uid phase. Analogous definitions for molar concentrations of other species

D = liquid-phase diffusivity of molecular chlorine, sq. cm./sec.

H = Henry's law constant for molecular chlorine, (g.moles)/(liter) (atm.)

h = height of the short wetted-wall column, cm.

K = equilibrium constant for chlorine hydrolysis, (g.moles/liter)^2

k_F = reaction rate constant, (sec.)$^{-1}$

k_L = liquid-phase absorption coefficient in the presence of the simultaneous chemical reaction, cm./sec.

k_L^* = liquid-phase absorption coefficient that would exist if no chemical reaction accompanied the absorption process, cm./sec.

M = $k_F D/(k_L^*)^2$

r = rate of chlorine hydrolysis, g.moles/(sec.) (liter)

T = temperature, °K. or °C.

y = mole fraction of chlorine in the gas phase

Γ = mass flow rate of liquid per unit perimeter of the column, g./(min.) (cm.)

η = $K/(Cl_2)^2_i$

ξ = liquid-phase density-viscosity product divided by this same product for water at 25°C.

ϕ = k_L/k_L^*

Subscripts

i = gas-liquid interface

LITERATURE CITED

1. Adams, F. W., and R. G. Edmonds, *Ind. Eng. Chem.*, **29**, 447 (1937).
2. Boelter, L. M. K., *Trans. Am. Inst. Chem. Engrs.*, **39**, 557 (1943).
3. Brian, P. L. T., J. F. Hurley, and E. H. Hasseltine, *A.I.Ch.E. Journal*, **7**, 226 (1961).
4. Connick, R. E., and Yuan-tsan Chia, *J. Am. Chem. Soc.*, **81**, 1280 (1959).
5. Danckwerts, P. V., *Trans. Faraday Soc.*, **46**, 300 (1950).
6. Gilliland, E. R., R. F. Baddour, and P. L. T. Brian, *A.I.Ch.E. Journal*, **4**, 223 (1958).
7. Habib, A. G., S.M. thesis, Mass. Inst. Technol., Cambridge, Massachusetts (1957).
8. Hatta, S., *Technical Reports, Tohoku Imp. Univ.*, **8**, 1 (1928-29) and **10**, 119 (1932).
9. James, W. A, and A. R. Gordon, *J. Chem. Phys.*, **7**, 963 (1939).
10. Lifshitz, Assa, and B. Perlmutter-Hayman, *J. Phys. Chem.*, **64**, 963 (1960).
11. Peaceman, D. W., Sc.D. thesis, Mass. Inst. Technol., Cambridge, Massachusetts (1951).
12. Sherwood, T. K., and F. A. L. Holloway, *Trans. Am. Inst. Chem. Engrs.*, **36**, 39 (1940).
13. Sherwood, T. K., and R. L. Pigford, "Absorption and Extraction," 2 ed., McGraw-Hill, New York (1952).
14. Shilov, E., and S. Solodushenkov, *Acta Physicocimica (USSR)*, **20**, 667 (1945).
15. Van Krevelen, D. W., and P. J. Hoftijzer, *Rec. trav. chemi*, **67**, 563 (1948).
16. Vivian, J. E., and D. W. Peaceman, *A.I.Ch.E. Journal*, **2**, 437 (1956).
17. Vivian, J. E., and R. P. Whitney, *Chem. Eng. Progr.*, **43**, 691 (1947).
18. Whitney, R. P., and J. E. Vivian, *Ind. Eng. Chem.*, **33**, 741 (1941).
19. Yakovkin, A., *J. Russ. Phys. Chem. Soc.*, **32**, 673 (1900).

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Experimental Determination of Critical Temperatures and Pressures of Mixtures: the Methane-Ethane-*n*-Butane System

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An experimental unit has been designed and constructed for the study of critical phenomena in multicomponent systems. This unit has been built to utilize a new visual PVT cell capable of operating at temperatures up to 300°F. and pressures to 10,000 lb./sq. in. abs. This cell is of the liquid piston type with mercury as the pressurizing fluid and affords unobstructed visual observation of its contents. The dependability of the unit has been tested on two mixtures of ethane and *n*-butane. Phase equilibria data were obtained, which in turn were used to establish the critical temperature and pressure.

