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Title TESTING OF VAPOR-LIQUID EQUILIBRIUM DATA FOR
THERMODYNAMIC CONSISTENCY

Abstract approved 

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Redlich and Kister have developed two methods for evaluating thermodynamic consistency of vapor-liquid equilibrium data. These same authors also developed a power series for classifying systems according to the number of coefficients required to define the data. Stockett found it was difficult to classify systems by this method. Macan suggested that the power series be replaced by a series of orthogonal polynomials, namely the Legendre polynomials, which Macan found to represent the data better. Unfortunately when evaluating these series for the area test, only the magnitude is obtained.

The I. B. M. 1620 digital computer was used to check the thermodynamic consistency of seventy-two sets of experimental data.

The results of this investigation indicated that the majority of the data satisfied the slope test, but did not satisfy the area test. It

was also found that the percentage of the area, as well as the magnitude should be used in evaluating the area test.

TESTING OF VAPOR-LIQUID EQUILIBRIUM
DATA FOR THERMODYNAMIC CONSISTENCY

by

RICHARD PATRICK FRUTIGER

A THESIS

submitted to

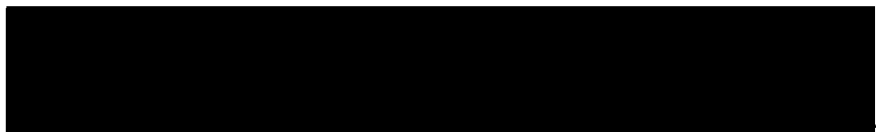
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MASTER OF SCIENCE

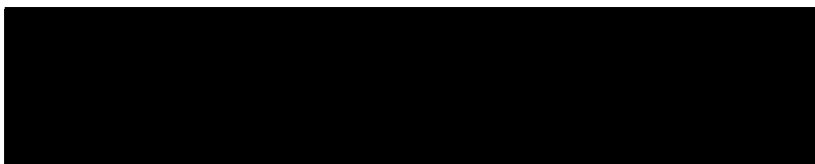
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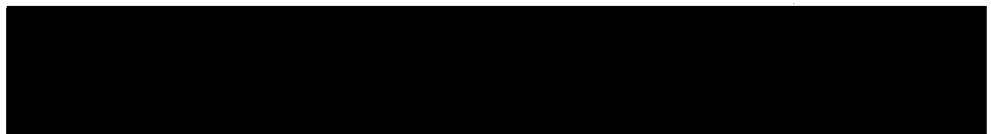


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TESTING OF VAPOR-LIQUID EQUILIBRIUM DATA FOR THERMODYNAMIC CONSISTENCY

INTRODUCTION

Binary vapor-liquid equilibrium data are very valuable in the design of costly distillation equipment. With the trend toward more complex separation processes, the need for accurate data on which to base the design calculations becomes more important.

The literature contains a vast amount of vapor-liquid equilibrium data either at constant pressure or temperature. Unfortunately in many instances different sets of data for the same system will disagree considerably. In order to evaluate the reported information, the data must be tested for its thermodynamic consistency.

Redlich and Kister (33), (34) proposed two methods for testing this data using thermodynamic relationships. The first method, known as the area test, consisted of evaluating the net area under the curve representing the logarithmic ratio of the activity coefficients versus the mole fraction of the more volatile component in the liquid phase. The second method, known as the slope test, consisted of evaluating the slope of the dew point curve at each experimental point. It was suggested by Redlich and Kister (33), (34) that this second method be used to pinpoint any inconsistencies in the data.

Redlich and Kister also proposed that the logarithmic ratio of the activity coefficients be represented by a power series for

classifying the systems and for smoothing the data. A system would be classified according to the number of coefficients required to define the data. Stockett (40) found in general that at least five terms are required to classify a system using this power series. It was concluded by Stockett that it would be rather difficult to classify binary systems in the manner Redlich and Kister suggested. Macan (23) proposed that a series of orthogonal polynomials, namely the Legendre polynomials, be used to classify the systems in place of the power series. This series had the advantage of representing the consistent data better, as well as having the area test indicated by the first coefficient of the series.

Unfortunately when the area test is determined using either of these proposed series, only the magnitude of the difference in the areas is obtained. Herington (12) pointed out that the percentage of the total area, as well as the magnitude, should be involved in the area test. The importance of this can be seen from the data in Table 1 for systems 21 and 32. The magnitude of the area test for these two systems are -.0147 and -.0157 respectively while the percentage of the total area for the respective systems are 25.9 percent and 4.6 percent indicating that system 32 is more reliable.

Using the I. B. M. 1620 digital computer the published data for some seventy-two sets of experimental data were evaluated for

thermodynamic consistency by the slope test and the area test using the orthogonal polynomials. The total area for each set of data was also determined using a planimeter.

THEORY

The basic expression for the partial pressure of a component in solution is represented by Raoult's law and is expressed as

$$P = P^{\circ}x. \quad (1)$$

For the vapor phase the general expression relating the composition of the vapor to the total pressure is known as Dalton's law and is expressed as

$$P = \pi y. \quad (2)$$

A combination of Raoult's and Dalton's law yields the basic equation used for predicting vapor-liquid equilibria. This equation is expressed as

$$\pi y = P^{\circ}x \quad (3)$$

and is applicable only for systems containing both ideal solutions and ideal vapors. Since such systems rarely exist, it is necessary then to correct for the non-ideality.

In order to correct for the deviation of the vapor-phase from ideality, Lewis and Randall (21, p. 154) proposed that fugacity be used in place of the pressure terms in equation (3). When operating near atmospheric pressure the fugacity can generally be taken equal to the pressure since for most substances the deviation from ideality

is small and the use of either is acceptable.

The deviation of the liquid phase is generally more important, since in most cases even at low pressure most liquids deviate from ideality. To correct for the non-ideality of solutions a correction factor was proposed by Lewis and Randall which could be incorporated directly in the equilibrium relationship of equation (3). This factor is called the activity coefficient and is expressed as

$$\gamma = \frac{y\pi}{xP^0} \quad (4)$$

In a binary mixture, the activity coefficients are related by the Duhem equation

$$x_1 \left[\frac{\partial \log \gamma_1}{\partial x_1} \right]_{\pi, t} + (1-x_1) \left[\frac{\partial \log \gamma_2}{\partial x_1} \right]_{\pi, t} = 0. \quad (5)$$

The laborious amount of calculation required to solve Duhem's equation makes it rather impractical for calculating the activity coefficients precisely. Consequently approximation formulas like the equations of Margules (36, p. 54-56), Scatchard (36, p. 59), van Laar (36, p. 56-60) and others have been devised for predicting the activity coefficients from experimental data. This procedure, however, does introduce some uncertainty as to whether the deviation of the original values calculated from equation (4) from the smoothed values are due to experimental errors or the insufficient validity of

the approximation formula.

Since experimental data are to be used for calculating the activity coefficients, it is necessary to employ some method for smoothing the data as well as checking the thermodynamic consistency.

