EVALUATION OF BENEDICT'S EQUATION FOR CALCULATION OF CRITICAL PRESSURES OF HYDROCARBON MIXTURES

BY

THOMAS W. OWENS

A THESIS
SUBMITTED TO THE FACULTY OF
THE DEPARTMENT OF CHEMICAL ENGINEERING
OF
NEWARK COLLEGE OF ENGINEERING

IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE
IN CHEMICAL ENGINEERING

NEWARK, NEW JERSEY

1955

ABSTRACT

Owens, Thomas W. - Evaluation of Benedict's Equation for Calculation of Critical Pressure of Hydrocarbon Mixtures - Thesis, submitted to Newark College of Engineering, January 24, 1955.

An introduction to the problem of critical pressure calculations of mixtures is presented, followed by a brief history of prior work in this field. Mentioned in the history are the correlations of Watson and Nelson, Smith and Watson, Mayfield, Kuratta and Katz, Benedict, and Edmister. Another section contains a series of tables showing critical pressure calculated by Benedict's equation as contrasted to other data appearing in the literature. An evaluation of the equation is then made from the comparisons.

Included are curves of the values shown in the tables and a series of curves depicting the deviation of these values from the experimental.

APPROVAL OF THESIS

FOR

DEPARTMENT OF CHEMICAL ENGINEERING
NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: ______________________________

____

____

NEWARK, NEW JERSEY
JANUARY, 1955

PREFACE

The Benedict equation for calculating critical pressures of hydrocarbon mixtures was applied to available literature data for comparison of results with other prior calculation methods.

ACKNOWLEDGEMENTS

I would hereby like to acknowledge and express my appreciation to the following:

1. Prof. M. Frederick who helped immeasurably through his timely assistance and guidance.

2. Dr. J. Joffe who originated this topic along with several others for selection.

3. Dr. C. Mantell and other members of the Graduate School and Chemical Engineering Department, all of whom made this thesis possible.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

Knowledge, or more properly, lack of knowledge concerning critical properties of hydrocarbons has resulted in great interest in this field for the past thirty years. The petroleum industry as a whole has been extremely desirous of learning more about this subject. No single factor (8) is of greater practical importance in cracking-plant design than the computations of volumes of liquids and vapors at cracking-zone conditions. Small errors become very important because the stocks are at or near their critical points and a small misjudgment may shift the behavior of the material from that of a vapor to that of a liquid. To accomplish the intelligent design of petroleum refining equipment, knowledge of the critical properties of hydrocarbon mixtures, particularly as a function of properties readily determinable, is paramount as the critical pressure in particular cannot be easily determined directly.

In particular, the use of equilibrium constants in phase equilibria computations has required an increase in the knowledge of the critical point. The limits of the two-phase region and the relative amounts of vapor and liquid within this region are of particular interest since these mixtures are similar in properties to the effluents from distillate wells.

Direct experimental$^{(7)}$ determination of the critical constants is not only inconvenient but frequently misleading unless properly determined by competent experimentalists in this field. Some of the factors that can cast doubt on these determinations may stem from the experimental equipment, purity of substance, background of investigation, and the stability of such compounds near the critical point.

As has been mentioned, the critical point is important in making phase equilibria estimates. It is an important point on the phase diagram$^{(3)}$ because it defines the conditions above which there is no distinction between coexistent phases. Although the critical temperature of mixtures may be correlated or estimated with relative ease and accuracy, the critical pressure is a much more complex property and is difficult to predict. Of interest in this topic are the pseudo-critical pressure and the critical pressure. The pseudo-critical pressure is an imaginary point which may be readily determined as approximately proportional to the mol fractions of the pure components. The critical pressure, while being an actual experimentally determinable point, frequently assumes a value considerably higher than that of any of the pure components of the mixture. Many correlators have attempted to determine the pseudo-critical pressure and then relate this empirically to the actual or true critical pressure.

The more important correlations to date are summarized in this presentation. Evaluation of Benedict's(1) correlation will also be presented and will be compared with other literature values.

SUMMARY OF PREVIOUS CORRELATIONS

Watson and Nelson(10)

Several methods of estimating critical pressures have been proposed. Watson and Nelson, in 1933, proposed an adoption of an existing method for finding the critical pressure of a pure hydrocarbon utilizing a Cox vapor pressure chart. Knowing the critical temperature of a pure hydrocarbon, the critical pressure could be found by drawing a line on this chart and connecting the normal boiling point of the compound with the convergence point of the hydrocarbon vapor pressure curves. The pressure at which this line crossed the abscissa of the critical temperature was the critical pressure.

The molal average boiling point of hydrocarbon mixtures also plot as straight lines on the Cox chart with the same point of convergency as the pure hydrocarbons. Also the slopes of the initial equilibrium vaporization points plot as straight lines but with less slope than the boiling point curve. The authors found that by joining the A.S.T.M. 10% point with a point approximately 20% past the critical temperature isotherm on the average boiling point line, the approximate critical pressure could be found. This is the absolute pressure reading where the 10% line crosses the critical temperature isotherm.

At the time the Watson and Nelson method was proposed there was very little published data on the critical pressures of hydrocarbon mixtures. The accurate determination of such pressures was quite difficult and exacting and the authors had little to work with, both in devising their method and later in testing it.

Smith and Watson(9)

The correlations and methods presented by Smith and Watson claimed to be advantageously based on and applicable to both pseudo-critical and true critical properties for all widths of boiling range and any type of mixture. The authors felt that because a true critical pressure of a mixture is intermediate in composition and higher in value than any constituent, the true critical pressure could not be correlated as a function of only two average properties. Kay(5) has previously indicated that no such maximum existed for pseudo-critical pressures which were approximately proportional to mol fraction in binary mixtures. The authors then proceeded to correlate true and pseudo-critical pressures by means of a series of charts.

The true molal, mean and weight average boiling points and A.P.I. gravity were first determined. From a plot of weight average boiling points versus true critical temperature for a family of A.P.I. gravities, the true critical temperature was determined. From the same figure, the pseudo-critical temperature was determined using the true molal average boiling point. The ratio of true to pseudo-critical temperature was then calculated. From another plot relating the two, the ratio of true to pseudo-critical pressure was found. Two more plots were formed linking respectively, mean average boiling point and A.P.I. gravity with pseudo-critical pressure, and molecular weight and A.P.I. gravity with pseudo-critical pressure. From one of these plots the pseudo-critical was determined and the true critical pressure calculated from the previously determined ratio.

Mayfield(6)

Mayfield in 1942 proposed a new method of determining critical pressures empirically, for binary normal hydrocarbon mixtures. He pointed out that whereas all critical temperatures of such mixtures lie between the critical temperatures of the two pure components, the critical pressures may be far in excess of either pure component. He also observed that the deviations of the true critical from the additive critical pressure coincide with the ratios of the molecular weights of the pure components.

In his analysis, Mayfield selected a known binary normal hydrocarbon system and proceeded to graph the true critical pressure of the mixture against the weight composition. Then he drew in the expected or pseudo-critical pressure curve based on the weight percentages of the components and the true critical pressures of the pure components. The difference between the true and the additive critical pressure of the mixture at any concentration he designated as P_{CD} and by simple mathematical analysis presented the following equation:

$$P_{CD} = P_{CM} - P_{CH} - \frac{\% L}{100} (P_{CL} - P_{CH})$$

The only unknowns in this equation are P_{CD} and P_{CM} so that by determining the P_{CD} of any unknown mixture or concentration the true P_{CM} can be found.

For the systems studied, Mayfield found that all the deviations pass through a maximum. When he plotted $\frac{P_{CD}}{\text{max } P_{CD}}$ against the weight percent of the heavier component for all of his known systems, a fairly good curve resulted with a peak at the fifty percent ordinate. With this curve, the P_{CD} can be found knowing the maximum P_{CD}. By plotting maximum P_{CD} against a ratio including the critical temperature and number of carbon atoms for both components, on log-log paper he was able to draw a straight line through points representing all his known systems. By means of the two curves and the equation plus a knowledge of the components and their weight concentrations, the critical pressure of the mixture may be found.

By a very similar process, with another equation and similar curves, Mayfield developed another method for calculating critical pressures which he calls the temperature method. The methods differ in his drawing of the additive curve and the equation derived therefrom.

Kuretta and Katz(4)

The first attempt by Kuratta and Katz to correlate critical pressures of natural gas and gasoline mixtures was tried using the Smith and Watson method. Since the volatile mixtures could not be brought into line with the petroleum fractions, the authors decided that some variable, important in the volatile mixtures having relatively high critical pressures became much less significant in the petroleum fractions with relatively low critical pressures. They concluded that the missing variable was molecular weight. From Smith and Watson's other variables a series of curves were drawn relating the ratio of $\frac{(T_c)({}_pP_c)}{P_c}$ to pseudo-critical temperature for a series of molecular weights. For mixtures of known constituents, the pseudo-critical pressure can be calculated by multiplying the mol fraction of the constituent by its critical pressure. For unknown petroleum mixtures, the pseudo-critical pressure may be found by one of the Smith and Watson methods.

Benedict(1)

Benedict's equation was presented by Edmister(2) as being the first to attempt to account for the effect of concentrations of components in a mixture. This method, similar to Mayfield's, attempts to calculate the critical pressure as a conversion of the pseudo-critical pressure by empirical consideration of the atmospheric boiling points of the constituents alone. This equation has been used in this presentation to calculate critical pressures of binary and complex hydrocarbon mixtures for which data is available in the literature. Results of the calculations were then compared with other published correlations.

Benedict's equation is:

$$P_{CM} = {}_pP_c \left(9 \left[\frac{\Sigma\, x_i \left(\frac{T_{bi}}{100}\right)^2}{\Sigma\left(x_i \left(\frac{T_{bi}}{100}\right)\right)^2} - 1 \right] + 1 \right)$$

where P_{CM} = critical pressure of mixture

${}_pP_c$ = pseudo-critical pressure of mixture $= \Sigma x_i\, P_{ci}$

T_{bi} = atmospheric boiling point of ith component

x_i = mol fraction of ith component

Edmister (2)

In the same article in which he presented the Benedict equation, Edmister offered two more methods for calculating critical pressure for which he claims approximate values only. Both methods are adaptions of critical locus curves related to the various critical pressures and temperatures appearing on the border curve. Also, both methods are aimed at actually estimating convergence pressure, which at the critical temperature is the critical pressure.

CALCULATIONS AND CONCLUSIONS

Tables 1 - 8 show a series of binary hydrocarbon mixtures. Included in the tables are the experimentally observed literature values of critical pressure as well as the calculated values from the Benedict equation and other calculations taken from the literature. Table 9[II] shows three series of natural gas and natural gasoline mixtures again with experimentally observed and calculated literature values plus the calculated Benedict values. Because the calculations are somewhat tedious, they were set up on a systematic basis as shown in tables 10 and 11 in the appendix. Accuracy was obtained by use of a calculator and by carrying out the calculations to the number of places shown in the table.

Observation of the correlated values of critical pressures in tables 1 - 8 indicate that the two empirical methods set up by Mayfield have by far the greatest accuracy for the type mixtures shown. The average overall Mayfield deviation was 1.2 per cent by the weight method and 1.3 per cent by the temperature method. Comparative deviation values by the other methods are Benedict, 3.0 per cent; Kuratta and Katz, 3.0 per cent; and Smith and Watson, 8.6 per cent. With one exception, the Mayfield calculated

---

[II] See table 12 for composition of mixtures.

average critical pressure was closer to the experimentally observed value than any of the other methods. The one exception was the C_5H_{12} - C_7H_{16} mixture series where the Benedict critical pressure value showed the closest correlation with an average deviation of 0.5 per cent.

From the above observations, one may conclude that the Mayfield method is preferable for calculating the critical pressure of binary normal hydrocarbon systems. However, this method has been set up for binary systems only. Mayfield believes that the $\frac{P_{CD}}{\text{max. } P_{CD}}$ plots will hold for branched paraffin, olefins, and cyclic system but that the maximum P_{CD} curves will not. Perhaps when more data becomes available, new curves covering the different classes of compounds can be formed for the maximum P_{CD} curves. In any case, (because of the binary feature) the excellent method of Mayfield will have limited use over the gamut of volatile mixtures existing in the petroleum and organic fields.