Critical temperatures and pressures have been determined for six different compositions of the methane-ethane-*n*-butane system. These mixtures consisted of two series, each of three compositions differing only in methane content. The data obtained from them, in conjunction with previously reported critical values for the binaries of this system, have been utilized to generate the complete critical locus for the ternary system. The results for the six mixtures of this study have been compared with critical values predicted by methods available in the literature.

The present state of the field concerned with critical constants of hydrocarbon systems for the most part can be divided into two main classifications. A good deal of work is reported for binary systems (*6*), and for the other extreme considerable information is presented for complex mixtures (*8*). Although all of this information is basic and has been used extensively for correlation of critical properties, a gap exists between these two extremes. Experimental data on three- and four-component systems available in the literature are limited (*2*, *4*, *5*, *16*).

The majority of the critical data presented for these systems is a by-product of vapor-liquid equilibrium studies and frequently is not presented in a useful manner. At this time it appears appropriate to undertake a systematic study of these properties as particularly applied to a specific system. A background of this type on several systems is highly desirable in order to bridge the gap presently existing

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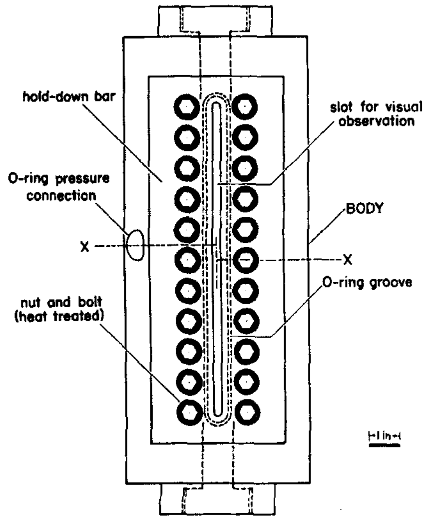

Fig. 1. Schematic diagram of visual PVT cell without closures.

between the binary and complex hydrocarbon systems.

EXPERIMENTAL EQUIPMENT

A survey of the literature has presented several experimental units for the determination of critical constants of multicomponent systems. These units possess a common characteristic in that they use a liquid type of piston in order to vary the volume and thus the pressure at constant temperature. These can be divided into two basic categories; the principal difference between them lies in the ability to observe visually the system confined in the unit. Excellent examples of the nonvisual type are those of Sage and Lacey (*18, 19, 20*) which were specifically designed for volumetric and phase equilibria studies and include sampling facilities for analysis of the coexisting vapor and liquid phases. Critical temperatures and pressures are determined indirectly by extrapolation of vapor-liquid equilibrium data.

Visual types of equipment are basically the same but do not require sampling facilities and afford direct observation of the mixture under study. Two foremost groups involved in this area of activity are those of Kay and Katz. The equipment of Kay (*11*) is essentially a modification of that of Andrews (*1*) and Young (*22*) and has been used primarily for vapor-liquid equilibrium and critical studies of binary systems by the dew- and bubble-point method. This type of equipment is restricted to binaries for vapor-liquid equilibrium studies; however its application can be extended for the determination of criticals for systems containing more than two components. Katz and co-workers (*9, 10, 15*) have employed a visual technique to establish the critical points of natural gas and gasoline mixtures and also carbon dioxide-paraffin systems. The equipment designed and constructed for these studies is essentially of the same basic type as that of Katz and Kurata (*9*).

Visual PVT Cell

The cell utilized in this investigation is shown schematically in Figures 1 and 2, and a photographic view is presented as Figure 3. The essential features of this cell include a stainless steel body 6 in. in diameter and closures rated at 10,000 lb./sq. in., a full-length glass window mounted in a tool steel hold-down bar, an unsupported-area (Bridgman type) closure, and an O-ring pressure seal for the glass viewing window.