Redlich and Kister (33), (34) have proposed a method using Scatchard's (38) "excess free energy" equation as a starting point. The Scatchard "excess free energy" equation is expressed as

$$Q = x_1 \log \gamma_1 + (1 - x_1) \log \gamma_2. \quad (6)$$

At the boundary conditions of $x_1 = 0$ and $x_1 = 1$ the excess free energy equals zero, since at these points where only pure components exist no mixing effects occur.

Differentiation of equation (6) with respect to x_1 gives

$$\frac{dQ}{dx_1} = \log \gamma_1 - \log \gamma_2 + x_1 \frac{\partial (\log \gamma_1)}{\partial x_1} + (1 - x_1) \frac{\partial (\log \gamma_2)}{\partial x_1}. \quad (7)$$

According to the Duhem equation (5) the sum of the last two terms is zero and equation (7) becomes

$$\frac{dQ}{dx_1} = \log \frac{\gamma_1}{\gamma_2}. \quad (8)$$

Integrating equation (8) between the definite limits $x_1 = 0$ and $x_1 = 1$, where $Q = 0$ at both points, there is obtained

$$Q = \int_0^1 \log \frac{y_1}{y_2} dx_1 = 0. \quad (9)$$

Redlich and Kister (33), (34) proposed equation (9) as one of the tests for thermodynamic consistency of the experimental data. The activity coefficients are calculated using equation (4) and the area calculated by plotting the ratio of the activity coefficients on the ordinate and the mole fraction x_1 of the more volatile component as the abscissa. In order for the data to be thermodynamically consistent the net area under the curve between $x_1 = 0$ and $x_1 = 1$ must equal zero. The area test is strictly applicable only at constant temperature and pressure, but for practical purposes it can be extended to systems with moderate boiling ranges. Unfortunately, the area test does not establish inconsistencies in the data with absolute certainty, but it does indicate whether a system requires further investigation before the data can be accepted.

Redlich and Kister (33), (34) proposed a second test, the "slope test", to try and pinpoint the inconsistencies in the experimental data. The equation for this test is obtained by logarithmically differentiating equation (4) and substituting into equation (5) to obtain

$$\left[\frac{x_1}{y_1} - \frac{1-x_1}{1-y_1} \right] \frac{dy_1}{dt} - \left[x_1 \frac{d \ln P_1^0}{dt} + (1-x_1) \frac{d \ln P_2^0}{dt} \right] = 0. \quad (10)$$

This equation becomes after rearrangement

$$\frac{dt}{dy} = \frac{0.4343(x_1 - y_1)}{y_1(1 - y_1)} \left[x_1 \frac{1}{\frac{d \log P_1^o}{dt}} + (1 - x_1) \frac{1}{\frac{d \log P_2^o}{dt}} \right] \quad (11)$$

This equation has the restriction of being applicable only at constant temperature and pressure, but for practical purposes it is also extended to systems with moderate boiling ranges.

Equation (11) may be used to calculate the slopes of the dew point curve (y vs. t) at the various experimental points. Any point is considered to be inconsistent if the slope is not tangent to the curve passing through the points. If either y is higher or x lower than it should be, the calculated slope will be greater than the experimental slope. The reverse is true if y is lower or x is higher than it should be.

Redlich and Kister (33), (34) suggested that a convenient way to represent the function Q was by a power series in x_1 . Since $Q = 0$ for $x_1 = 0$ and $x_1 = 1$, it was necessary for each term in the series to contain the factor $x_1(1 - x_1)$. Also it was desirable to develop a series symmetric with respect to the two components. The variable $(2x_1 - 1)$ was chosen since it was the simplest of its kind. Applying these conditions the series expansion for Q becomes

$$Q = x_1(1-x_1) \left[B + C(2x_1 - 1) + D(2x_1 - 1)^2 + E(2x_1 - 1)^3 \right]. \quad (12)$$

Differentiating equation (12) yields

$$\begin{aligned} \frac{dQ}{dx_1} &= B(1-2x_1) + C[-1+6x_1(1-x_1)] \\ &+ D(2x_1-1)[-1+8x_1(1-x_1)] \\ &+ E(2x_1-1)^2[-1+10x_1(1-x_1)]. \end{aligned} \quad (13)$$

Setting equation (13) equal to equation (9) yields

$$\begin{aligned} \log \frac{y_1}{y_2} &= B(1-2x) + C[-1+6x_1(1-x_1)] \\ &+ D(2x_1-1)[-1+8x_1(1-x_1)] \\ &+ E(2x_1-1)^2[-1+10x_1(1-x_1)]. \end{aligned} \quad (14)$$

The coefficients of this series are ideal for classifying systems, since each of the higher terms are corrections for the terms of lower order. Redlich and Kister (33, p. 346) suggested there are five different types of classification ranging from the case of a perfect solution, where all the coefficients are zero, to the case of a highly imperfect solution which would require all four coefficients.

Using the Alwac III - E digital computer, Stockett (40) calculated the coefficients to equation (14) for experimental data ranging from nearly perfect to extremely imperfect. In all cases the author found that at least four terms were required to represent the data.

The author also concluded that in order to classify binary systems as

suggested by Redlich and Kister, one must have beforehand some idea as to which classification the system in question belongs.

Macan (23) suggested that the function $\log(\gamma_1/\gamma_2)$ might be represented better by a series of orthogonal polynomials, such as the Legendre polynomials represented as

$$\log \frac{\gamma_1}{\gamma_2} = aP_0(x_1) + bP_1(x_1) + cP_2(x_1) + dP_3(x_1) + eP_4(x_1) \quad (15)$$

where (25, p. 260)

$$P_0(x_1) = 1, \quad (16)$$

$$P_1(x_1) = 1 - 2x_1, \quad (17)$$

$$P_2(x_1) = 1 - 6x_1 + 6x_1^2, \quad (18)$$

$$P_3(x_1) = 1 - 12x_1 + 30x_1^2 - 20x_1^3 \quad (19)$$

and

$$P_4(x_1) = 1 - 20x_1 + 90x_1^2 - 140x_1^3 + 70x_1^4. \quad (20)$$

Using the Alvac III - E digital computer Macan calculated the coefficients for both the Legendre polynomial and the Redlich and Kister series. Macan found that the Legendre polynomial defines the function $\log(\gamma_1/\gamma_2)$ very satisfactorily even though the experimental data may be thermodynamically inconsistent, while the Redlich - Kister

series gives as good results only if the experiment data are consistent. The Legendre polynomial also has the advantage over the Redlich - Kister series in that the first coefficient represents the area test for thermodynamic consistency.