The remaining correlations have been developed so as not to be limited to binary mixtures. Of the three other methods shown on tables 1 - 8, there is little to choose between the Benedict and the Kuratta and Katz values. Both show an overall average deviation of 3.0 per cent. The Benedict average deviation values were the more erratic of the two covering a range of $\pm$ 0.5 per cent for the C_5H_{12} - C_7H_{16} series to $\pm$ 7.3 per cent for the C_2H_6- C_7H_{16} series.

The Kuratta and Katz average deviation range was ± 1.9 per cent to ± 4.0 per cent.

Previous work in the critical point field has indicated that the deviation of the actual critical pressure of a mixture from the weighted average critical pressure or pseudo-critical pressure, is influenced by several factors. Among those which increase the deviation of the critical pressure, or in other words, form a high critical loci curve include: (a) wide boiling width between lightest and heaviest components; (b) a high ratio of molecular weight of pure components; (c) a wide difference in critical temperature of pure components; (d) few intermediate components.

In an effort to determine the extent of their influence, the above listed factors applicable to binary systems, namely a, b and c, have been incorporated into the following table. This table lists the systems studied with associated experimental critical pressure values as well as the corresponding calculated pseudo-critical pressure. The difference of these pressures should then follow the pattern set by appropriate numerical values for the influencing factors.

System	Highest Experimental P_c	Corresponding ${}_pP_c$	$P_c - {}_pP_c$	Aver. Dev. Benedict	Diff. in Boil. Points °R	Mol. Wgt. ratio	Diff. in T_c °R
CH_4 -C_3H_8	1468	656	812	3.6	215	2.75	323
CH_4 -C_4H_{10}	1924	646	1273	3.6	290	3.63	422
C_2H_6 -C_4H_{10}	842	657	185	3.6	158	1.93	216
C_2H_6 -C_7H_{16}	1263	640	623	7.3	336	3.33	423
C_3H_8 -C_4H_{10}	638	597	41	0.6	75	1.32	100
C_4H_{10}-C_7H_{16}	596	519	77	1.8	178	1.72	207
C_3H_8 -C_5H_{12}	671	590	81	1.7	141	1.64	181
C_5H_{12}-C_7H_{16}	492	463	29	0.5	112	1.39	126

The above table does not correlate any of the three factors to one hundred per cent agreement. However, it is readily apparent that the influence of increased values of all three of the factors definitely raises the critical locus curve. Correlation probably would be better if the maximum points in all the curves could be used for the comparison. Actually, the highest experimental points available were used which vary in their degree of closeness to the maximum critical pressure values of the mixture.

Also noteworthy in the above table is the significant influence of the critical pressure minus the pseudo-critical pressure totals on the average deviations computed by the Benedict equation. Here again, agreement is not one hundred per cent consistent. However, the fact that the maximum average deviation corresponds directly to the difference between boiling points of components is important as it is this property plus the mol weight which Benedict utilizes in his equation.

In general, critical pressure calculations of binary mixtures by the Benedict method appear to give results on the high side whereas the Kuratta and Katz values are more liable to be on the low side. Another observation that may be made is that the maximum calculated deviation in the critical pressure is more likely to occur for the 50 per cent by weight mixture which in turn represents the maximum true critical pressure deviation from the weighted average. There is also a tendency for the Kuratta and Katz results to bracket the experimental figures more so than the Benedict values.

Figures 1 to 8 in the appendix show critical pressure curves of actual versus calculated values for the binary mixtures shown. Figures 9 to 16 show the per cent deviation of critical pressures from the experimentally determined values of the same binary mixtures. Examination of the curves shown in figures 1 to 8 shows that samples were chosen in most cases so that a reasonably accurate curve through the maximum could be drawn. However, three of the series contained values approaching the maximum from one side only and another had too few points in the maximum region to do other than approximate this area.

The deviation curves shown in figures nine to sixteen show a repetitive type curve for the Benedict deviations in four of the systems. As can be seen in the figures, the four deviation curves approach zero deviation at both ends and recede towards the center. Perhaps three of the other four would fall into the same pattern if, as is evident on the critical pressure curves, the samples had been continued to give results on both sides of the maximum critical pressure. To some degree, the curves of the Kuratta and Katz deviations follow the curvature of the Benedict curve but generally displaced in the negative direction.

Table 9 shows experimental and calculated critical pressure values for three series of complex natural gas and gasoline mixtures. In all three series, the Kuratta and Katz correlation shows exceptionally good consistency with the experimental value. On the other hand, the Benedict correlation shows satisfactory agreement for the "B" series only. The "B" series is a less complex mixture of natural gas and normal butane with fewer intermediate components than the "S" and "T" series. From this observation, the Kuratta and Katz correlation seems to hold promise for complex mixture evaluation but the Benedict equation is more limited in scope.

An attempt was made to determine if by chance the concentration of the most prevalent component in the complex mixture might be in a more accurate range of the Kuratta and Katz method but no conclusion of this sort could be drawn. This was done by checking the prevalent component of the complex mixtures in the binary curves to check the deviations in the areas where this component was most concentrated.

Table 1

CRITICAL PRESSURE - CALCULATED AND EXPERIMENTAL

CH_4 - C_3H_8 SYSTEM

Mol % CH_4	(6) Experi-mental	Benedict Calc.	Benedict % Dev	(4) Kuratta&Katz Calc.	(4) Kuratta&Katz % Dev.	(9) Smith&Watson Calc.	(9) Smith&Watson % Dev	(6) Mayfield-wgt Calc.	(6) Mayfield-wgt % Dev	(6) Mayfield-temp Calc.	(6) Mayfield-temp % Dev.
70	1468	1471	+ 0.2	1420	- 3.3	1640	+ 10.5	1456	- 0.8	1444	- 1.6
60	1406	1440	+ 2.4	1385	- 1.5	1607	+ 14.3	1395	- 0.8	1382	- 1.7
50	1292	1354	+ 4.8	1270	- 1.7	1363	+ 5.5	1284	- 0.6	1273	- 1.5
40	1158	1227	+ 6.0	1180	+ 1.9	1176	+ 1.4	1145	- 1.1	1149	- .8
30	1018	1079	+ 6.0	1060	+ 4.1	1180	+ 15.9	1010	- .8	1011	- .7
20	891	934	+ 4.8	947	+ 6.3	798	- 11.3	875	- 1.8	868	- 2.6
10	766	774	+ 1.0	783	+ 2.2	--	--	744	- 2.9	715	- 6.7
		Av.dev.	3.6	Av.dev.	3.0	Av.dev.	9.8	Av.dev.	1.3	Av.dev.	2.2

Table 2

CRITICAL PRESSURE - CALCULATED AND EXPERIMENTAL

CH_4 - C_4H_{10} SYSTEM

Mol % CH_4	(6) Experimental	Benedict Calc.	Benedict % Dev	(4) Kuratta&Katz Calc.	Kuratta&Katz % Dev.	(9) Smith&Watson Calc.	Smith&Watson % Dev.	(6) Mayfield-wgt Calc.	Mayfield-wgt % Dev	(6) Mayfield-temp Calc.	Mayfield-temp % Dev
78.4	1924	1815	- 5.7	1770	- 8.0	2200	+ 14.3	1959	+ 1.8	1915	- 0.5
70.7	1901	1818	- 4.4	1890	- 0.6	2110	+ 11.0	1903	+ 0.1	1932	+ 1.6
60.8	1799	1733	- 3.7	1720	- 4.4	2360	+ 31.2	1744	- 3.1	1779	- 1.1
47.5	1537	1512	- 1.6	1443	- 6.1	1709	+ 11.2	1446	- 5.9	1441	- 6.2
28.7	1093	1123	+ 2.7	1060	- 3.2	1125	+ 2.9	1056	- 3.6	1005	- 8.1
		Av.dev.	3.6	Av.dev.	4.5	Av.dev.	14.1	Av.dev.	2.9	Av.dev.	3.5

Table 3

CRITICAL PRESSURE - CALCULATED AND EXPERIMENTAL

C_2H_6 - C_4H_{10} System

Mol % C_2H_6	(6) Experimental	Benedict		(4) Kuratta&Katz		(9) Smith&Watson		(6) Mayfield-wgt		(6) Mayfield-temp	
		Calc.	% Dev	Calc.	% Dev	Calc.	% Dev	Calc.	% Dev	Calc.	% Dev
94.7	759	773	+ 1.8	740	- 2.5	767	+ 1.1	760	+ 0.13	761	+ 0.26
82.2	827	855	+ 3.4	798	- 3.5	813	- 1.7	829	+ 0.24	834	+ 0.85
65.8	842	881	+ 4.6	820	- 3.3	887	+ 5.4	845	+ 0.36	848	+ 0.71
45.1	781	819	+ 4.9	786	+ 0.64	843	+ 7.9	782	+ 0.13	786	+ 0.64
17.5	646	667	+ 3.3	645	- 0.15	655	+ 1.4	644	- 0.31	646	+ 0.0
		Av.dev.	3.6	Av.dev.	2.0	Av.dev.	3.5	Av.dev.	0.23	Av.dev.	0.49

Table 4

CRITICAL PRESSURE - CALCULATED AND EXPERIMENTAL

C_2H_6 - C_7H_{16} System

Mol % C_2H_6	(6) Experi-mental	Benedict Calc.	Benedict % Dev	(4) Kuratta&Katz Calc.	Kuratta&Katz % Dev	(9) Smith&Watson Calc.	Smith&Watson % Dev	(6) Mayfield-wgt Calc.	Mayfield-wgt % Dev	(6) Mayfield-temp Calc.	Mayfield-temp % Dev.
96.8	850	885	+ 4.1	807	- 5.1	927	+ 9.1	880	+ 3.5	866	+ 1.9
88.7	1132	1175	+ 3.8	1065	- 5.9	1232	+ 8.8	1151	+ 1.7	1134	+ 0.2
77.1	1263	1325	+ 4.9	1230	- 2.6	1580	+ 25.0	1243	- 1.6	1265	+ 0.2
58.7	1106	1225	+ 10.7	1105	- 0.1	1431	+ 29.4	1083	- 2.1	1120	+ 1.3
26.5	682	770	+ 12.9	690	+ 1.2	875	+ 13.6	675	- 1.0	690	+ 1.2
		Av.dev.	<u>7.3</u>	Av.dev.	<u>3.0</u>	Av.dev.	<u>17.2</u>	Av.dev.	<u>2.0</u>	Av.dev.	<u>1.0</u>

Table 5

CRITICAL PRESSURE - CALCULATED AND EXPERIMENTAL

C_3H_8 - C_4H_{10} System

Mol % C_3H_8	(6) Experi-mental	Benedict Calc.	Benedict % Dev	(4) Kuratta&Katz Calc.	Kuratta&Katz % Dev	(9) Smith&Watson Calc.	Smith&Watson % Dev	(6) Mayfield-wgt Calc.	Mayfield-wgt % Dev	(6) Mayfield-temp Calc.	Mayfield-temp % Dev.
85.5	631	630	- 0.16	609	- 3.5	608	- 3.6	632	+ 0.16	635	+ 0.63
69.4	638	632	- 0.90	607	- 4.9	--	--	638	0.0	641	+ 0.47
51.6	630	622	- 1.3	597	- 5.2	649	+ 3.0	630	0.0	629	- 0.16
33.9	609	606	- 0.5	583	- 4.3	613	+ 0.66	610	+ 0.16	607	- 0.33
20.3	588	587	- 0.25	580	- 1.4	564	- 4.1	589	+ 0.17	587	- 0.17
		Av.dev.	0.6	Av.dev.	3.9	Av.dev.	2.9	Av. dev.	0.1	Av.dev.	0.35

Table 6

CRITICAL PRESSURE - CALCULATED AND EXPERIMENTAL

C_4H_{10} - C_7H_{16} System

Mol % C_4H_{10}	Experimental (6)	Benedict Calc.	Benedict % Dev.	Mayfield-wgt (6) Calc.	Mayfield-wgt % Dev.	Mayfield-temp (6) Calc.	Mayfield-temp % Dev.
94	576	575	- 0.17	567	- 1.6	570	- 1.0
80.1	596	608	+ 2.0	586	- 1.7	591	- .84
63.1	584	600	+ 2.7	578	- 1.0	579	- .85
42.5	538	553	+ 2.8	532	- 1.1	533	- .93
15.9	452	458	+ 1.3	449	- .66	449	- .66
		Av. dev.	1.8	Av.dev.	1.2	Av.dev.	0.9