The working volume is cylindrical, 1 in. in diameter and slightly more than 10 in. in length, of approximately 145-cc. volume. The hole is bored off-center to prevent pressure distortion of the cell which could put undue strains on the glass. The window is Herculite tempered glass. This window fits in the hold-down bar with tolerances of the glass, and the copper and tool steel shims kept within 0.001 in. of the depth of the slot in the hold-down bar.

The pressure seal between the glass window and the cell body is made with an O-ring, which sets the upper temperature limit of 300°F., located in a groove surrounding the slot for visual observation. To affect a tight seal nitrogen pressure is applied behind the O-ring and is always kept at least 1,000 lb./sq. in. higher than the internal cell pressure. A cross-sectional view of the cell showing the O-ring and its pressure connection is shown in Figure 2.

The Bridgman type of end closure is presented in the cross-section view of the head shown in Figure 2. This type of closure possesses the excellent feature of sealing tighter with increasing pressure, since increased pressure results in greater compression of the Teflon gasket. Each piece of the closure was machined from a different type of stainless steel to minimize the possibility of galling. In addition all pieces were coated with molybdenum disulfide-graphite lubricant.

Auxiliary Equipment

The entire layout of the experimental unit is presented schematically in Figure 4. The basic pressurizing system consists of a mercury pump (250-cc. capacity, 25,000 lb./sq. in.) used to introduce and remove mercury from the PVT cell via the charging cell. Pressures are measured with two 16-in. gauges. The low-pressure gauge, to 2,500 lb./sq. in., can be disconnected by closing valve G-1. The gauges were calibrated with a dead-weight tester, connected through valve G-5. The details concerning calibration and height differentials of mercury are presented elsewhere (*7*).

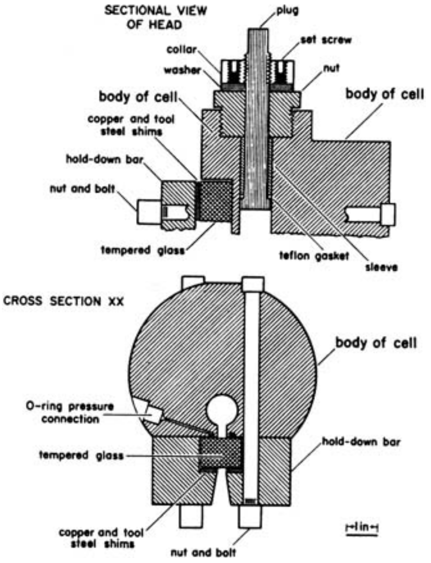

Fig. 2. Detail drawing of visual PVT cell.

An auxiliary pressurizing system supplies compressed nitrogen behind the O-ring seal in the visual PVT cell. This is accomplished by compressing nitrogen with mercury delivered from the O-ring pump into the nitrogen-mercury separator.

Evacuating facilities are provided by a mechanical fore-pump in conjunction with a mercury diffusion pump. Absolute pressures are measured with a vacuum thermocouple gauge. The vacuum system can be tied into either the main pressurizing system through valve V-4 or the O-ring pressurizing system through valve V-5.

Air bath facilities are used to maintain constant temperature around the PVT cell. These thermostating facilities consist of two insulated chambers, one inside the other, provided with hinged doors. Each door is provided with a long window of Herculite plate glass to afford a visual observation of the PVT cell contents. The PVT cell is mounted on a rocker trunnion in the inner chamber. The main heat is supplied in the outer chamber by twelve 500-w. (maximum) strip heaters, manually controlled by autotransformers. Control in the outer chamber is effected with an on-off controller operating a 500-w. heater. This arrangement enables maintenance of temperature within ± 2°F. in the outer chamber. The inner chamber operates with a 200-w. heater a few degrees above the temperature level of the outer chamber. This 200-w. heater is controlled by a sensitive tem-