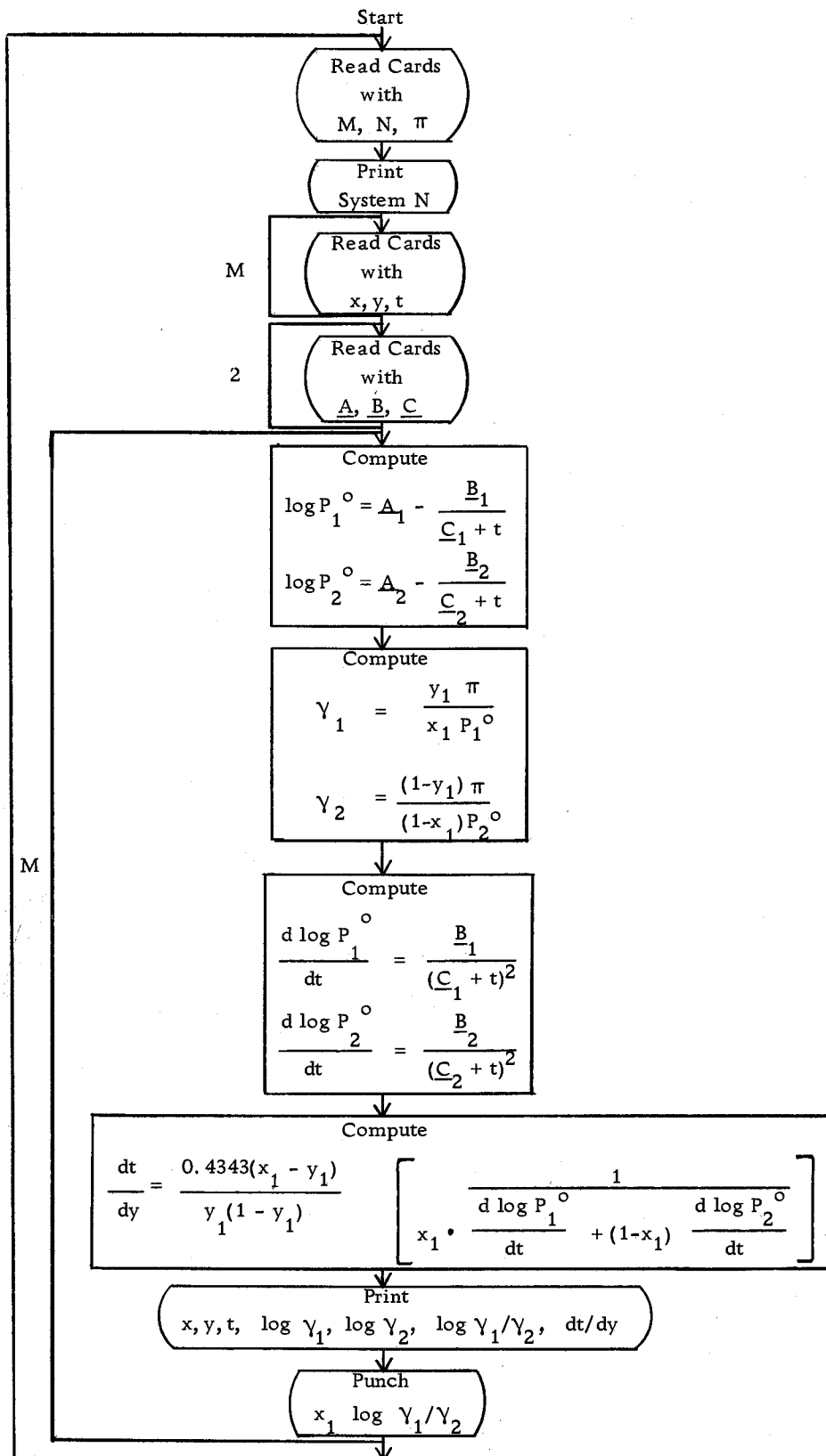
DISCUSSION OF COMPUTER PROGRAMS

To test seventy-two sets of vapor-liquid equilibrium data for thermodynamic consistency would be a very laborious job if it were not for digital computers. The mathematical relationships used for testing the consistencies were programmed for the I. B. M. 1620 digital computer using Fortran language. The calculations were split into two parts which are illustrated in their general form in Figures 1 and 2. The actual programs, in complete detail, are included in the appendix.

The first diagram illustrates the general procedure the computer followed in evaluating the slope of the dew point curve using equation (11) for the slope test and the activity coefficients for the area test using equation (4). In order to apply either of these mathematical relationships, it was first necessary to obtain vapor pressure data for each of the binary systems under consideration. The Antoine equation

$$\log P^{\circ} = \frac{A}{C+t} - \frac{B}{C+t} \quad (21)$$

was used to evaluate the vapor pressure at various temperatures. The constants for the Antoine equation were readily available (19, p. 1424-1438).



SCHEMATIC DIAGRAM OF FIRST PROGRAM

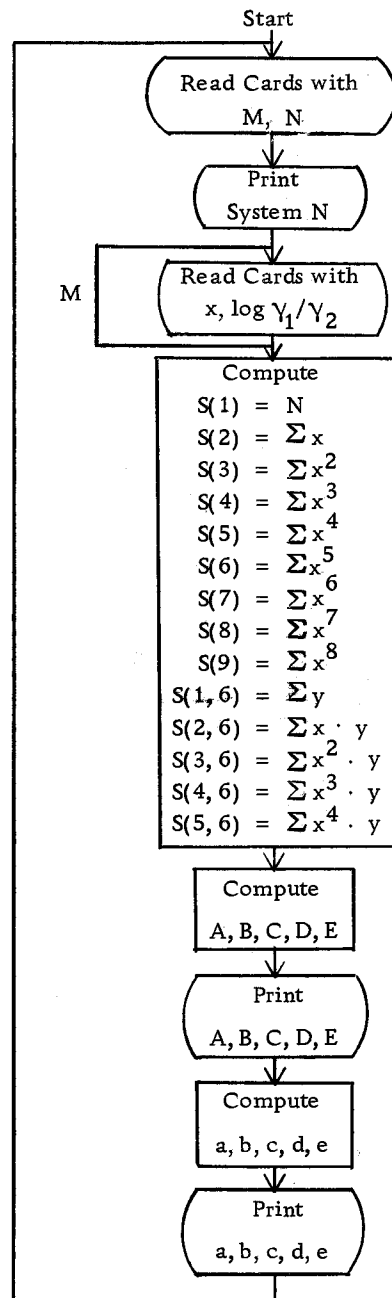
Figure 1

In order to allow application of the program to more than one system, it was necessary to provide a means for entering new (x, y, t) data as well as the pressure of the system and Antoine constants for the two components. Consequently, the first step in the program is to read the pressure and number of data points into the computer. The computer then proceeds to read the correct number of (x, y, t) data cards followed by the Antoine constants for the two components.

After the necessary data had been read into the computer, it proceeded to compute the vapor pressures and activity coefficients, as well as the slope for each experimental point. After all the necessary results had been computed the computer proceeded to type them out in tabulated form. As part of the first program the data cards for the second program were prepared by the computer. The last statement in the program then returned the computer to the first statement, namely the reading in of new data.