Table 7

CRITICAL PRESSURE - CALCULATED AND EXPERIMENTAL

C_3H_8 - C_5H_{12} System

Mol % C_3H_8	(6) Experi-mental	Benedict Calc.	% Dev.	(4) Kuratta&Katz Calc.	% Dev.	(9) Smith&Watson Calc.	% Dev.	(6) Mayfield-wgt Calc.	% Dev	(6) Mayfield-temp Calc.	% Dev.
81.9	664	674	+ 1.5	641	- 3.5	670	+ 0.9	661	- 0.5	665	+ 0.15
79.2	671	678	+ 1.0	658	- 1.9	692	+ 3.1	664	- 1.0	678	+ 1.0
55.6	648	664	+ 2.5	635	- 2.0	681	+ 5.1	652	+ 0.6	658	+ 1.5
35.0	608	620	+ 2.0	610	+ 0.3	649	+ 6.7	602	- 1.0	605	- 0.5
		Av.dev.	1.7	Av.dev.	1.9	Av.dev.	3.9	Av.dev.	0.8	Av.dev.	0.8

Table 8

CRITICAL PRESSURE - CALCULATED AND EXPERIMENTAL

C_5H_{12} - C_7H_{16} System

Mol % C_5H_{12}	(6) Experimental	Benedict Calc.	Benedict % Dev.	(4) Kuratta&Katz Calc.	(4) Kuratta&Katz % Dev	(9) Smith&Watson Calc.	(9) Smith&Watson % Dev.	(6) Mayfield-wgt Calc.	(6) Mayfield-wgt % Dev	(6) Mayfield-temp Calc.	(6) Mayfield-temp % Dev.
74.7	492	491	- 0.2	487	- 1.0	518	+ 5.3	504	+ 2.4	493	+ 0.2
55.8	480	479	- 0.2	473	- 1.5	513	+ 6.9	481	+ 0.2	481	+ 0.2
25.5	445	440	- 1.1	431	- 3.1	461	+ 3.5	441	- 0.9	438	- 1.6
		Av.dev.	0.5	Av.dev.	1.9	Av.dev.	5.2	Av.dev.	1.2	Av.dev.	0.7

Table 9

CRITICAL PRESSURE - CALCULATED AND EXPERIMENTAL

Natural Gas and Gasoline Mixtures

Mixture	P_c (4) Experimental	Benedict Calc.	Benedict % Dev.	Kuratta & Katz (4) Calc.	Kuratta & Katz (4) % Dev	Smith & Watson (4) Calc.	Smith & Watson (4) % Dev.
S-2	2387	2027	- 15.1	2160	- 9.5	3120	+ 31.0
S-3	2574	2252	- 12.5	2585	+ 0.4	2475	- 3.8
S-4	2537	2237	- 11.8	2540	+ 0.1	2940	+ 15.9
S-5	2615	2039	- 22.0	2680	+ 2.5	2700	+ 3.2
		Av.dev.	15.3	Av.dev.	3.1	Av.dev.	13.5
T-1	2605	2122	- 18.6	2640	+ 1.3	3020	+ 15.9
T-3	2675	2185	- 18.3	2610	- 2.4	2910	+ 8.8
T-4	2730	2314	- 15.2	2790	+ 2.2	3120	+ 14.3
T-5	2900	2295	- 20.8	2910	+ 0.3	2820	- 2.8
		Av.dev.	18.2	Av.dev.	1.6	Av.dev.	10.5

Table 9
(cont'd)

CRITICAL PRESSURE - CALCULATED AND EXPERIMENTAL

Natural Gas and Gasoline Mixtures

Mixture	P_c (4) Experimental	Benedict Calc.	% Dev.	Kuratte & Katz (4) Calc.	% Dev.	Smith & Watson (4) Calc.	% Dev.
B-1	1826	1808	- 1.0	1840	+ 0.8	1960	+ 7.3
B-2	1797	1799	+ 0.1	1788	- 0.5	1955	+ 8.8
B-3	1796	1764	- 1.8	1800	+ 0.2	1870	+ 4.1
B-4	1706	1725	+ 1.1	1705	- 0.1	1775	+ 4.0
		Av.dev.	1.0	Av.dev.	0.4	Av.dev.	6.1

APPENDIX

Table 10

CRITICAL PRESSURE - BENEDICT EQUATION

Sample Calculations - CH_4 - C_4H_{10} System

Gases	Mol Wgt	Wgt %	Mols	Mol %	Pcp		$\frac{Tb}{100}$	$x_i\left(\frac{Tb}{100}\right)$	$\left(\frac{Tb}{100}\right)^2$	$\left(x_i \frac{Tb}{100}\right)^2$
CH_4	16	50	3.125	78.37	673	527.4	2.01	1.583	4.04	3.166
C_4H_{10}	58	50	.862	21.63	550.1	116.8	4.91	1.042	24.1	5.116
			3.987			644.2		2.625		8.282
CH_4	16	40	2.50	70.74		476.1		1.429		2.858
C_4H_{10}	58	60	1.034	29.26		161.0		1.437		7.052
			3.534			637.1		2.866		9.910
CH_4	16	30	1.875	60.83		409.4		1.229		2.458
C_4H_{10}	58	70	1.207	39.17		215.5		1.923		9.440
			3.082			624.9		3.152		11.898

Table 10
(Cont'd)

CRITICAL PRESSURE - BENEDICT EQUATION

Sample Calculations - CH_4 - C_4H_{10} System

Gases	Mol Wgt	Wgt %	Mols	Mol %	Pcp	$\frac{Tb}{100}$	$x_i\left(\frac{Tb}{100}\right)$	$\left(\frac{Tb}{100}\right)^2$	$\left(x_i \frac{Tb}{100}\right)^2$
CH_4	16	20	1.250	47.54	319.9		.960		1.921
C_4H_{10}	58	80	1.379	52.46	288.6		2.576		12.643
			2.629		608.5		3.536		14.564
CH_4	16	10	0.625	28.72	193.3		.580		1.160
C_4H_{10}	58	90	1.552	71.28	392.1		3.500		17.178
			2.177		585.4		4.080		18.338

Table 11

CRITICAL PRESSURE - BENEDICT EQUATION

Sample Calculations - CH_4 - C_4H_{10} System

Wgt % (I) CH_4	Ppm	a	b	b^2	$\frac{a}{b^2}$	c	$c \neq 1$	Pcm
50	644.2	8.282	2.625	6.891	1.202	1.818	2.818	1815
40	637.1	9.910	2.866	8.214	1.206	1.854	2.854	1818
30	624.9	11.898	3.152	9.935	1.197	1.773	2.773	1733
20	608.5	14.564	3.536	12.503	1.165	1.485	2.485	1512
10	585.4	18.338	4.080	16.646	1.102	.918	1.918	1123

$$a = x_1 \left(\frac{Tb}{100}\right)^2$$

$$b = x_1 \left(\frac{Tb}{100}\right)$$

$$c = 9\left(\frac{a}{b^2} - 1\right)$$

Ppm = pseudo-critical pressure of mixture

Pcm = critical pressure of mixture

Pcp = pseudo-critical pressure times the mol fraction of each component

(I) See Table 10

EXPLANATION OF CALCULATIONS

Benedict's equation,

$$P_{CM} = {}_pP_c \left(9 \left[\frac{\Sigma \; x_i \left(\frac{T_{bi}}{100} \right)^2}{\Sigma \left(x_i \; \frac{T_{bi}}{100} \right)^2} - 1 \right] + 1 \right)$$

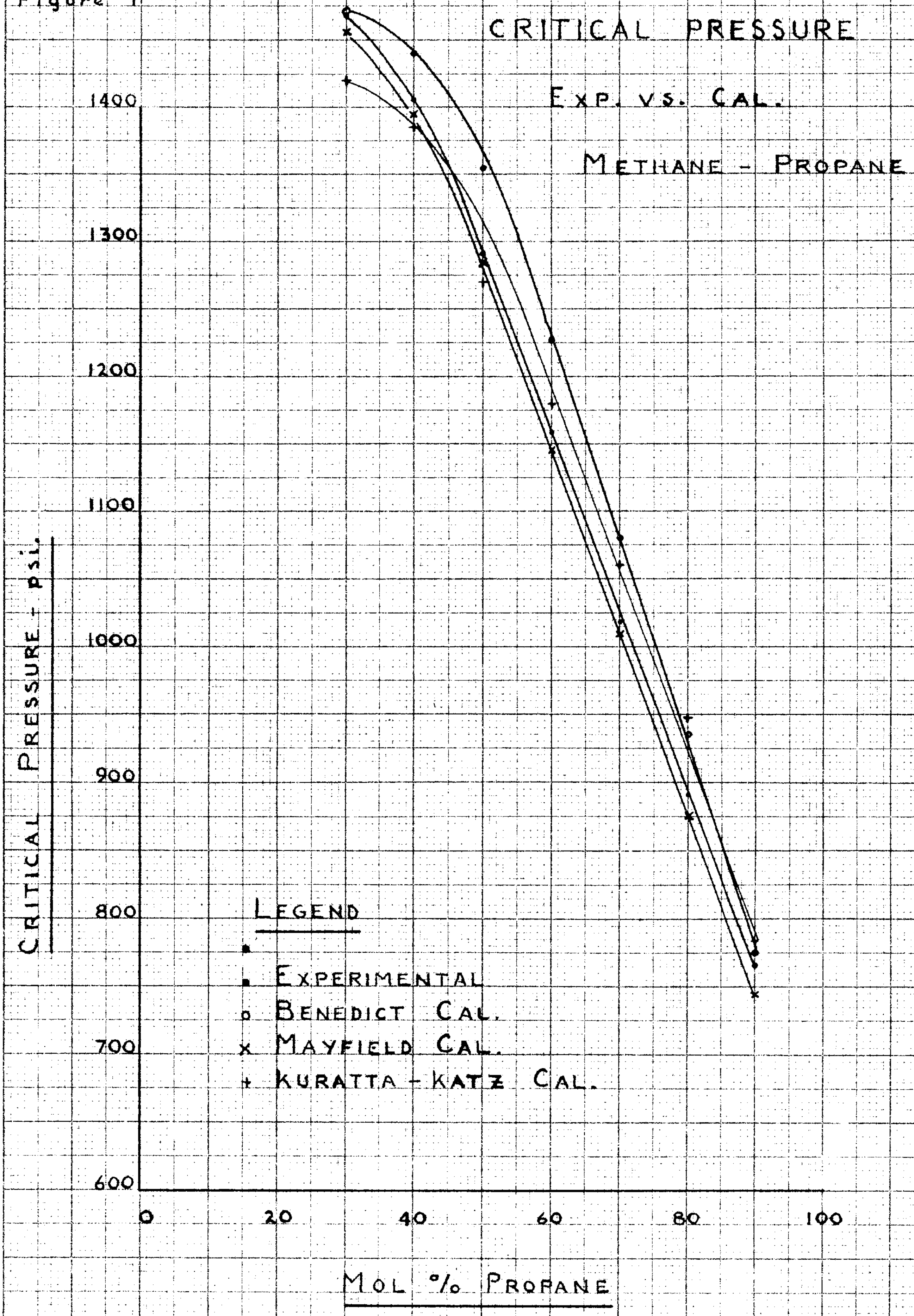
requires a knowledge of the numerical values of the atmospheric boiling points and the critical pressure of the components involved. Both of these properties are readily available for the systems studied. Also required is knowledge of the mol per cent of the mixture components or a combination of the weight per cent and the molecular weight. The latter was given in the literature for the mixtures studied and the mol per cent calculated. In the Pcp column in table 10 is shown the critical pressure of the components for the first mixture only, and also the pressure of each component contributing to the pseudo-critical pressure of the mixture which is the total of the component pressures. The component pressures represent the mol fraction of the component critical pressures in these calculations. The atmospheric boiling points are divided by one hundred and inserted into the table. This value is then multiplied by the mol fraction and squared as required to fit the equation. The sums of the mixture values were then inserted into table 11 and the mathematics of the equation carried out in a simplified, organized and routine manner as shown.