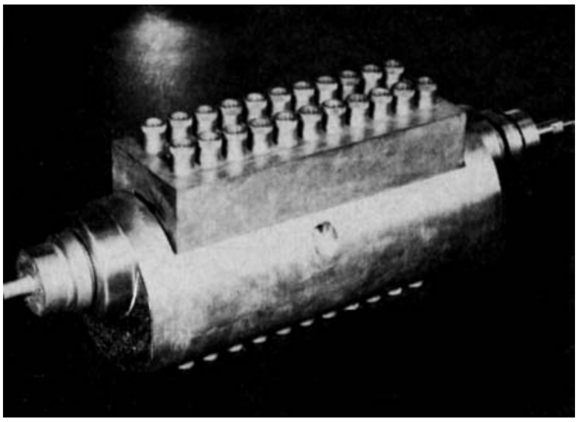

Fig. 3. Side view of assembled PVT cell.

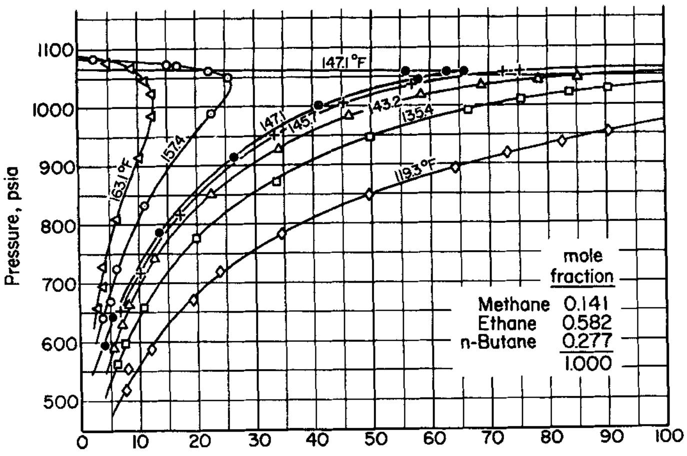

Fig. 5. Liquid volume per cent isotherms for Charge 2.

perature controller utilizing a resistance thermometer located in the inner chamber; this arrangement enables maintenance of temperature within 0.1°F. Air circulation in the outer chamber is accomplished with a centrifugal blower and duct work. The inner chamber was provided with fan blades mounted on rotating shafts. Temperatures in the experimental unit are measured with 14-gauge copper-constantan thermocouples, three of which are inserted in deep holes drilled in the visual PVT cell and four located in the constant temperature baths. These thermocouples are connected to an L and N type K-2 potentiometer, external galvanometer, and an ice point reference junction. Calibration of these thermocouples was made with a National Bureau of Standards certified platinum resistance thermometer used in conjunction with a precision bridge.

The different components of a mixture are charged into the charging cell. A sampling system for withdrawal of small samples for analysis is provided and consists of glass expansion, leveling, and sampling bulbs. The charging and sampling procedures are described in some detail below, and the entire experimental unit and procedure is described in greater detail elsewhere (*7*).

EXPERIMENTAL PROCEDURE

After the PVT cell and main pressurizing system are completely evacuated, the hydrocarbon constituents are introduced by means of the charging cell. The heavy components are charged first, usually as liquids, followed by noncondensable gases available in high pressure cylinders. After charging, mercury is pumped into the PVT cell. The temperature of the system is then adjusted to the desired value and allowed to reach thermal equilibrium overnight.

Actual phase equilibria measurements are commenced by first pressurizing the system with mercury until a homogeneous single phase is obtained. The pressure is then decreased decrementally into the two-phase region. Volumetric data are taken for the total system and the liquid present at any one pressure. Details of the procedure used to establish the volumetric data are presented elsewhere (*7*). After each decrease in pressure the cell is rocked on its trunnion to insure equilibrium, and the temperature and pressure are recorded. The decrease in pressure is continued until the mercury reaches the bottom of the PVT cell. With the same charge this procedure is repeated at different temperatures until enough isotherms are obtained to completely define the phase diagram of the mixture in the critical region, in a manner similar to that used by Katz and Kurata (*9, 13*).