Figure 2 illustrates the general procedure followed in calculating the coefficients of the Legendre polynomial. Before these coefficients, however, could be computed it was necessary to express the function $\log (\gamma_1/\gamma_2)$ in the form of a power series expressed as

$$\log \gamma_1/\gamma_2 = A + Bx + Cx^2 + Dx^3 + Ex^4. \quad (22)$$



SCHEMATIC DIAGRAM OF SECOND PROGRAM

Figure 2

Using the method of least squares and solving the system of linear equations, the coefficients for equation (22) were computed. Next the coefficients of equation (15) were evaluated using the two very important properties of orthogonality, namely

$$\int_0^1 P_m(x)P_n(x)dx = 0 \quad (23)$$

when $m \neq n$, and

$$\int_0^1 P_m^2(x)dx = \frac{1}{2m+1} \quad (24)$$

when $m = n$. The five coefficients were calculated using the following equations

$$a = \int_0^1 P_0(x) \cdot \log \frac{\gamma_1}{\gamma_2} dx \quad (25)$$

$$b = 3 \cdot \int_0^1 P_1(x) \cdot \log \frac{\gamma_1}{\gamma_2} dx \quad (26)$$

$$c = 5 \cdot \int_0^1 P_2(x) \cdot \log \frac{\gamma_1}{\gamma_2} dx \quad (27)$$

$$d = 7 \cdot \int_0^1 P_3(x) \cdot \log \frac{\gamma_1}{\gamma_2} dx \quad (28)$$

$$e = 9 \cdot \int_0^1 P_4(x) \cdot \log \frac{\gamma_1}{\gamma_2} dx. \quad (29)$$

In each equation (25-29) the function $\log (\gamma_1/\gamma_2)$ was replaced by the power series of equation (22). Evaluation of the coefficient "a" of equation (25) resulted in a measure of the area test for thermodynamic consistency of the smoothed data.

DISCUSSION OF RESULTS

The calculated results for the seventy-two sets of experimental vapor-liquid data, involving forty-seven systems, are presented in Table 1. These systems were chosen at random from the vast supply of equilibrium data recorded in literature and consisted of twenty azeotropic systems and twenty-seven non-azeotropic systems. The variation in boiling interval for the two types of systems were 0.6 to 32.3 degrees centigrade for azeotropes and 2.9 to 91.5 degrees centigrade for non-azeotropes. Recorded in Table 1 are the two components making up the binary system, the reference to where the data were obtained, the boiling points of the two components, the magnitude of the area test, the percentage this magnitude is of the total area, the rating of the slope test, and the coefficients for the Legendre polynomial.

Using a planimeter, the area under the curve ($\log \gamma_1/\gamma_2$ vs. x_1) was determined, when feasible, for all seventy-two sets of data. The planimeter was used to measure the distance around a square of known area encompassing the curve and also the curve and two sides bounding the curve. The area under the curve was obtained by multiplying the ratio of these two distances times the area of the measured square. This procedure was carried out for the area under the curve on both

TABLE 1

CALCULATED RESULTS										
System	Ref.	B. P. ° C	Area Test			Coefficient of Legendre Polynomial				
			Magnitude	% of total area	Slope test	a	b	c	d	e
1. Acetic Acid-Dimethylaniline	8	118.1 194.2	.0413	31.0	Fairly good	.0506	.2573	-.0004	-.0151	.0412
2. Acetone-Cyclohexane*	17	56.2 80.7	-.0285	8.8	Good (poor at azeo.)	-.0252	.6143	-.1663	-.0652	.0117
3. Acetone-Ethanol	11	56.2 78.4	-.0311	24.6	Fairly good	-.0372	.2316	.0679	-.0070	.0213
4. Acetone-Methanol*	10	55.6 64.1	.0150	11.6	Fairly good	.0127	.2514	-.0257	-.0380	-.0134
5. Acetone-Methanol*	29	56.2 64.7	.0139	8.2	Poor	.0324	.2932	.0810	-.0572	.0421
6. Acetone-Methanol*	1	56.2 64.7	-.0193	13.8	Fairly good (poor at azeo.)	-.0155	.2781	-.0059	.0111	.0002
7. Acetone-Methyl Ethyl ketone	31	56.2 79.6	-.0057 (scattered)	20.8	Fairly good (some scattering)	-.0158	.0481	-.0316	-.0163	-.0543
8. Acetone-Water	31	56.2 100.0	-.0086	2.2	Good	.0201	.7209	.2147	.0170	.0928
9. Acetone-Water	32	56.2 100.0	.0205	5.0	Good	.0298	.8061	.1015	.0494	.0326
10. Acetone-Water	2	56.2 100.0	.0311	7.7	Good	.0299	.8059	.0882	.0556	-.0149

* Indicates Azeotropes.

Table 1 (Continued)

System	Ref.	B. P. ° C	Area Test		Slope test	Coefficient of Legendre Polynomial				
			Magnitude	% of total area		a	b	c	d	e
11. Acetone- Water	30	56.2 100.0	.0306	7.7	Fairly good	.0366	.7937	.1041	.0347	-.0167
12. Benzene- Cyclohexane*	35	80.1 80.7	-.0101	13.5	Fairly good	-.0096	.1436	-.0036	-.201	.0123
13. Benzene- Cyclohexane*	39	80.1 80.7	-.0031	4.0	Good	-.0013	.1539	-.0074	.0095	.0064
14. Benzene- Cyclohexane*	41	80.1 80.7	.0092	10.2	Fairly good	.0127	.1867	.0324	.0326	.0137
15. Benzene- Methylcyclo- hexane	28	80.1 100.9	-.0174	25.2	Very good	-.0212	.1295	-.0443	-.0234	-.0122
16. Benzene- Methylcyclo- hexane	39	80.1 100.9	-.0221	33.0	Good	-.0240	.1361	-.0110	.0140	.0031
17. Benzene- 2, 4-Di- methylpentane*	35	79.8 80.2	0.0	0	Good (data scattered)	.0006	.2407	-.0512	.0351	-.0060
18. Cellosolve- Ethylbenzene*	27	135.1 136.2	.0260	11.8	Good	.0252	.4371	.0378	.0066	-.0033
19. Cyclohexane- Methylcyclo- hexane	35	80.7 100.9	scattered	---	Very poor	---	---	---	---	---
20. Cyclohexane- Toluene	28	80.7 110.6	-.0283	41.4	Very good	-.0379	.1545	-.0663	.0369	-.0345

Table 1 (Continued)

System	Ref.	B. P. ° C	Area Test		Slope test	Coefficient of Legendre Polynomial				
			Magnitude	% of total area		a	b	c	d	e
21. Cyclohexane- Toluene	39	80.7 110.6	-.0147	25.9	Very good	-.0155	.1134	-.0001	-.0016	.0091
22. Cyclopentane- Benzene	28	49.3 80.1	-.0082	11.3	Very good	-.0100	.1450	.0040	-.0046	.0204
23. Ethyl Acetate- Benzene	4	77.2 80.1	-.0054	24.0	Fairly good	-.0054	.0418	.0085	-.0008	.0045
24. Ethyl Acetate- Ethanol*	7	77.2 78.4	.0059	3.3	Poor	.0021	.3609	-.0401	.0445	-.0613
25. Ethyl Acetate- Ethanol*	27	77.2 78.4	-.0102	5.5	Fairly good	-.0119	.3682	-.0261	.0298	.0053
26. Ethyl Acetate- n-propanol	27	77.2 97.2	Very positive	---	Fairly good	---	---	---	---	---
27. Ethyl Acetate- Isopropanol*	27	77.2 82.4	.0006	0.6	Poor (little data)	.0035	.2143	.0010	.0206	-.0059
28. Ethyl Acetate- Toluene	4	77.2 110.6	-.0080	19.2	Very good	-.0084	.0786	-.0061	.0045	.0002
29. Ethyl Acetate- p-xylene	4	77.2 138.4	-.0050	5.5	Very good	-.0063	.1863	-.0082	.0210	-.0026
30. Ethanol- Benzene*	18	78.3 80.1	-.0036	1.1	Good	-.0019	.6571	.1064	.0270	.0174
31. Ethanol- Benzene*	15	78.1 79.7	-.0312	9.4	Fairly good (poor at azeo.)	-.0278	.6777	.0370	.0185	-.0293