Table 12

COMPOSITION OF NATURAL GAS AND GASOLINE MIXTURES$^{(4)}$

	Components - Mol % of total								
Mixture Designation	Nitrogen	Carbon Dioxide	Methane	Ethane	Propane	Butanes	Pentanes	Hexanes	Heptanes
S-2	0.58	---	78.80	5.90	3.15	2.66	4.25	2.52	2.14
S-3	0.53	---	72.40	5.42	3.00	3.10	7.10	4.56	3.88
S-4	0.54	---	72.80	5.46	3.02	3.07	6.88	4.38	3.75
S-5	---	---	59.70	8.90	5.00	4.90	9.30	12.20	---
T-1	0.38	0.45	83.00	3.76	1.44	0.89	4.36	3.08	2.63
T-3	0.38	0.44	81.50	3.72	1.41	1.02	5.01	3.54	3.03
T-4	0.36	0.43	78.40	3.55	1.36	1.30	6.31	4.47	3.82
T-5	0.30	0.35	64.30	2.94	1.11	2.52	12.30	8.71	7.47
B-1	0.33	0.38	70.65	3.23	1.22	24.20	---	---	---
B-2	0.30	0.35	65.24	2.98	1.13	30.0	---	---	---
B-3	0.28	0.34	61.30	2.80	1.06	34.22	---	---	---
B-4	0.27	0.32	58.25	2.66	1.01	37.50	---	---	---

Figure 1



CRITICAL PRESSURE

EXP. VS. CAL.

METHANE - PROPANE

Figure 2

CRITICAL PRESSURE

EXP. VS. CAL.

METHANE - BUTANE

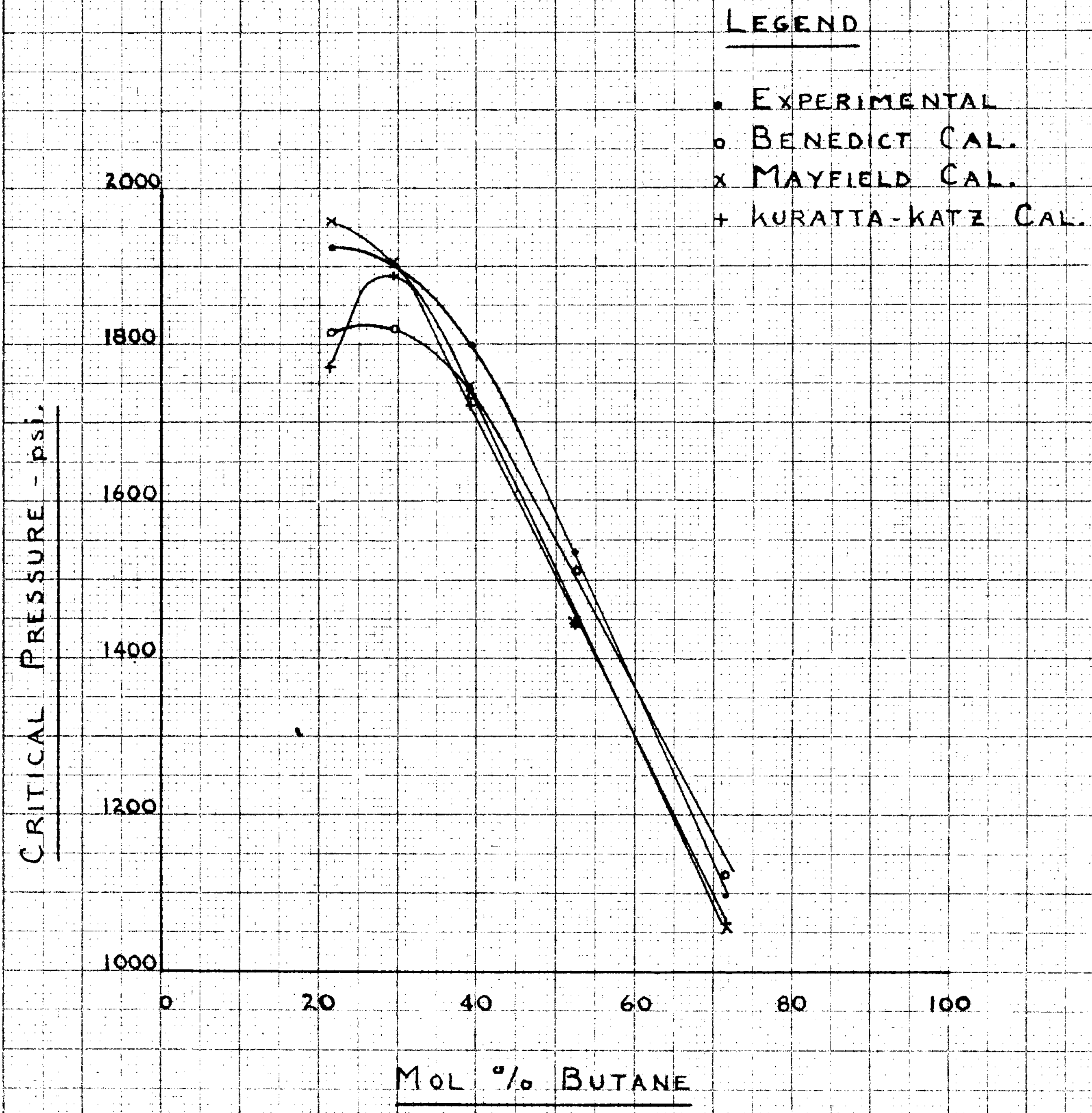


Figure 3

CRITICAL PRESSURE

EXP. VS. CAL.

ETHANE - BUTANE

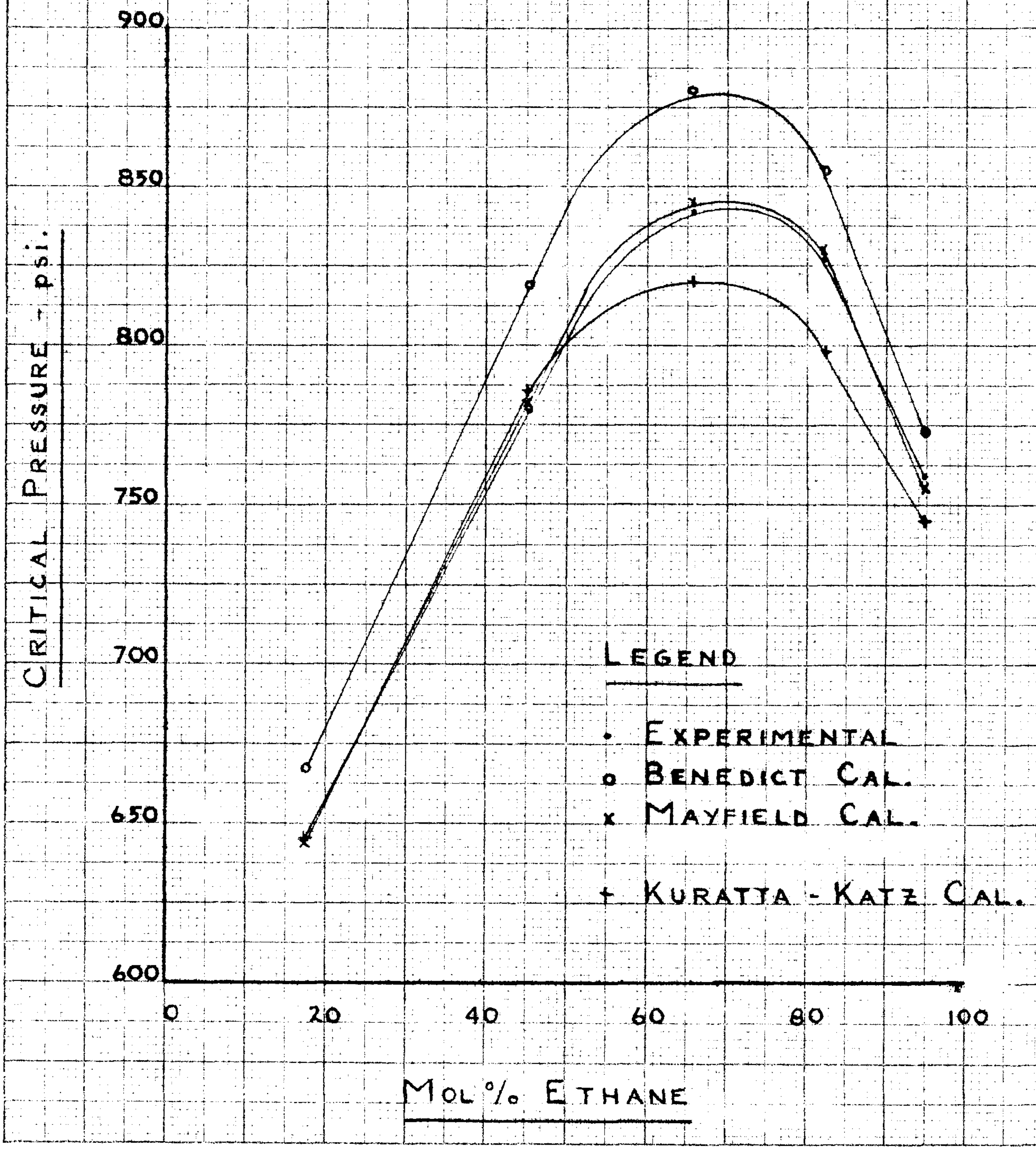
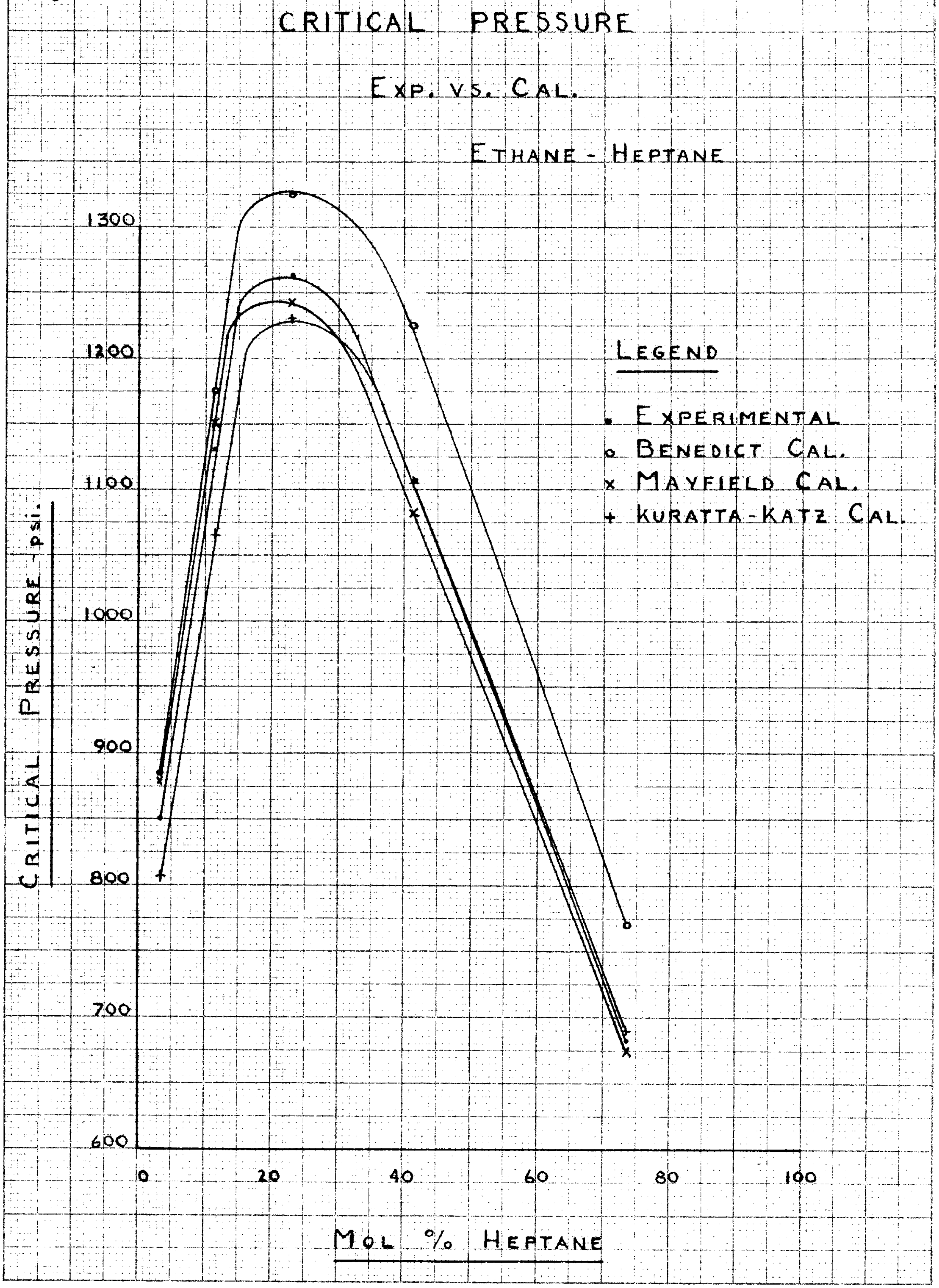


Figure 4


CRITICAL PRESSURE

Exp. vs. Cal.