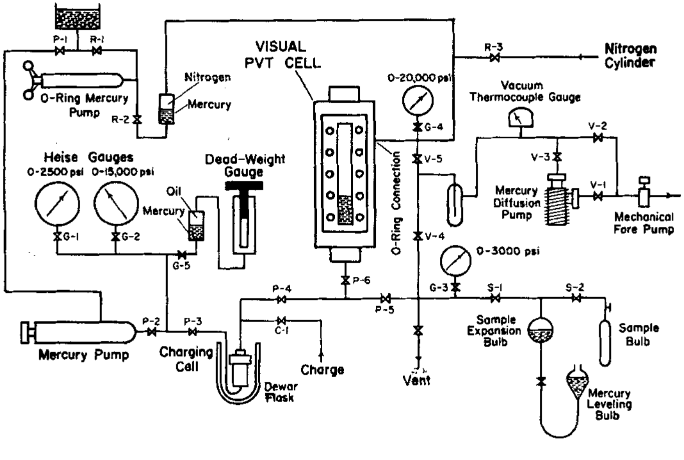

Fig. 4. Schematic diagram of experimental unit for studies in the critical region.

Upon completion of phase equilibria measurements the temperature in the cell is raised somewhat above the cricondentherm prior to sample withdrawal for composition analysis. Also all lines bounded by valves P-4, V-4, S-1, and the vent are heated by means of insulated heating tapes. This precaution is taken in order to avoid the possibility of phase separation when the pressure is decreased. The pressure of the system is decreased by withdrawing the merucry completely from the cell to valve P-4. Samples are then trapped in the evacuated line between valves P-5 and S-1 and are then expanded into the sample expansion bulb. After the sample has been adequately mixed by raising and lowering the mercury level in the expansion bulb, the gas is introduced into the evacuated sample bulb at slightly above atmospheric pressure. These samples are then analyzed for composition with a mass spectrometer.

EXPERIMENTAL INVESTIGATIONS

In order to test the reliability of the equipment the critical region phase behavior of two mixtures of the ethane—*n*-butane system was investigated. This system was selected because it was previously studied by Kay (*12*) and also because it represents one of the binaries of the methane—ethane—*n*-butane system to be investigated in

Table 1. Critical Temperature and Pressures for Methane-Ethane-*n*-Butane Mixtures

Charge	Mole fraction Methane	Ethane	*n*-Butane	T_c, °F.	P_c lb./sq.in.abs.
1	0.095	0.626	0.279	162	1,017
2	0.141	0.582	0.277	146	1,065
3	0.190	0.560	0.250	130	1,118
4	0.112	0.372	0.516	225	992
5	0.216	0.321	0.463	192	1,218
6	0.452	0.229	0.319	114	1,700

this study. The first mixture, of 0.602 mole fraction ethane, yielded a critical temperature of 207°F. and a critical pressure of 837 lb./sq. in. abs.; the second, of 0.874 mole fraction ethane, produced critical values of 130°F. and 814 lb./sq. in. abs. Neither of these compositions was among the five studied by Kay. However from a plot of Kay's data critical values were obtained of 204°F. and 832 lb./sq. in. abs. for the first mixture and 131°F. and 806 lb./sq. in. abs. for the second. The good agreement found here showed the equipment to be operating reliably.

The Methane-Ethane-n-Butane System

The minimum guaranteed purities of the hydrocarbons were as follows:

	mole %
methane	99.59
ethane	99.9
n-butane	99.91

The normal butane was charged first as a liquid; the ethane and methane, available at high pressure, were charged directly as gases.

In order to systematize the study of this ternary system two series of mixtures were investigated. Each series consisted of three different compositions differing only in methane content. The second and third mixtures of each series were obtained by adding methane to the initial charge to the system. Although all precautionary steps were taken in sampling and analysis, the ratio of the ethane and *n*-butane mole fractions of the two series of mixtures analyzed showed a slight variation.