Table 1 (Continued)

System	Ref.	B. P. ° C	Area Test			Coefficient of Legendre Polynomial				
			Magnitude	% of total area	Slope test	a	b	c	d	e
32. Ethanol- Benzene*	6	78.4 80.1	-.0157	4.6	Fairly good (not defined at azeo.)	-.0154	.6824	.1019	.0491	-.0105
33. Ethanol- Benzene*	6	78.4 80.1	-.0096	3.0	Fairly good (poor around azeo.)	-.0027	.6554	.0913	.0329	-.0276
34. Ethanol- Benzene*	6	78.4 80.1	-.0200	5.8	Fairly good (poor around azeo.)	-.0133	.6774	.0792	.0141	-.0017
35. Ethanol- Benzene*	43	78.4 80.1	-.0043	1.2	Fairly good (poor around azeo.)	-.0012	.7029	.1506	.0751	.0442
36. Ethanol- n-Butanol	2	78.4 118.0	scattered (very positive)	---	Poor	---	---	---	---	---
37. Ethanol- n-Butanol	11	78.4 118.0	scattered (very negative)	---	Fairly good	---	---	---	---	---
38. Ethanol- sec. -Butanol	11	78.4 99.5	scattered (very negative)	---	Fairly good	---	---	---	---	---
39. Ethanol- n-Heptane*	16	78.4 98.4	.0009	0.0	Poor (very poor at azeo.)	-.0070	1.0017	.0010	.1778	-.0449
40. Ethanol- Methyl Ethyl Ketone*	11	78.4 79.6	-.0083	6.7	Fairly good	-.0051	.2487	.0124	-.0038	.0257
41. Ethanol- Methyl n-propyl Ketone*	11	78.4 102.4	-.0190	25.5	Poor	-.0407	.3170	.0339	.0834	-.0257
42. Ethanol-n- Pentanol	11	78.4 138.1	scattered (very negative)	---	Very good	---	---	---	---	---
43. Ethanol- Toluene*	22	78.1 107.3	-.0236	6.8	Very good	-.0262	.6774	.0435	.0106	.0384

Table 1 (Continued)

System	Ref.	B. P. ° C	Area Test		Slope test	Coefficient of Legendre Polynomial				
			Magnitude	% of total area		a	b	c	d	e
44. Ethanol-Toluene *	18	78.3 110.6	-.0267	7.8	Very good	-.0247	.6845	.0277	.0192	-.0071
45. n-Heptane-Toluene	14	98.4 110.6	-.0117	18.3	Good	-.0108	.1186	.0164	-.0177	.0119
46. n-Heptane-Toluene	39	98.4 110.6	-.0090	14.1	Fairly good	-.0074	.1218	.0210	.0011	.0058
47. n-Heptane-Toluene	37	98.4 110.6	-.0004	0.7	Good	-.0006	.1169	.0177	-.0061	-.0044
48. Methanol-Butanol	13	64.7 118.0	(very positive)	---	Poor	.1208	.1808	-.0170	.0487	-.0361
49. Methanol-Carbon Tetrachloride *	14	64.7 76.8	-.0134	3.0	Good	.0029	.9230	.1637	.1461	.0677
50. Methanol-Ethyl Acetate *	27	64.7 77.2	-.0024	1.1	Good	.0037	.4525	-.0102	.0127	.0016
51. Methanol-Methyl Ethyl Ketone	13	64.7 79.6	.0035	2.2	Very poor	.0130	.3514	.0431	.0454	.0263
52. Methanol-Methyl Isobutyl Ketone	13	64.7 117.0	-.0259	12.0	Poor	-.0515	.4811	.0105	-.0600	.0840
53. Methanol-n-Pentanol	13	64.7 138.1	(very positive)	---	Fairly good	.1088	.1717	-.0702	.0474	.0021
54. Methanol-Methyl Propyl Ketone	13	64.7 102.4	-.0740	46.4	Poor	-.0769	.2970	-.0295	-.0068	-.0338

Table 1 (Continued)

System	Ref.	B. P. ° C.	Area Test		Slope test	Coefficient of Legendre Polynomial				
			Magnitude	% of total area		a	b	c	d	e
55. Methanol-n-Propanol	13	64.7 97.2	scattered (very positive)	---	Very poor	---	---	---	---	---
56. Methylcyclopentane-Benzene	28	71.8 80.1	-.0034	4.6	Very good	-.0040	.1450	.0186	-.0084	.0015
57. Methylcyclopentane-Benzene	9	71.8 80.1	.0021	2.9	Good	.0004	.1431	.0075	.0062	.0068
58. Methylcyclopentane-Toluene	28	71.8 110.6	-.0270	43.1	Very good	-.0340	.1325	-.0454	.0260	-.0355
59. Methyl Ethyl Ketone-Cyclohexane *	17	79.6 80.8	-.0008	0.0	Fairly good (poor around azeo.)	-.0083	.4710	-.0261	.0326	-.0600
60. Methyl Ethyl Ketone-Cyclohexane *	5	79.6 80.8	-.0029	1.3	Fairly good (poor around azeo.)	-.0021	.4577	.0756	.0383	.0040
61. Methyl Ethyl Ketone-Water *	31	79.6 100.0	-.0175	3.5	Poor	-.0252	1.0279	.2732	.1985	.0069
62. Methyl Ethyl Ketone-Water *	30	79.6 100.0	.0394	7.3	Very poor (little data)	.0097	1.0398	.2418	.1025	.0779
63. n-Octane-Cellosolve *	26	125.7 135.1	-.0036	1.0	Good	-.0152	.7056	.0309	.0010	.0170
64. 1-Octene-Ethylbenzene	42	121.3 136.2	.0051	16.4	Fairly good	.0084	.0673	.0261	.0145	.0016

Table 1 (Continued)

System	Ref.	B. P. ° C	Area Test		Slope test	Coefficient of Legendre Polynomial				
			Magnitude	% of total area		a	b	c	d	e
65. Isopropanol- [*] 2, 2, 4-Tri- methylpentane	3	82.4 99.2	-.0160	4.7	Fairly good	-.0156	.6690	.0065	.0091	-.0447
66. n-Propanol- [*] Water	27	97.2 100.0	.0189	5.7	Poor	---	---	---	---	---
67. Isopropanol- [*] Water	2	82.4 100.0	.0141	4.0	Fairly good (poor below azeo.)	.0075	.7023	.2549	.0844	.0218
68. Isopropanol- [*] Water	44	82.4 100.0	-.0075	2.2	Very good	-.0002	.6744	.2420	.0753	.0196
69. Isopropanol- [*] Water	20	82.4 100.0	(not enough data)	---	Very good (data given)	---	---	---	---	---
70. Isopropanol- [*] Water	15	82.4 100.0	.0142	3.7	Poor	.0186	.7989	.1805	.1799	.0026
71. Toluene-p- Cresol	24	110.7 202.2	.0170	13.1	Very good	.0625	.0953	.1285	-.1756	.1246
72. 2,2,5-Trimethyl- hexane Ethyl- benzene	42	136.2	.0108	14.7	Poor	.0216	.1204	.0423	-.0100	.0469

sides of the abscissa. The area test as given by equation (9) was then computed by adding the magnitude of the two areas together. To be thermodynamically consistent the sum of these two areas should equal zero. For each system that this did not occur, the percentage of the total area was computed by dividing the magnitude of the difference by the absolute sum of the areas under the curve.