Ethane - Heptane

Figure 5

CRITICAL PRESSURE

EXP. VS. CAL.

PROPANE - BUTANE

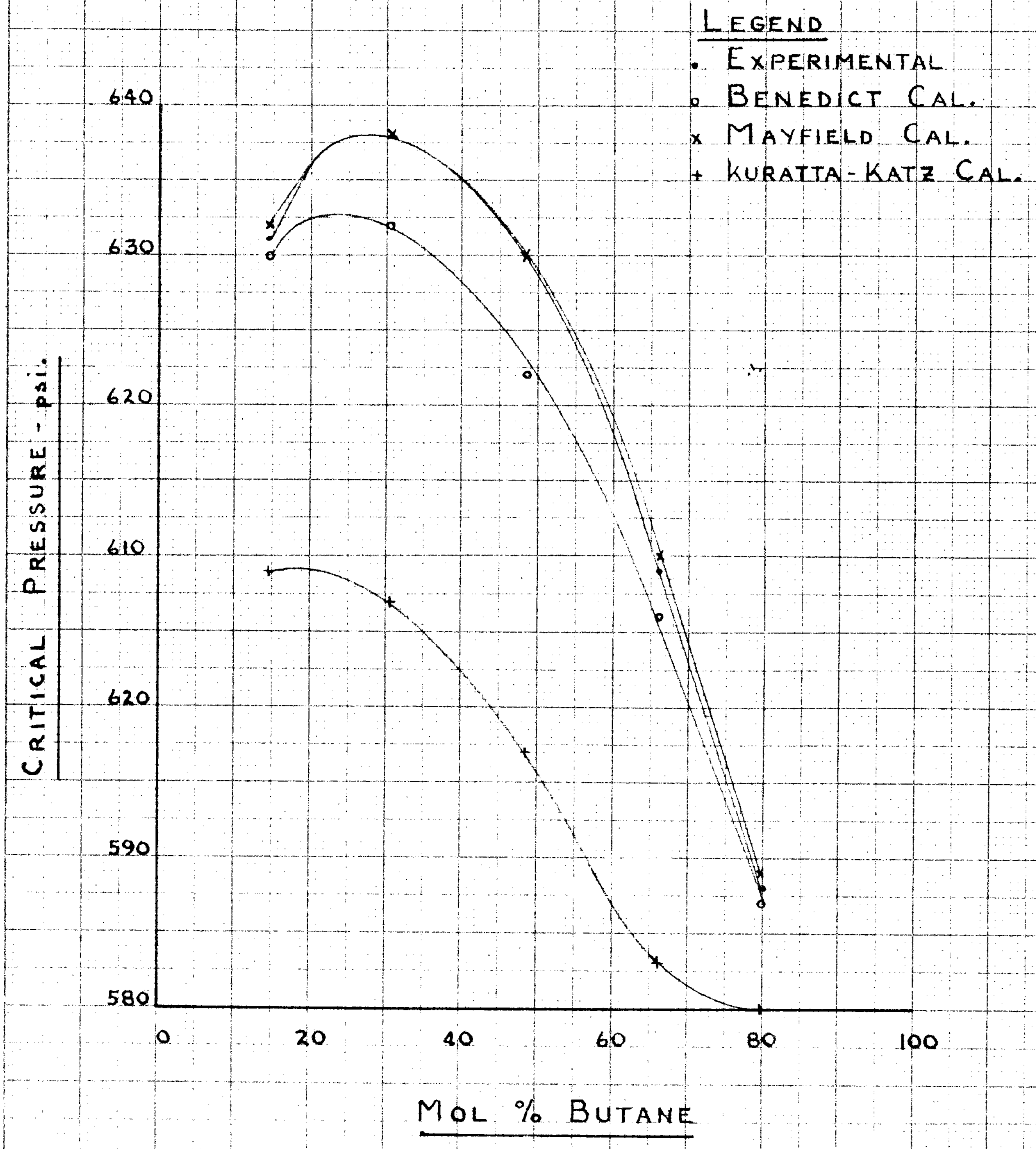
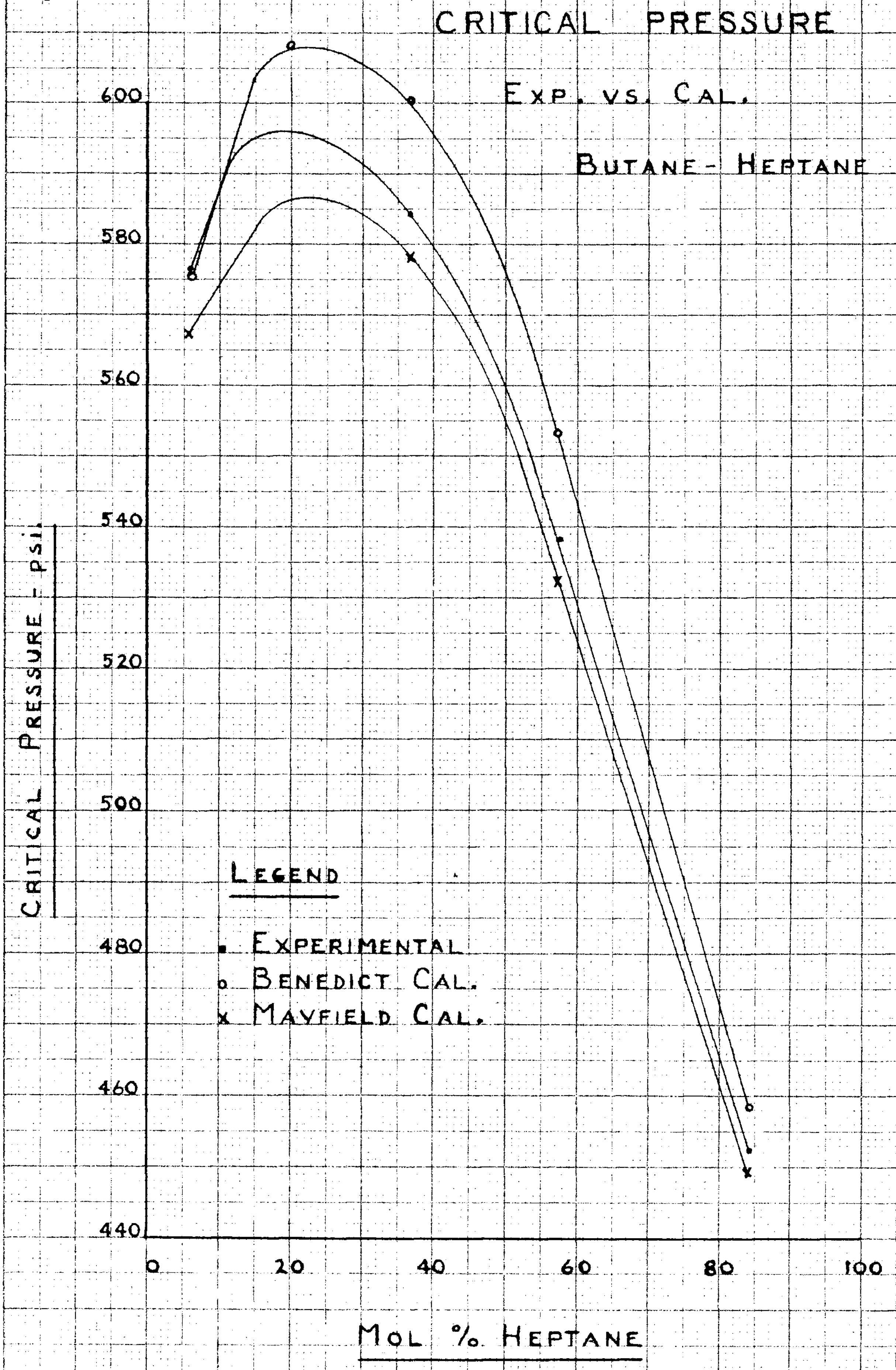


Figure 6



CRITICAL PRESSURE

EXP. VS. CAL.

BUTANE - HEPTANE

Figure 7

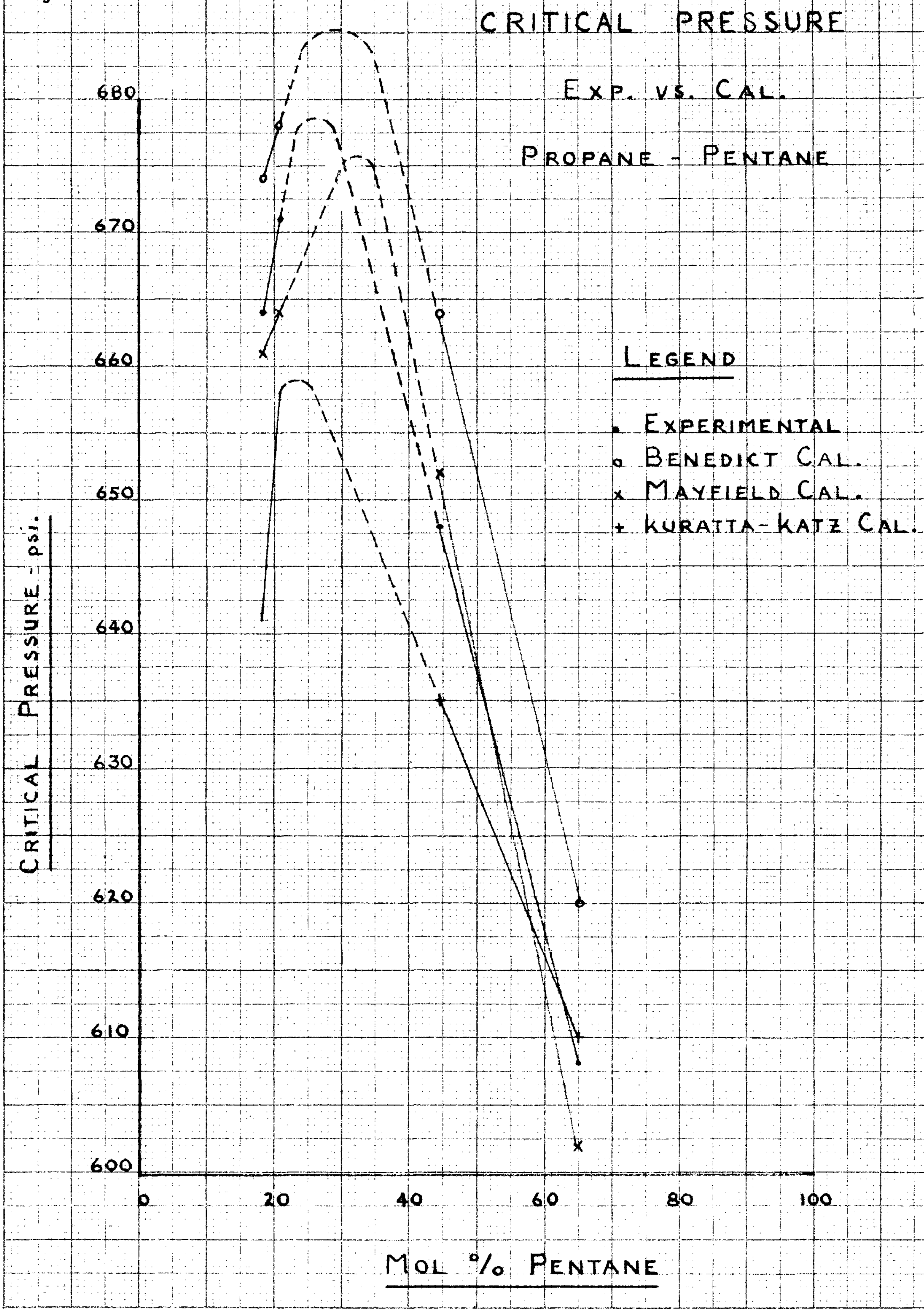

CRITICAL PRESSURE
EXP. VS. CAL.
PROPANE - PENTANE
LEGEND
• EXPERIMENTAL
o BENEDICT CAL.
x MAYFIELD CAL.
+ KURATTA-KATZ CAL.
CRITICAL PRESSURE - psi.
680
670
660
650
640
630
620
610
600
0
20
40
60
80
100
MOL % PENTANE

Figure 8

CRITICAL PRESSURE

EXP. VS. CAL.

