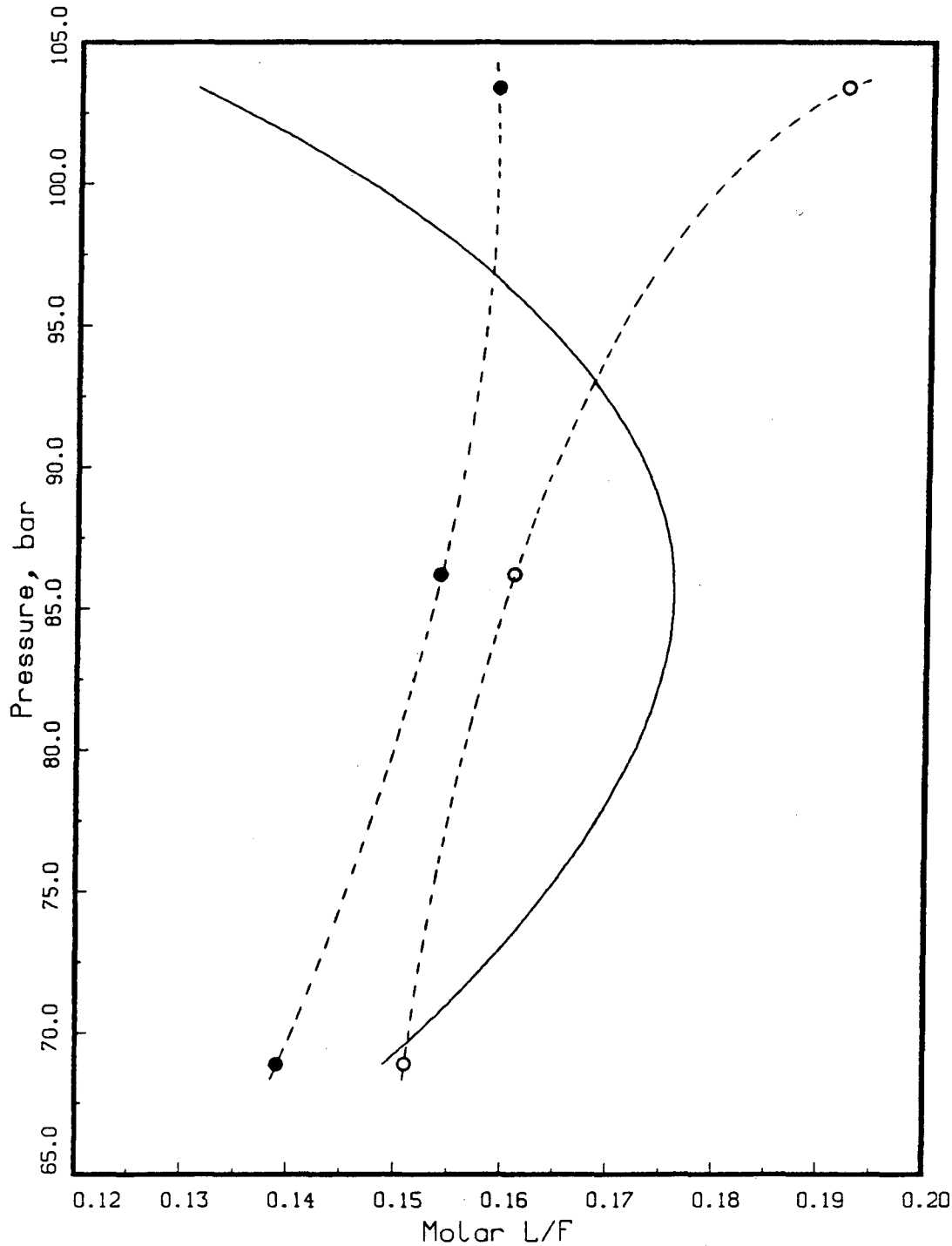


Fig. 3. Condensation curve for a simulated natural-gas mixture at 239K. Data by Oscarson, 1983: • direct measurement, o from experimental K-values and feed composition, --- interpolation. ___ Calculated using SRK equation.