Figures 5 and 6 represent the results for one of the six compositions studied. Figure 5 represents the data as obtained directly from visual observation of the liquid level in the PVT cell. Figure 6 represents a cross plot of Figure 5 onto the pressure-temperature plane and expresses the two-phase region in parameters of constant liquid volume per cent. The critical point is determined from Figure 6 as the point where all the liquid volume per cent lines converge. In a phase diagram of this type retrograde condensation is possible in the region between the critical temperature and the cricondentherm. With a similar procedure for the other five mixtures, the critical temperatures and pressures presented in Table 1 were obtained. These values should be reliable to within 1°F. and 2 lb./sq. in. abs.

Treatment of Data and Final Correlation

In order to obtain integral values of critical temperature and pressure the critical data resulting from each series of three charges were plotted in Figures 7 and 8. Since the ethane to *n*-butane ratio was held constant for each series, it was possible to utilize the composition parameter of Carter, Sage, and Lacey (*4*)

$$C = \frac{x_2}{x_2 + x_4}$$

where x_2 and x_4 represent mole fractions of ethane and *n*-butane, respectively. This parameter effectively relates the ethane and *n*-butane present in the ternary mixture; in the limit when no methane is present, it becomes simply the mole fraction of ethane in the binary system of ethane—*n*-butane. Accordingly the points on the ordinate axes at zero methane mole fraction were obtained from the information available for the binary system ethane—*n*-butane (*12*) at mole fractions of ethane equal to the parameter *C* for each of the two series investivated ($C = 0.415$ and $C = 0.687$).

The information of Figures 7 and 8 has been used to construct the final correlations presented in Figures 9 and 10. The points shown in these figures were obtained directly from Figures 7 and 8 and follow two straight lines converging to the methane vertex, representing the constant values of the parameter *C*. The critical data for the three associated binaries of the system (*3, 12, 17*) have been utilized to extend the available information to the sides of each triangular diagram. In order to complete these correlations, lines were drawn through the area rich in methane for temperatures below 100°F. by joining the points of the binary systems in a manner consistent with the behavior observed in the region above 100°F. Figures 9 and 10 thus define the critical temperatures

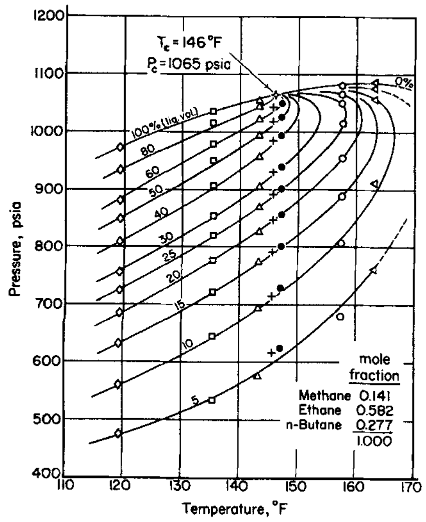

Fig. 6. Phase diagram for establishment of critical temperature and pressure of Charge 2.

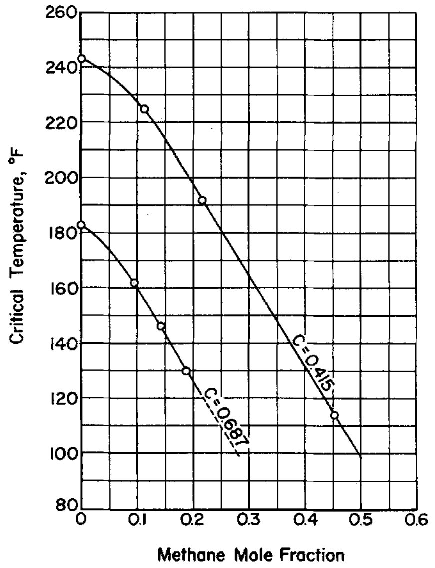

Fig. 7. Critical temperature-composition relationships for methane-ethane-*n*-butane mixtures.