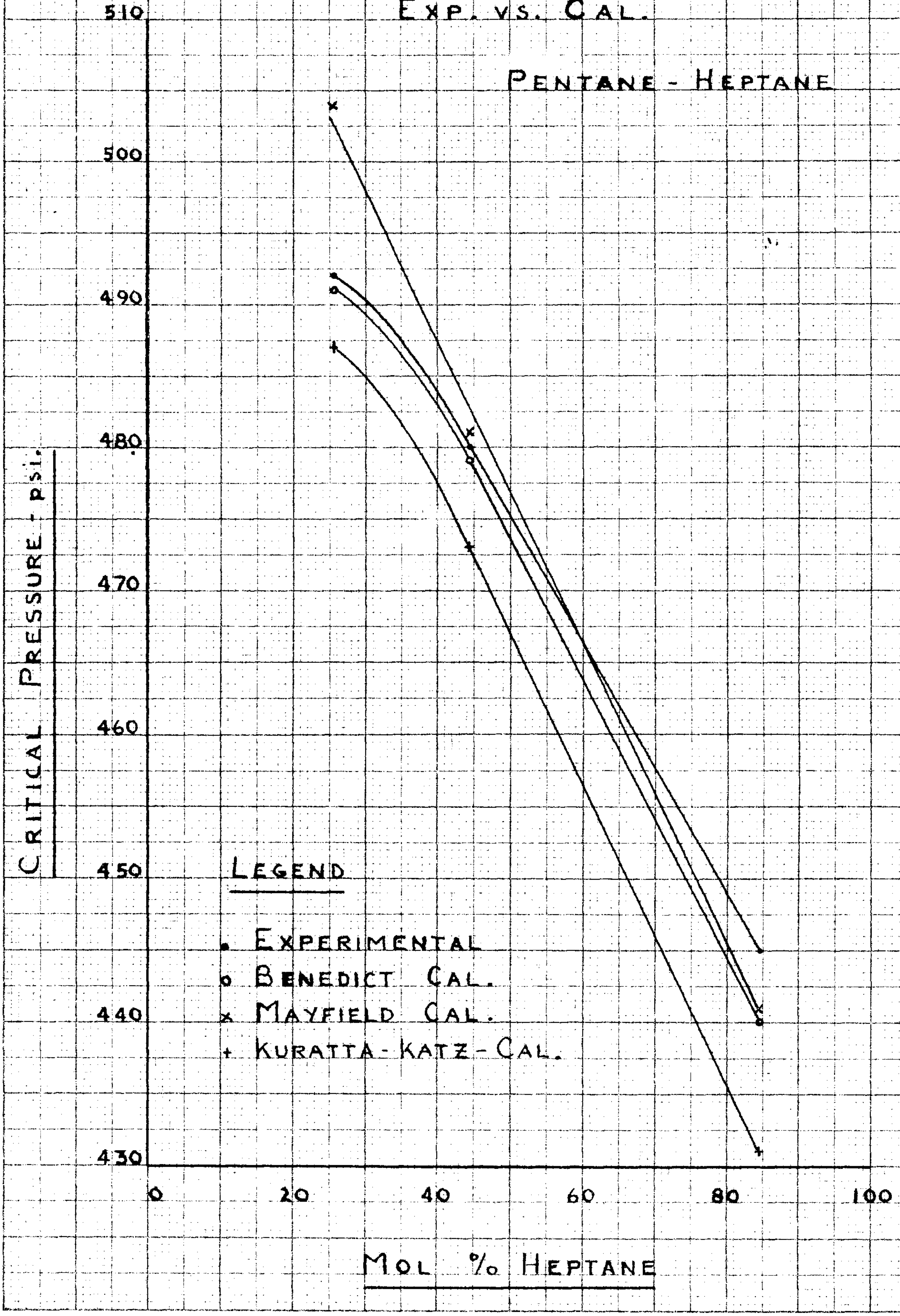


Figure 9

CRITICAL PRESSURE

DEVIATION FROM EXPERIMENTAL

METHANE - PROPANE

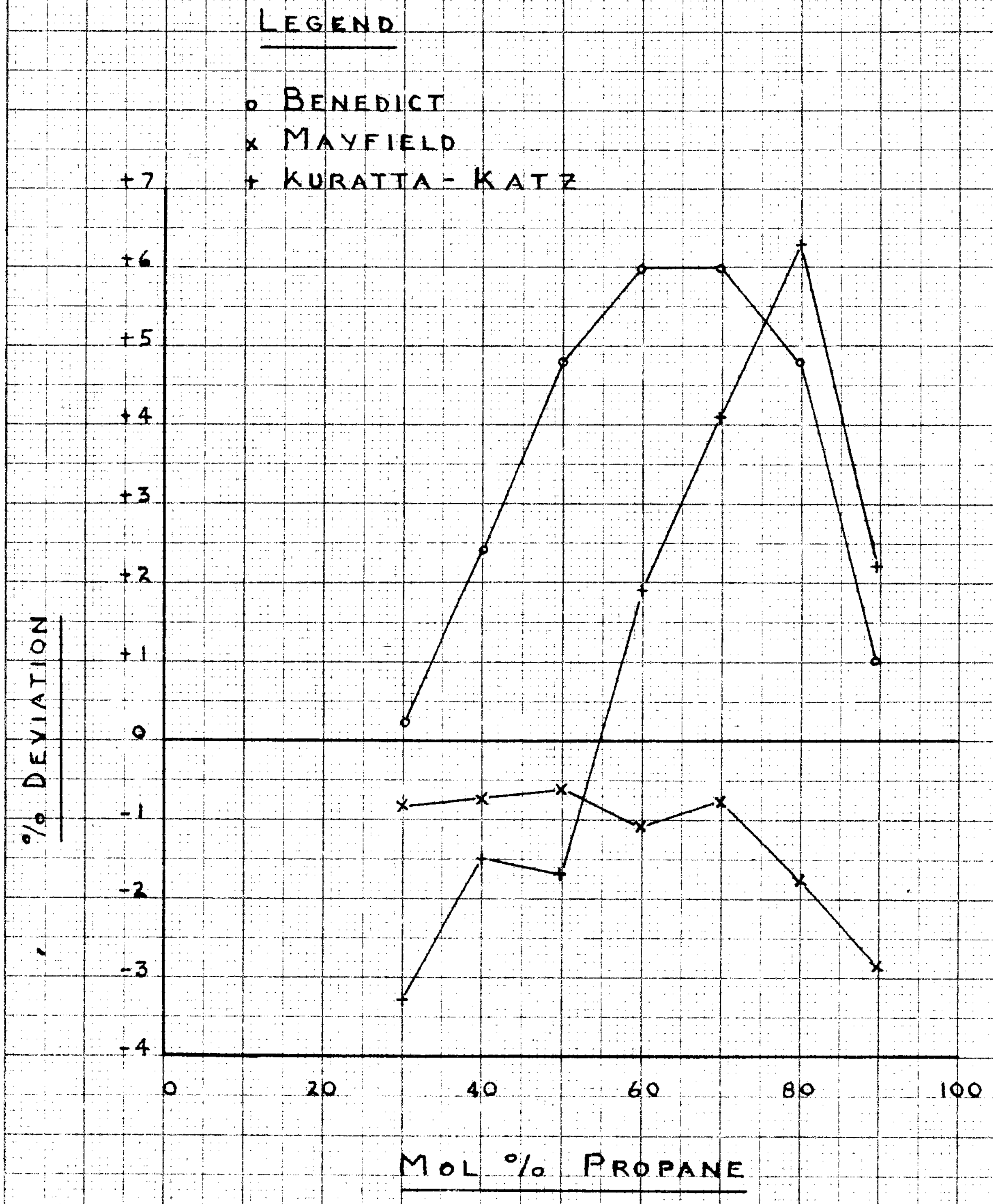


Figure 10

CRITICAL PRESSURE

DEVIATION FROM EXPERIMENTAL

METHANE - BUTANE

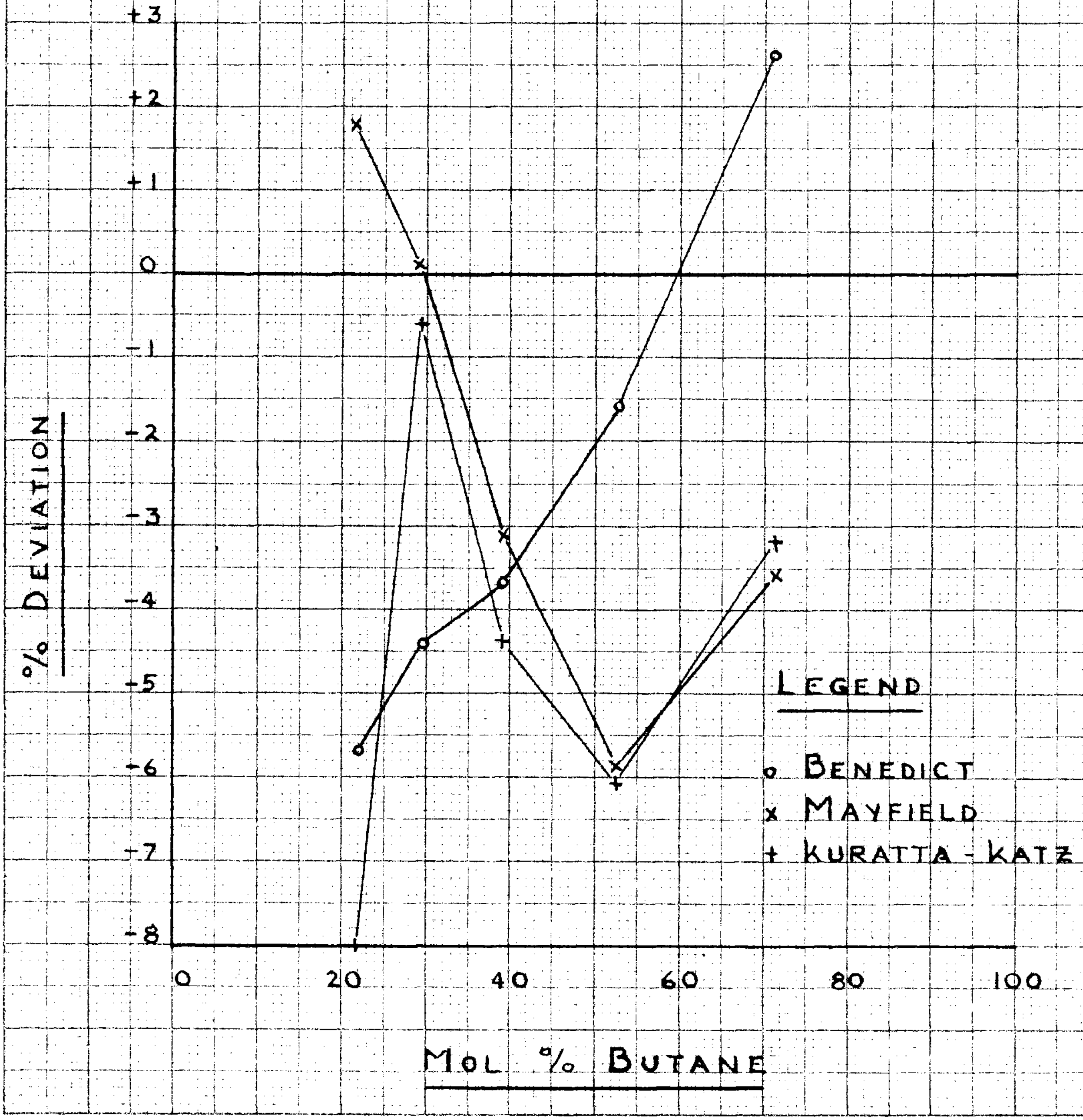