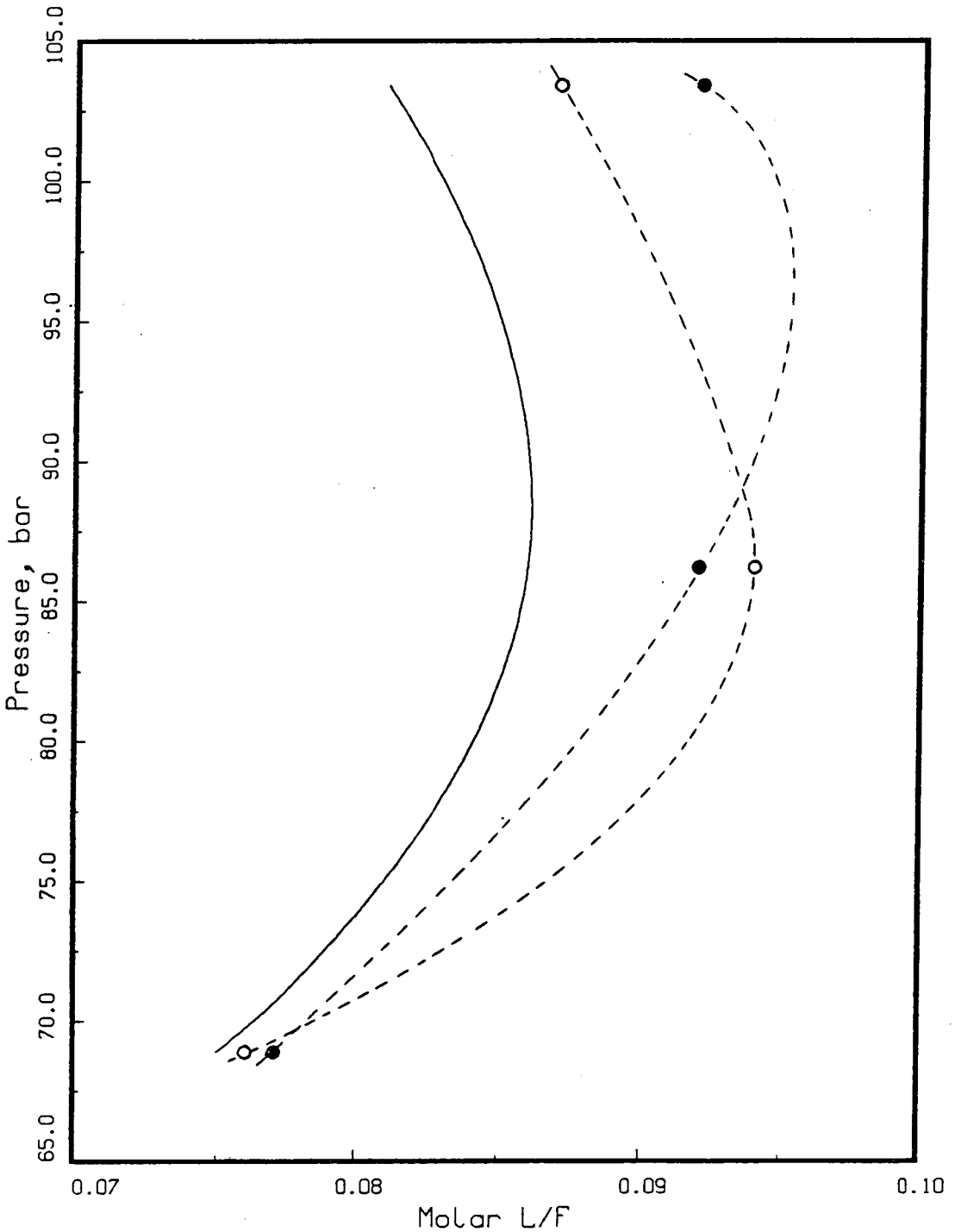


Fig. 4. Condensation curve for a simulated natural-gas mixture at 255K. Data by Oscarson, 1983: • direct measurement, o from experimental K-values and feed composition, --- interpolation. ___ Calculated using SRK equation.