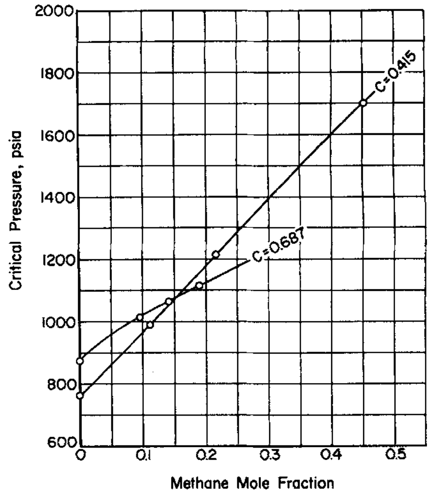

Fig. 8. Critical pressure-composition relationships for methane-ethane-*n*-butane mixtures.

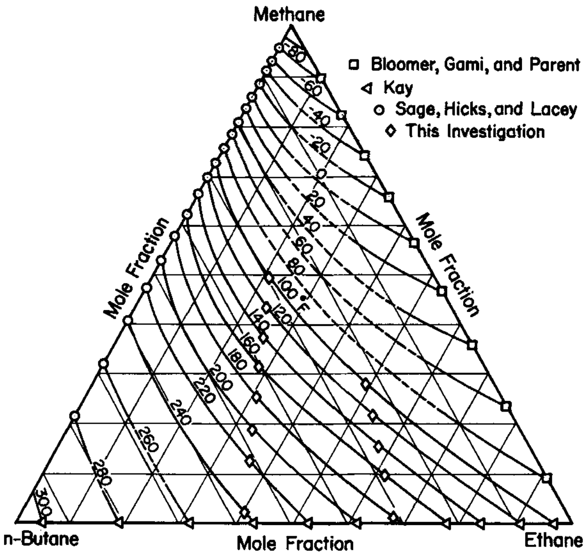

Fig. 9. Critical temperatures of the methane-ethane-*n*-butane system.

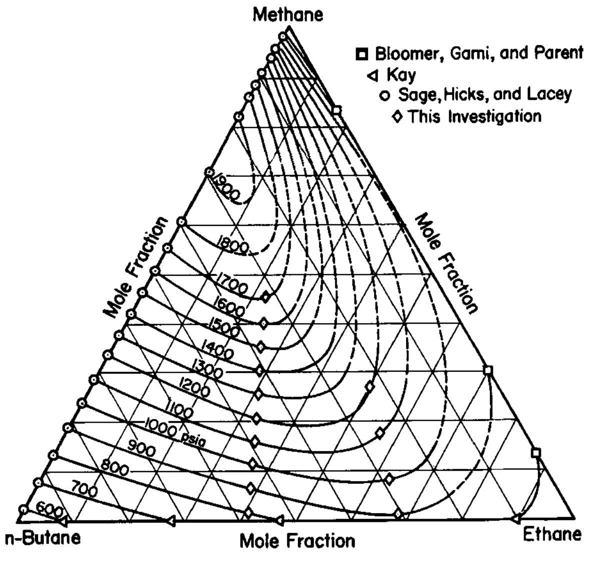

Fig. 10. Critical pressures of the methane-ethane-*n*-butane system.

and critical pressures for any composition of the ternary system methane—ethane—*n*-butane.