The slope at each experimental point on the dew point curve (t vs. y_1) were obtained using equation (11). These slopes were then used to draw a tangent line through each experimental point. Depending on how these tangent line fitted the actual curve drawn through the experimental points, a system was classified as one of the following: very good, good, fairly good, poor and very poor. Systems in which the calculated tangent agreed exceptionally well with the experimental curve, were classified as very good. The good classification was given to those systems whose calculated slope agreed quite well with the experimental curve, but whose data were somewhat scattered. Systems that had portions of the experimental curve undefined were generally classified as fairly good, while those with calculated slopes disagreeing with the experimental curve were classified as poor. The very poor classification was given those systems in which it was impossible to draw a curve through the experimental points and have a smooth curve. Any system classified as being fairly good or better,

was considered to have satisfied the requirements of the slope test.

The coefficients for the Legendre polynomial equation (15) were computed by replacing the function $\log (\gamma_1/\gamma_2)$ by the power series of equation (22) and solving equations (25) through (29). These coefficients represented all experimental points, since in smoothing the data with the power series all data points were included.

Table 2 consists of the experimental and calculated data for the system ethanol-toluene. The vapor composition for this system were obtained by solving the rigorous form of the Duhem equation(22) for a constant pressure process, using experimental temperature, liquid composition and heat of mixing data. The experimental boiling interval for this system was found to be 29.2 degrees centigrade. The area and slope tests which were derived from the Duhem equation for constant temperature and pressure, were used with these calculated data in order to determine whether the large boiling interval system could be evaluated as Redlich and Kister suggested. As can be seen from Figure 4 the slope test for this system was excellent. Although a smooth curve was easily drawn through the experimental points for the area test, the test itself exhibited a magnitude of -.0236 representing 6.8 percent of the absolute area. Since the area test required a net area of zero, these data would appear to be inconsistent. This conclusion, however, is incorrect since the data are known to be

TABLE 2

EXPERIMENTAL AND CALCULATED DATA

System 43: Ethanol-Toluene

Antoine Constants:

$$\underline{A}_1 = 8.04494 \quad \underline{A}_2 = 6.95464$$

$$\underline{B}_1 = 1554.3 \quad \underline{B}_2 = 1344.8$$

$$\underline{C}_1 = 222.65 \quad \underline{C}_2 = 219.482$$

Boiling Points:

Ethanol - 78.06° C

Toluene - 107.32° C

Total Pressure: 756 mmHg.

<u>x</u>	<u>y</u>	<u>t</u>	<u>log Y₁</u>	<u>log Y₂</u>	<u>log $\frac{Y_1}{Y_2}$</u>	<u>dt/dy</u>
.0050	.0803	107.32	.7490	.0042	.7447	-35.14
.0100	.1418	104.98	.7286	.0060	.7225	-36.77
.0150	.1871	103.20	.6988	.0075	.6912	-37.97
.0200	.2265	101.60	.6804	.0089	.6714	-39.14
.0250	.2605	100.18	.6653	.0102	.6550	-40.21
.0300	.2904	98.89	.6526	.0116	.6410	-41.20
.0400	.3415	96.62	.6325	.0140	.6185	-43.04
.0500	.3836	94.66	.6161	.0164	.5997	-44.67
.0751	.4638	90.71	.5842	.0219	.5623	-48.10
.1000	.5214	87.67	.5588	.0274	.5313	-50.78
.1500	.5902	83.81	.4996	.0405	.4590	-53.02
.2000	.6257	81.79	.4337	.0572	.3764	-51.91
.3000	.6717	79.32	.3302	.0952	.2350	-46.75
.4000	.7016	77.91	.2483	.1420	.1063	-39.09
.5000	.7189	77.26	.1732	.2051	-.0318	-28.90
.6000	.7278	77.03	.1034	.2916	-.1881	-16.98
.7900	.7900	76.79	.0237	.4624	-.4386	0.00
.8700	.8460	77.04	.0072	.5321	-.5248	4.69
.9000	.8749	77.20	.0043	.5534	-.5490	5.83
.9500	.9311	77.60	.0010	.5892	-.5882	7.46
.9900	.9851	78.06	-.0003	.6162	-.6165	8.44