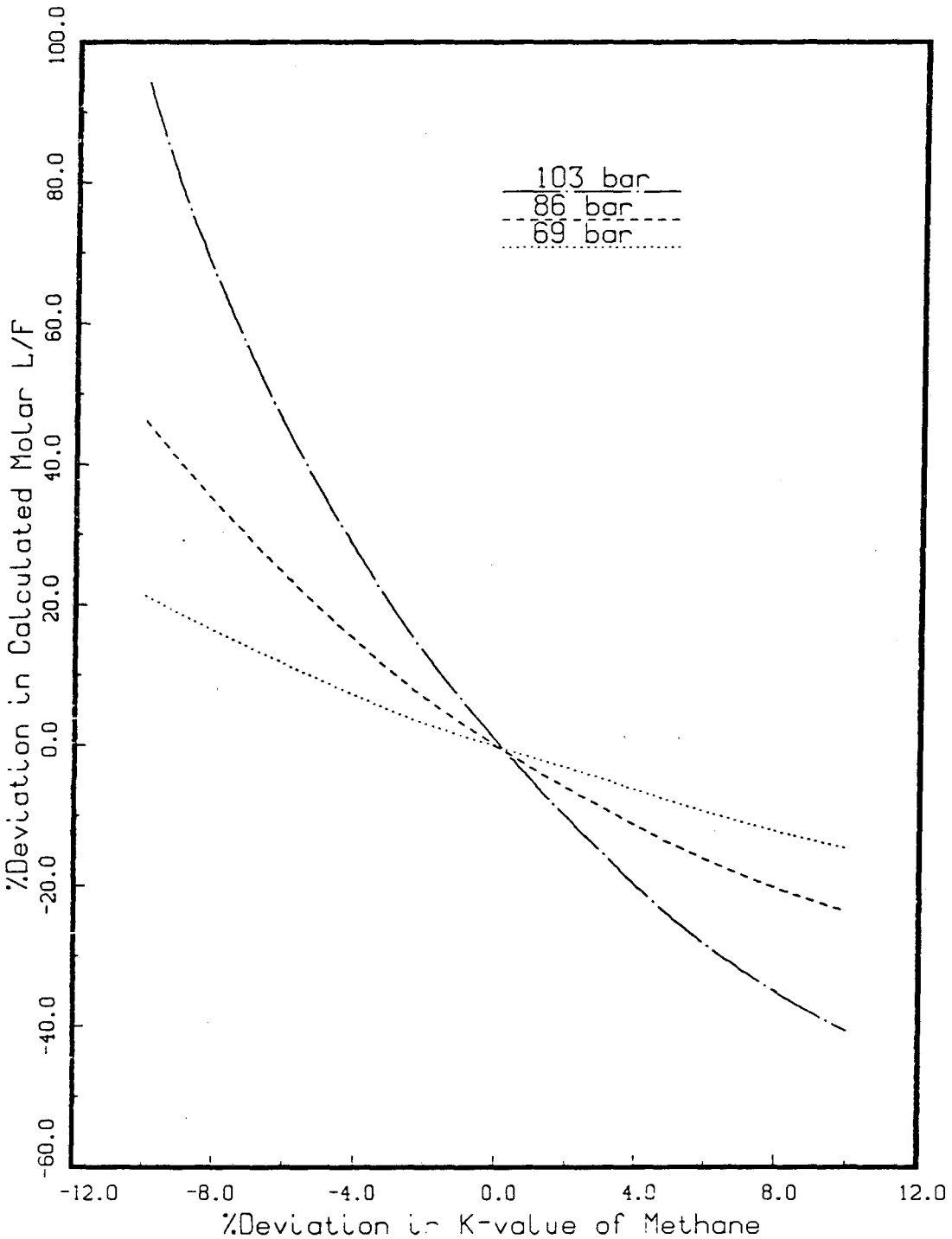


Fig. 5. The effect of K-values of methane on calculated molar L/F for the simulated natural-gas mixture at 239K.