Comparison with Literature Methods

Many methods for the prediction of critical temperatures and pressures of hydrocarbon mixtures are available in the literature. Of these, three methods are applicable to simple mixtures of known composition, such as those of this study. The methods used were those of Smith and Watson (*21*), Kurata and Katz (*13*), and Organick and Brown (*14*). Critical values were calculated by these methods and compared with the experimental critical temperatures and pressures of this investigation. Comparison showed that the method of Smith and Watson produced critical temperatures closest to those actually determined, with an average deviation of 1.8%. Deviations of 2.8 and 4.4% were obtained from the methods of Kurata and Katz and Organick and Brown, respectively. All correlations predicted critical temperatures invariably higher than the actual values. Comparison of critical pressures showed greater deviations than found for critical temperatures. Of the three methods, that of Organick and Brown gave the lowest deviation for the critical pressure, amounting to 5.0%. The Smith and Watson procedure yielded a 5.5% deviation, while that of Kurata and Katz produced a deviation of 7.9%. For the most part these methods produced critical pressures that were lower than those actually encountered; the agreement was poorest for mixtures with the highest methane content.

The final correlations, Figures 9 and 10, were also checked against the suggestion of Hadden (*8*) that a linear relationship can exist between critical pressure and a weight composition parameter, at constant critical temperature. The weight composition parameter W is defined in the same manner as the parameter C defined previously, except that weight fractions are employed instead of mole fractions. The comparison between the experimental results of this study and Hadden's suggested linear relationship has been made. It was found that agreement was almost exact at higher temperatures, whereas at lower temperatures deviations were noted with decreasing temperature. The poorest agreement occurred for low values of parameter W at lower temperatures; these again corresponded to mixtures with higher methane content.

These comparisons indicate the need for more experimental data on mixtures of the type examined in this investigation, especially systems containing methane.

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LITERATURE CITED

1. Andrews, Thomas, *Proc. Roy Soc. (London)*, **18**, 42 (1869).
2. Billman, G. W., B. H. Sage, and W. N. Lacey, *Trans. Am. Inst. Mining Met. Engrs.*, **174**, 13 (1948).
3. Bloomer, O. T., D. C. Gami, and J. D. Parent, *Inst. Gas Technol. Research Bull. No. 22* (1953).
4. Carter, R. T., B. H. Sage, and W. N. Lacey, *Trans. Am. Inst. Mining Met. Engrs.*, **142**, 170 (1941).
5. Dourson, R. H., B. H. Sage, and W. N. Lacey, *ibid.*, **151**, 206 (1943).
6. "Equilibrium Ratio Data Book," Natural Gasoline Association of America, Tulsa, Oklahoma (1957).
7. Forman, J. C., Ph.D. dissertation, Northwestern University, Evanston, Illinois (1960).
8. Hadden, S. T., *Chem. Eng. Progr. Symposium Ser. No. 7*, **49**, 53 (1953).
9. Katz, D. L., and Frederick Kurata, *Ind. Eng. Chem.*, **32**, 817 (1940).
10. Katz, D. L., D. J. Vink, and R. A. David, *Trans. Am. Inst. Mining Met. Engrs.*, **136**, 106 (1940).
11. Kay, W. B., *Ind. Eng. Chem.*, **30**, 459 (1938).
12. *Ibid.*, **32**, 353 (1940).
13. Kurata, Frederick, and D. L. Katz, *Trans. Am. Inst. Chem. Engrs.*, **38**, 995 (1942).
14. Organick, E. I., and G. G. Brown, *Chem. Eng. Progr. Symposium Ser. No. 2*, **48**, 97 (1952).
15. Poettmann, F. H., and D. L. Katz, *Ind. Eng. Chem.*, **37**, 847 (1945).
16. Reamer, H. H., B. H. Sage, and W. N. Lacey, *ibid.*, **44**, 1671 (1952).
17. Sage, B. H., B. L. Hicks, and W. N. Lacey, *ibid.*, 32, 1085 (1940).
18. Sage, B. H., and W. N. Lacey, *ibid.*, **26**, 103 (1934).
19. ————, *Trans. Am. Inst. Mining Met. Engrs.*, **136**, 136 (1940).
20. *Ibid.*, **174**, 102 (1948).
21. Smith, R. L., and K. M. Watson, *Ind. Eng. Chem.*, **29**, 1408 (1937).
22. Young, Sydney, *Sci. Proc. Roy. Dublin Soc.*, **12**, 374 (1909-10).

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