Figure II

CRITICAL PRESSURE

DEVIATION FROM EXPERIMENTAL

ETHANE - BUTANE

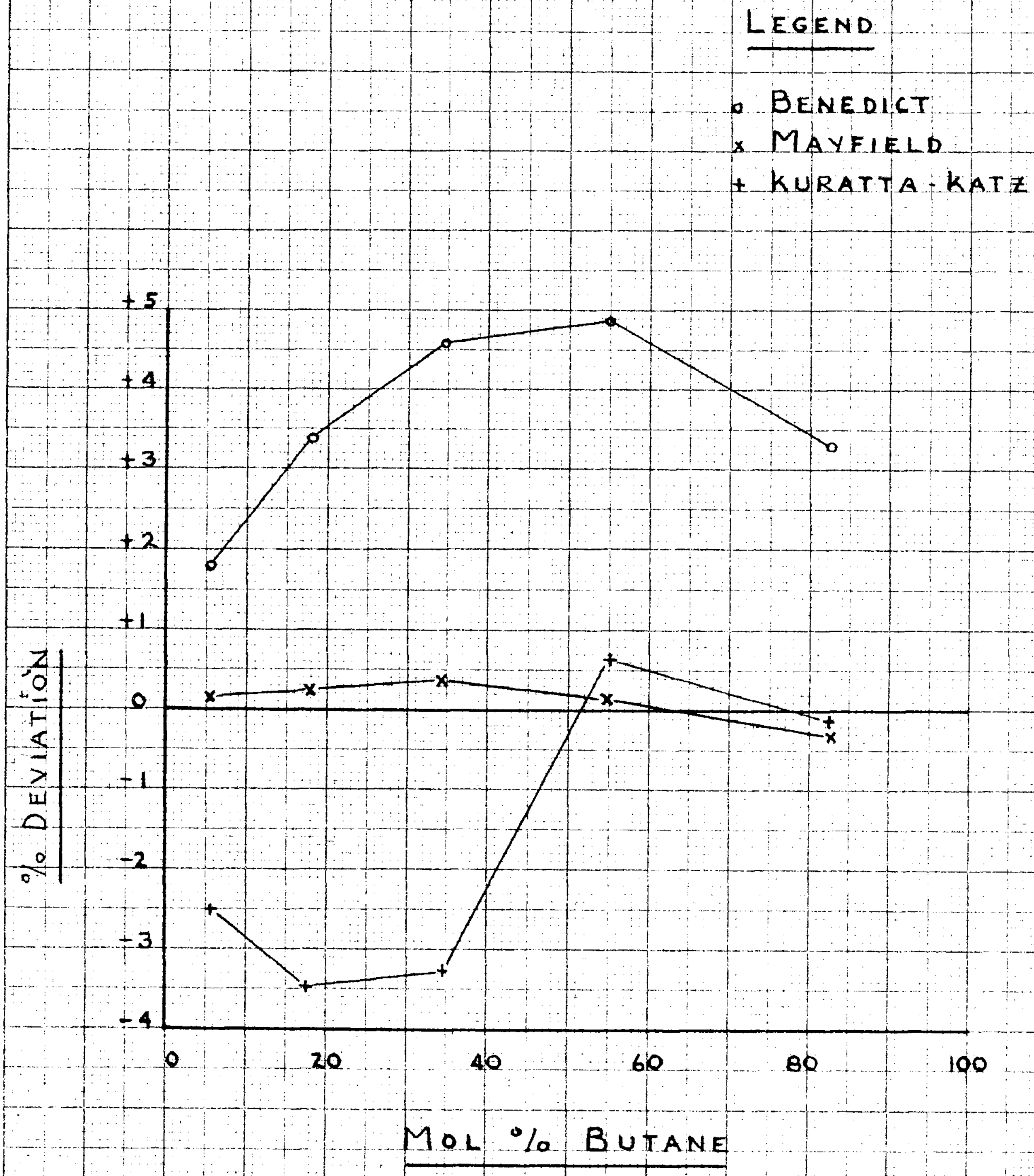


Figure 12

CRITICAL PRESSURE

DEVIATION FROM EXPERIMENTAL

ETHANE - HEPTANE

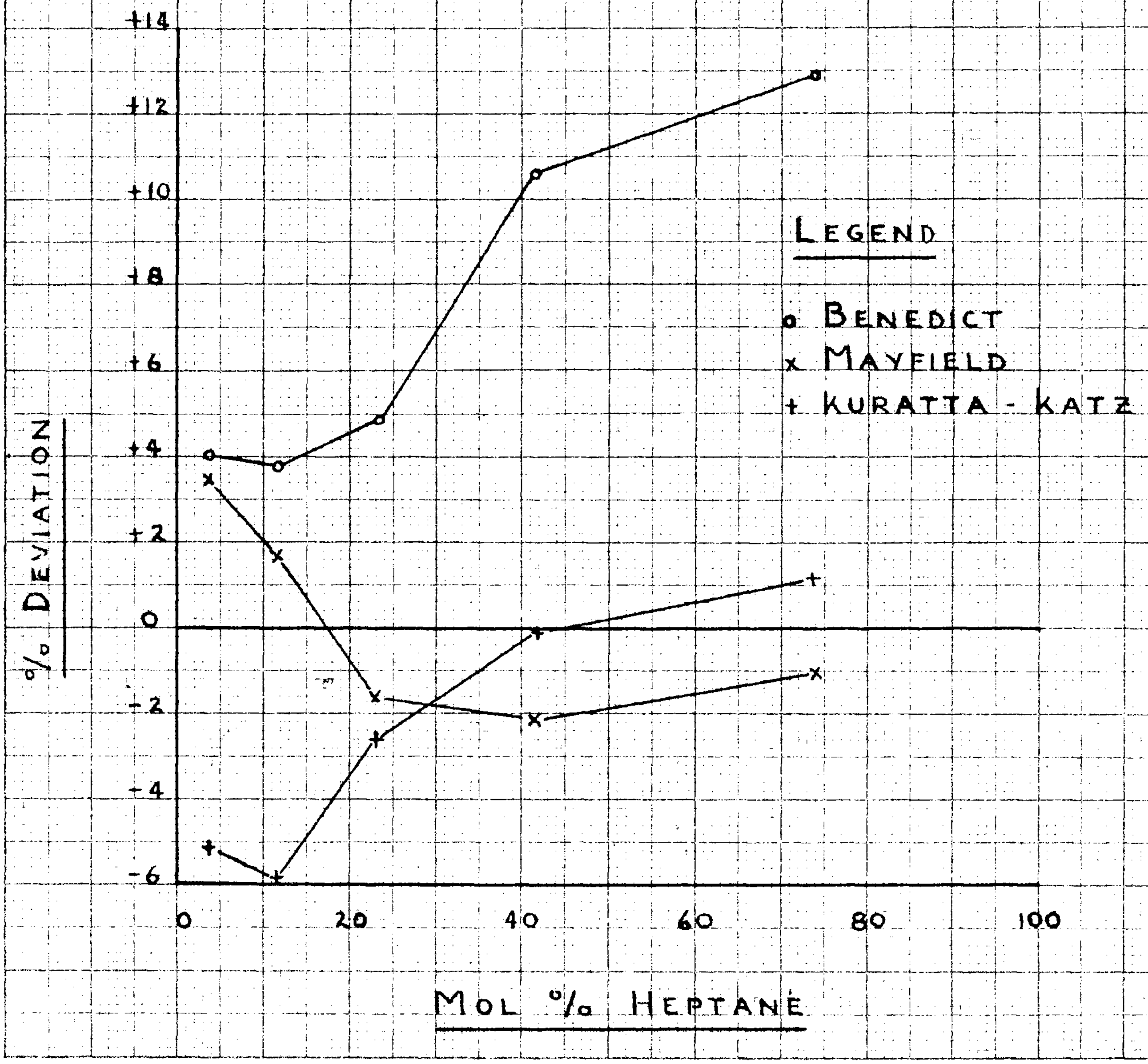
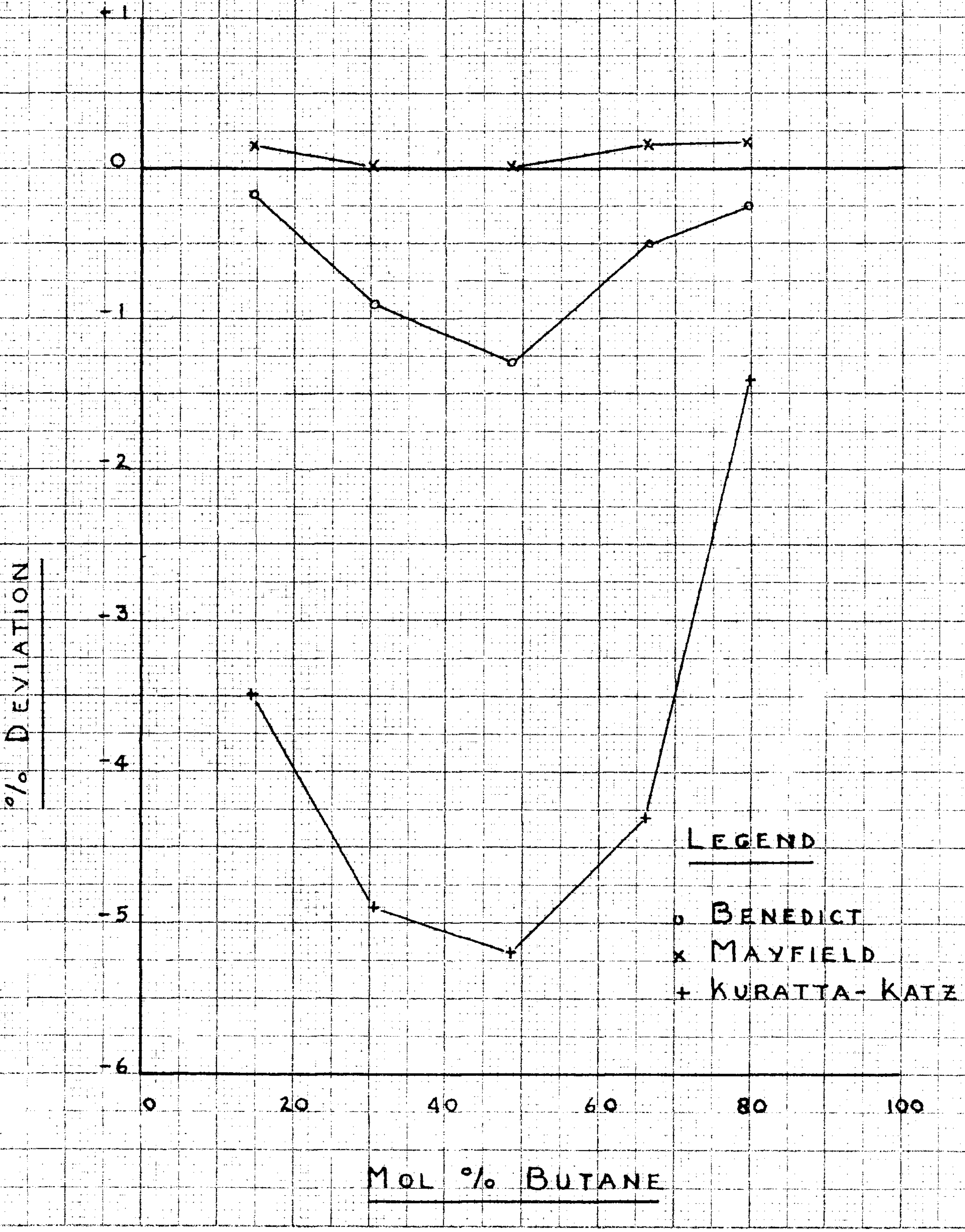