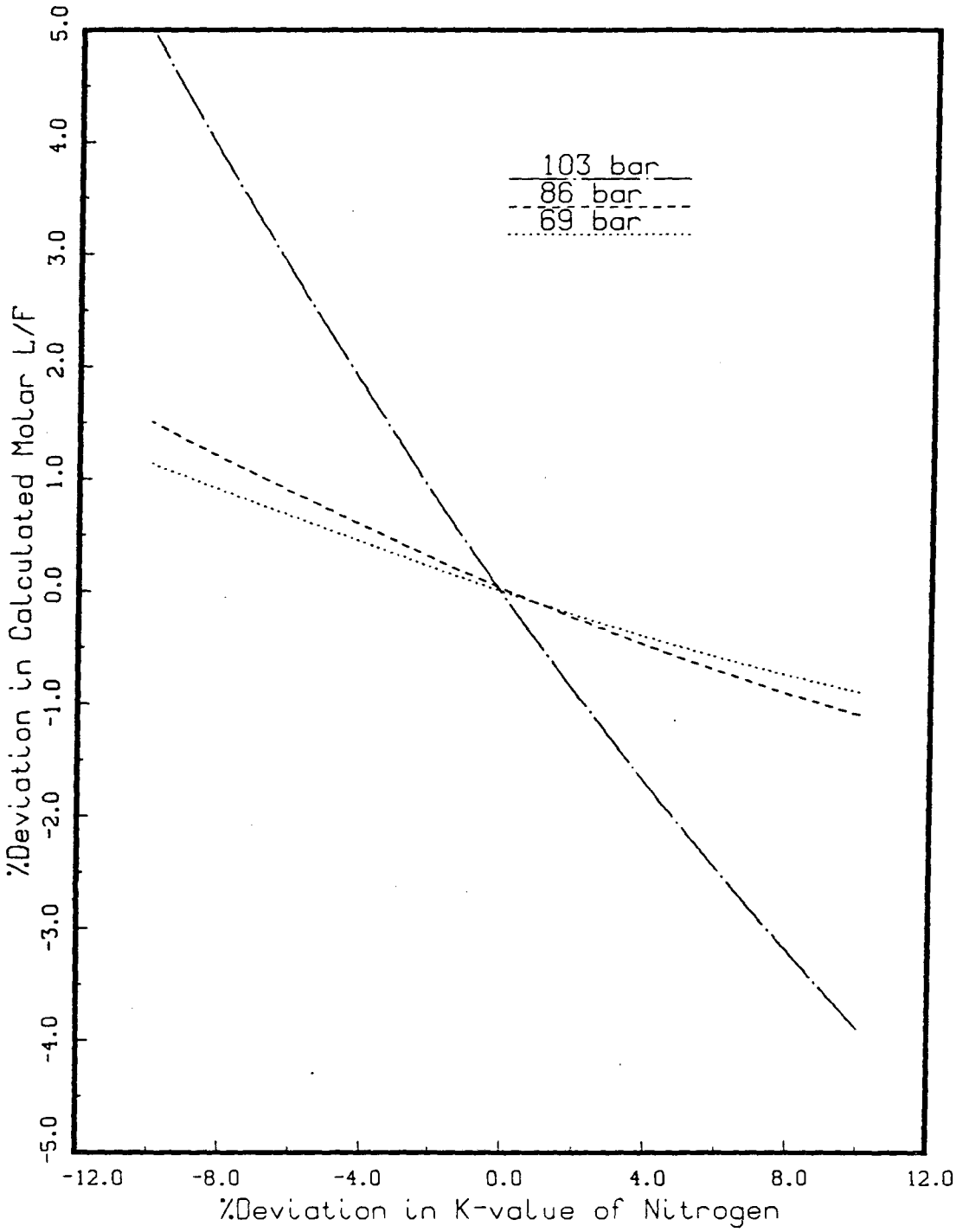


Fig. 6. The effect of K-values of nitrogen on calculated molar L/F for the simulated natural-gas mixture at 255K.