Area Test: -.0236

Percentage of Total Area: 6.8

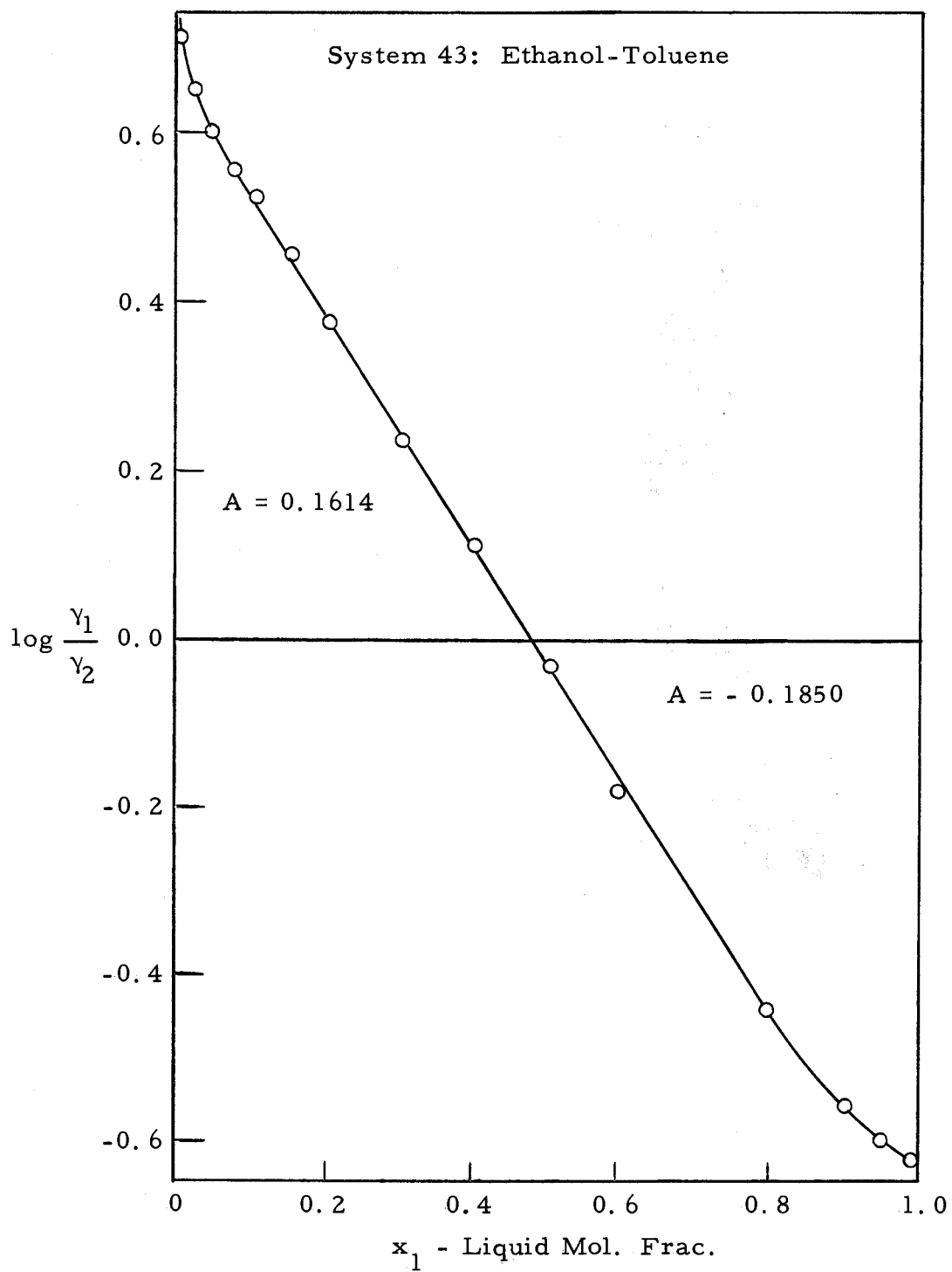
a = -.0262

b = .6774

c = .0435

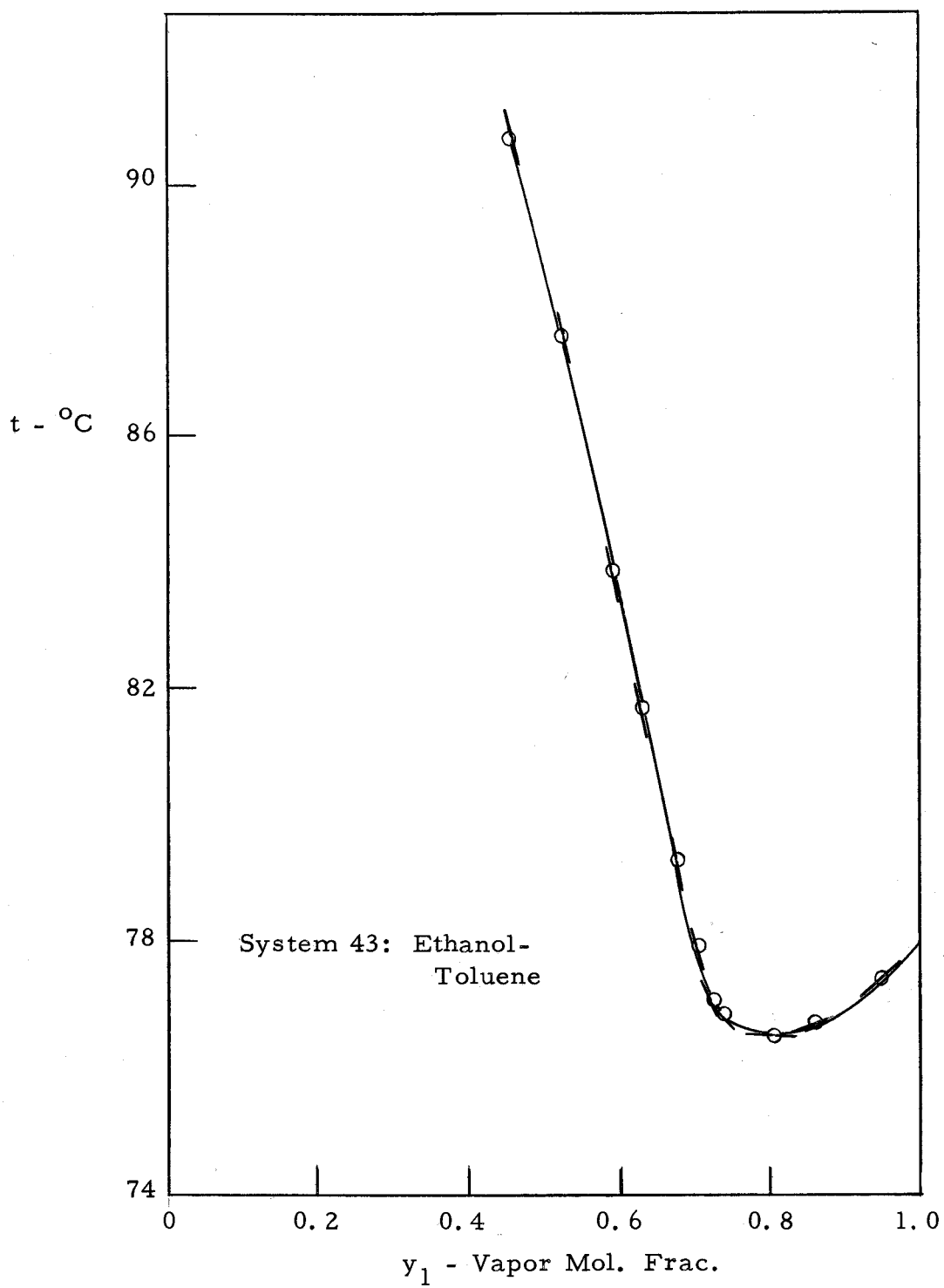
d = -.0106

e = .0384



EVALUATION OF AREA TEST

Figure 3



EXPERIMENTAL DEW POINT CURVE WITH CALCULATED SLOPES

Figure 4

definitely consistent. The question immediately arises then, as to why this inconsistency is implied by the area test.

This can best be answered by looking at the Duhem equation for a constant pressure process which is expressed as (41a)

$$x_1 \left[\frac{d \ln \gamma_1}{dx_1} \right] + (1-x_1) \left[\frac{d \ln \gamma_2}{dx_1} \right] = - \frac{\Delta H}{RT^2} \left[\frac{dt}{dx_1} \right]. \quad (30)$$

Redlich and Kister in the development of the two tests for thermodynamic consistency considered the last term of equation (30) to be negligible. Investigators felt that in general this term was rather small and consequently could be neglected unless the system had a large boiling interval. Since the term is made up of two factors, (dt/dx_1) and $(\Delta H/RT^2)$, neglecting the term actually requires the product to be negligible. Since very little information has been available on the heat of mixing, most authors presumed that (dt/dx_1) was the controlling influence of this term. However, this is not necessarily true.

Apparently the assumption that the term $-\frac{\Delta H}{RT^2} \left[\frac{dt}{dx_1} \right]$ can be neglected for the ethanol-toluene system is incorrect. Although the slope test proved to be satisfied, the area test when evaluated using the consistent data indicated the data were inconsistent. It might be concluded that at least with the area test the magnitude of the term must be known.