Figure 13



CRITICAL PRESSURE

DEVIATION FROM EXPERIMENTAL

PROPANE - BUTANE

Figure 14

CRITICAL PRESSURE

DEVIATION FROM EXPERIMENTAL

BUTANE - HEPTANE

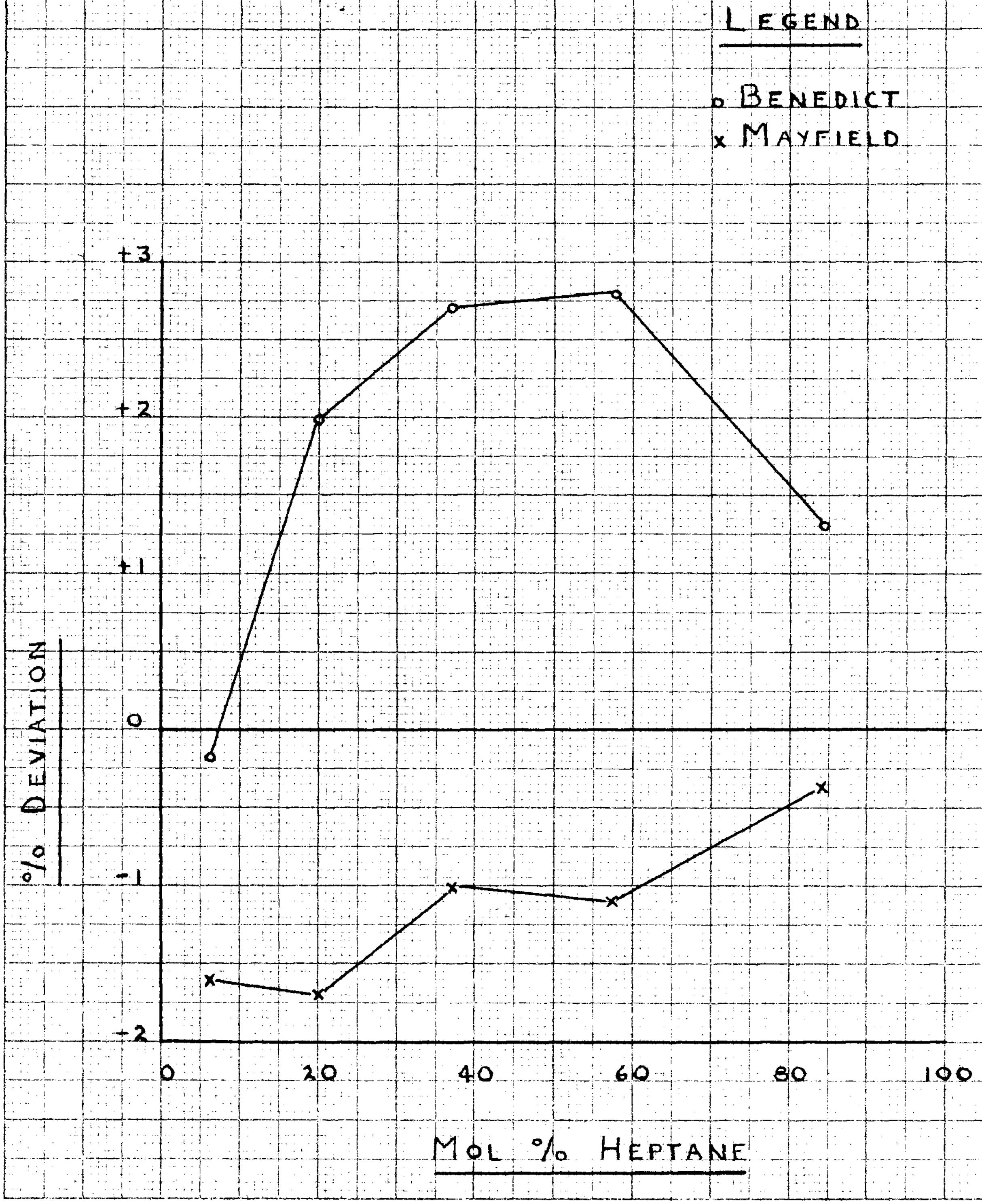


Figure 15

CRITICAL PRESSURE

DEVIATION FROM EXPERIMENTAL

PROPANE - PENTANE

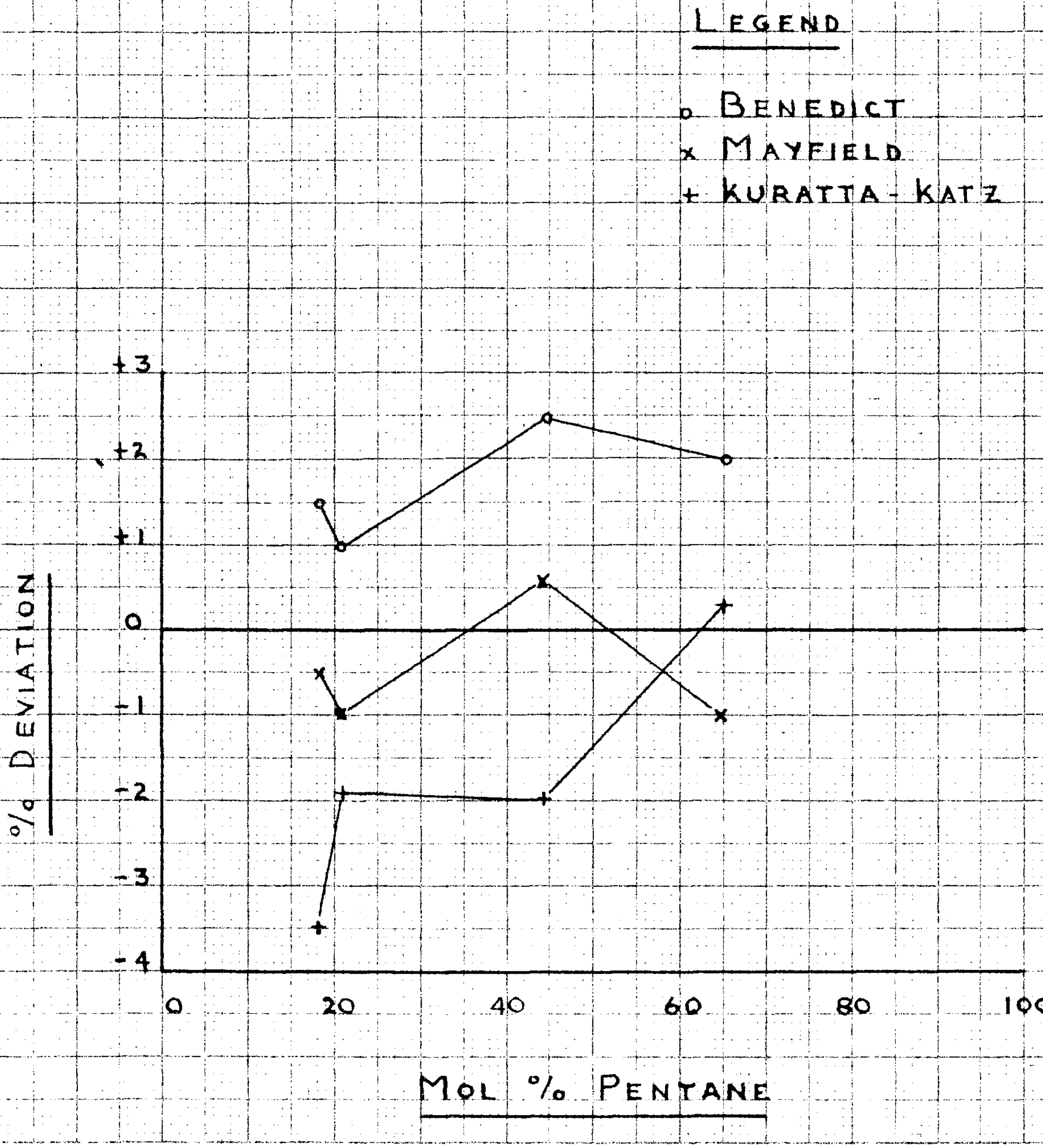


Figure 16

CRITICAL PRESSURE

DEVIATION FROM EXPERIMENTAL

PENTANE - HEPTANE

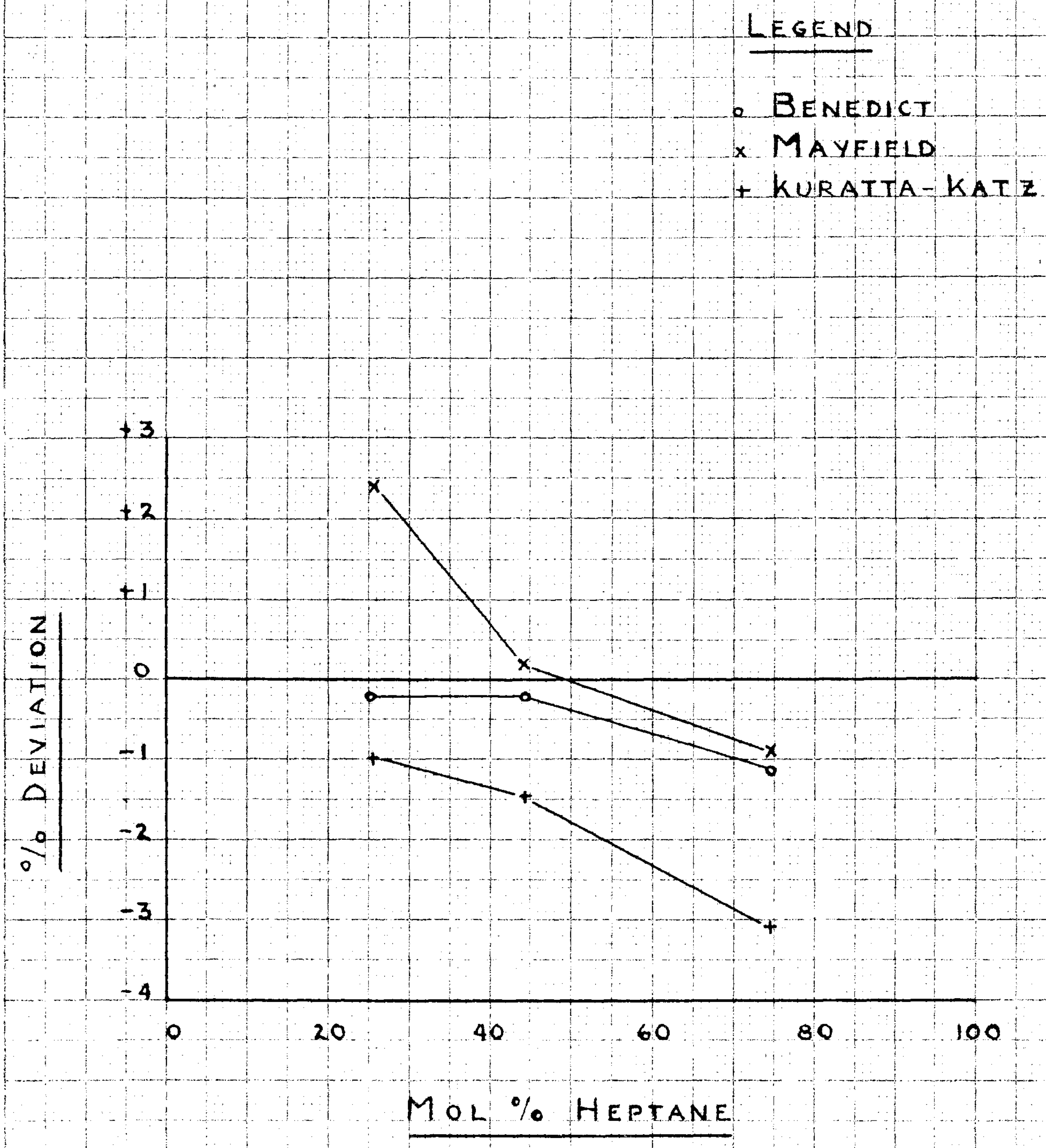


Table 13

LIST OF SYMBOLS

P_c - Critical pressure

$_{p}P_c$ - Pseudo-critical pressure

T_c - Critical temperature

P_{CD} - Difference in P_c between actual and additive law

P_{CM} - Critical pressure of a mixture

P_{CH} - Critical pressure of less volatile component

P_{CL} - Critical pressure of more volatile component

% L - Weight per cent of more volatile component

REFERENCES

(1) (Benedict, M.) - Edmister, Wayne C., "Applications of Thermodynamics to Hydrocarbon Processing" - Part XXII, <u>Petroleum Refiner</u>, September, 1949.

(2) Edmister, Wayne C., "Applications of Thermodynamics to Hydrocarbon Processing" - Part XXII, <u>Petroleum Refiner</u>, September, 1949.

(3) Edmister, Wayne C., "Applications of Thermodynamics to Hydrocarbon Processing" - Part XXIV, <u>Petroleum Refiner</u>, November, 1949.

(4) Kuratta, F. and Katz, D. L., "Critical Properties of Volatile Hydrocarbon Mixtures." Trans. Am. Inst. Chem. Eng. 1942

(5) Kay, W. B. - Ind. Eng. Chem., 28, 1014 (1936)

(6) Mayfield, F. D., "Critical States of Two Component Paraffin Systems," Ind. Eng. Chem. 35, 843, 1942.

(7) Michael, G. V. and Thodos, G., "Critical Temperatures and Pressures of Hydrocarbons," Chem. Eng. Progress Symposium Series, Vol. 49, No. 7, 1953.

REFERENCES (Cont'd)

(8) Nelson, W. L., Petroleum Refining Engineering, McGraw Hill, New York, 1941.

(9) Smith, R. L. and Watson, K. M., "Boiling Points and Critical Properties of Hydrocarbon Mixtures." Ind. Eng. Chem. 29, 1408, 1937.

(10) Watson, K. M. and Nelson, E. F., "Improved Methods for Approximating Critical and Thermal Properties of Petroleum Fractions." Ind. Eng. Chem. 25, 880, 1933.