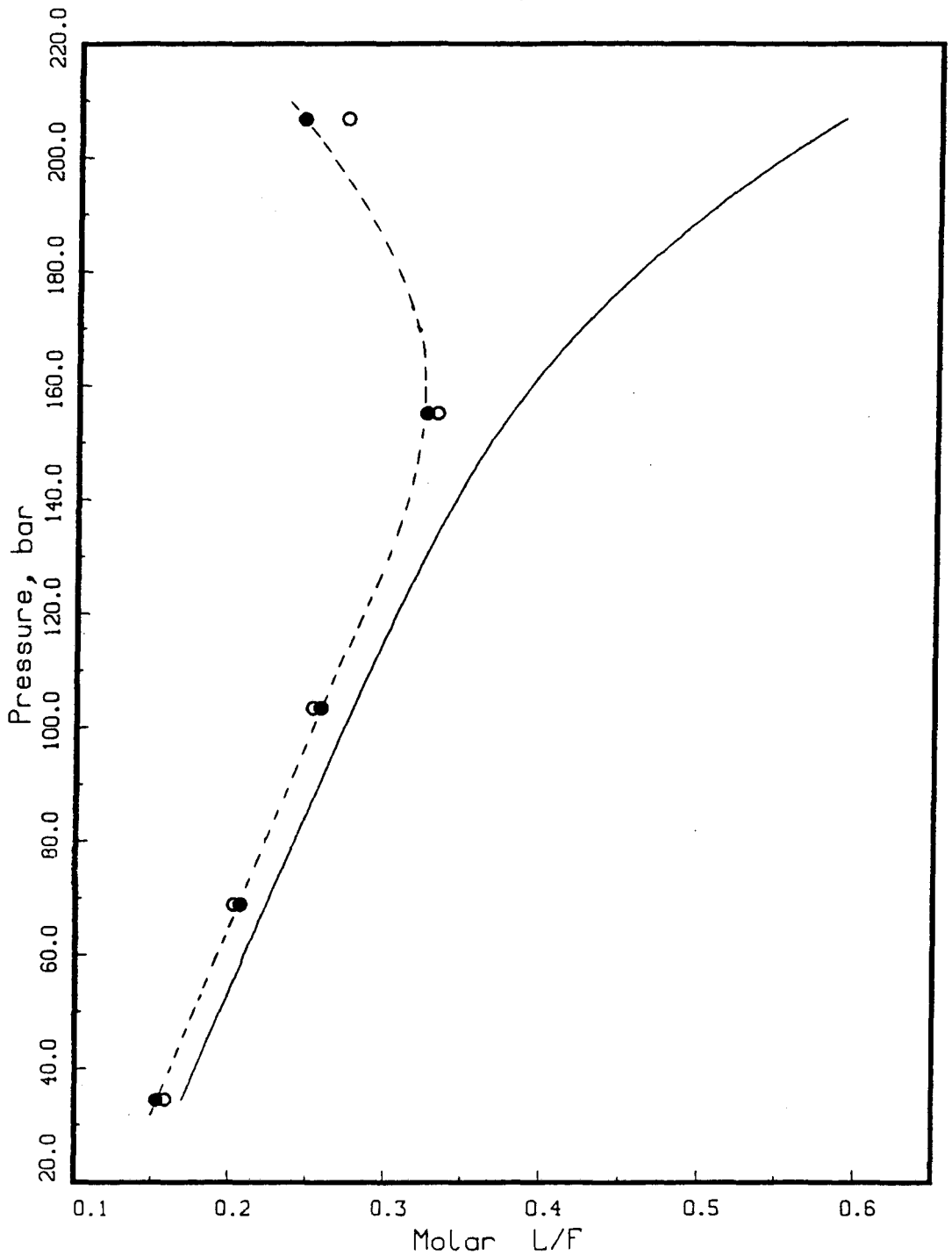


Fig. 7. Condensation curve for a real gas condensate at 311K. Data by Ng et al., 1986: • direct measurement, o from experimental K-values and feed composition, --- interpolation. ___ Calculated using SRK equation.

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720