An experimental set of data has also been obtained for the system ethanol-toluene. The calculated and experimental data of this system are presented in Table 3. In comparing the x-y data for the two sets of data over the ranges investigated, very close agreement is found to exist between them. As can be ascertained from Figures 3, 4, 5 and 6 both systems exhibited practically identical behaviors for the slope and area tests.

The majority of the other systems considered were found to satisfy the slope test for both azeotropes and non-azeotropes. Using a requirement that the magnitude of the absolute area be less than 10 percent as a guide for evaluating the area test it can be seen that the majority of the azeotropes satisfy this range, while the majority of the non-azeotropes do not. Here again the conclusion might be drawn that a possible reason for the general failure of the area test by both azeotropes and non-azeotropes is due to the fact that the rigorous form of the Duhem equation was not used in the development of the area test.

In looking over the magnitudes of the areas obtained in the area test for various systems, it appears that a relatively large variation exists in this value for different systems. As suggested by Redlich and Kister (33), (34) this was the basic test of thermodynamic consistency for binary systems. Herington (12) has suggested that the

TABLE 3

EXPERIMENTAL AND CALCULATED DATA

System 44: Ethanol-Toluene

Antoine Constants:

$$\underline{A}_1 = 8.04494 \quad \underline{A}_2 = 6.95464$$

$$\underline{B}_1 = 1554.3 \quad \underline{B}_2 = 1344.8$$

$$\underline{C}_1 = 222.65 \quad \underline{C}_2 = 219.482$$

Boiling Points:

Ethanol - 78.3° C

Toluene - 110.6° C

Total Pressure: 756 mmHg.

<u>x</u>	<u>y</u>	<u>t</u>	<u>log Y₁</u>	<u>log Y₂</u>	<u>log $\frac{Y_2}{Y_1}$</u>	<u>dt/dy</u>
.0666	.4478	91.06	.6150	.0259	.5891	-47.59
.0908	.5083	88.20	.5811	.0271	.5539	-50.46
.0985	.5224	87.45	.5697	.0289	.5408	-51.03
.1191	.5570	85.60	.5452	.0328	.5123	-52.52
.1576	.5991	83.40	.4914	.0409	.4505	-53.35
.2523	.6536	80.60	.3718	.0707	.3011	-49.89
.3469	.6830	79.10	.2781	.1134	.1647	-42.74
.4283	.7018	78.40	.2104	.1552	.0551	-35.45
.4890	.7141	77.95	.1681	.1925	-.0244	-29.60
.6330	.7444	77.30	.0853	.2975	-.2122	-15.37
.7310	.7751	77.04	.0448	.3808	-.3360	- 6.55
.8082	.8094	77.00	.0207	.4564	-.4357	- .20
.8794	.8554	77.15	.0055	.5357	-.5302	4.94
.9262	.8975	77.40	-.0004	.5957	-.5961	7.92
.9382	.9099	77.45	-.0009	.6160	-.6169	8.75
.9545	.9304	77.60	-.0013	.6346	-.6359	9.42

Area Test: -.0267

Percentage of Total Area: 7.8

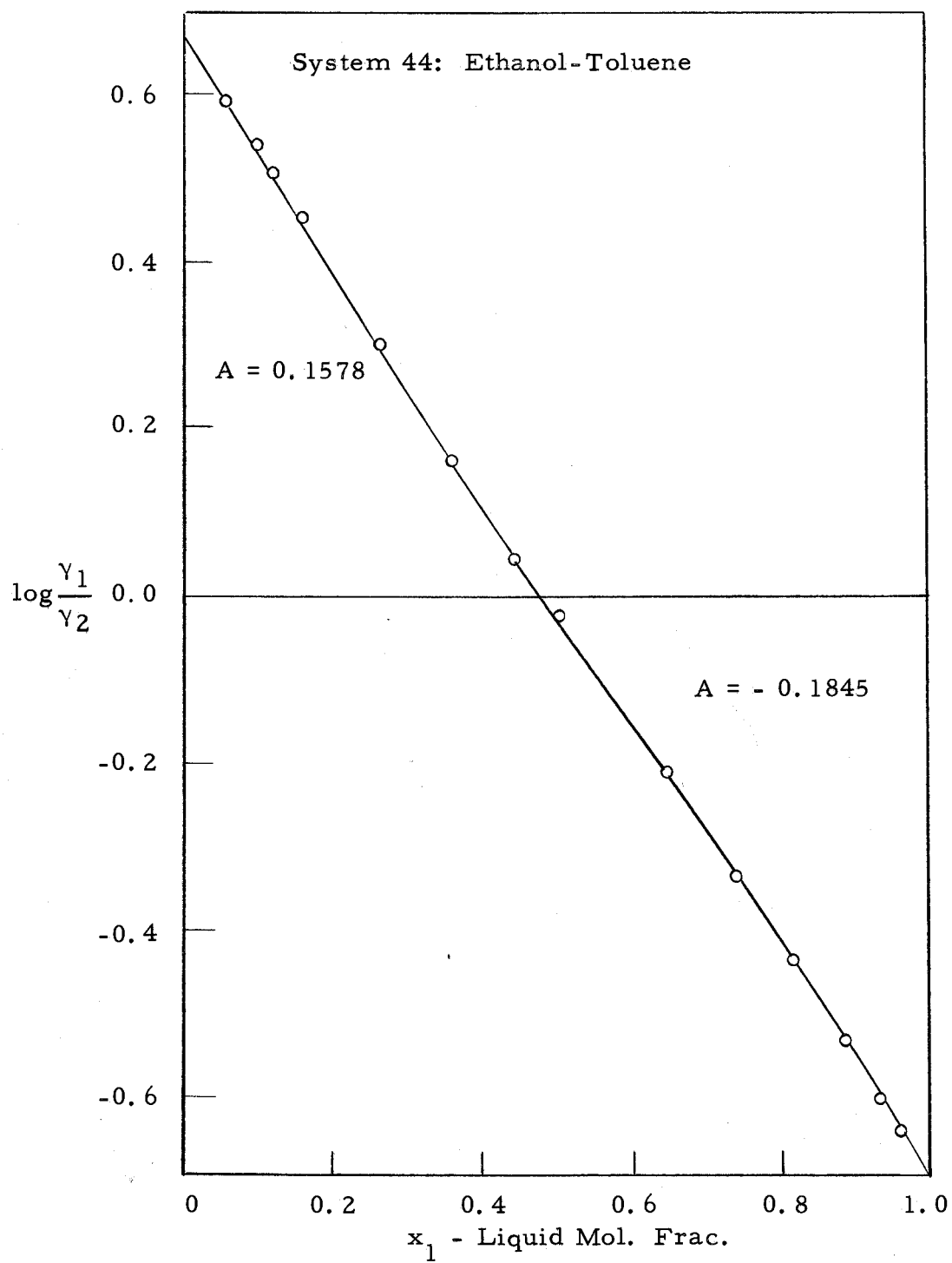
a = -.0247

b = .6845

c = .0277

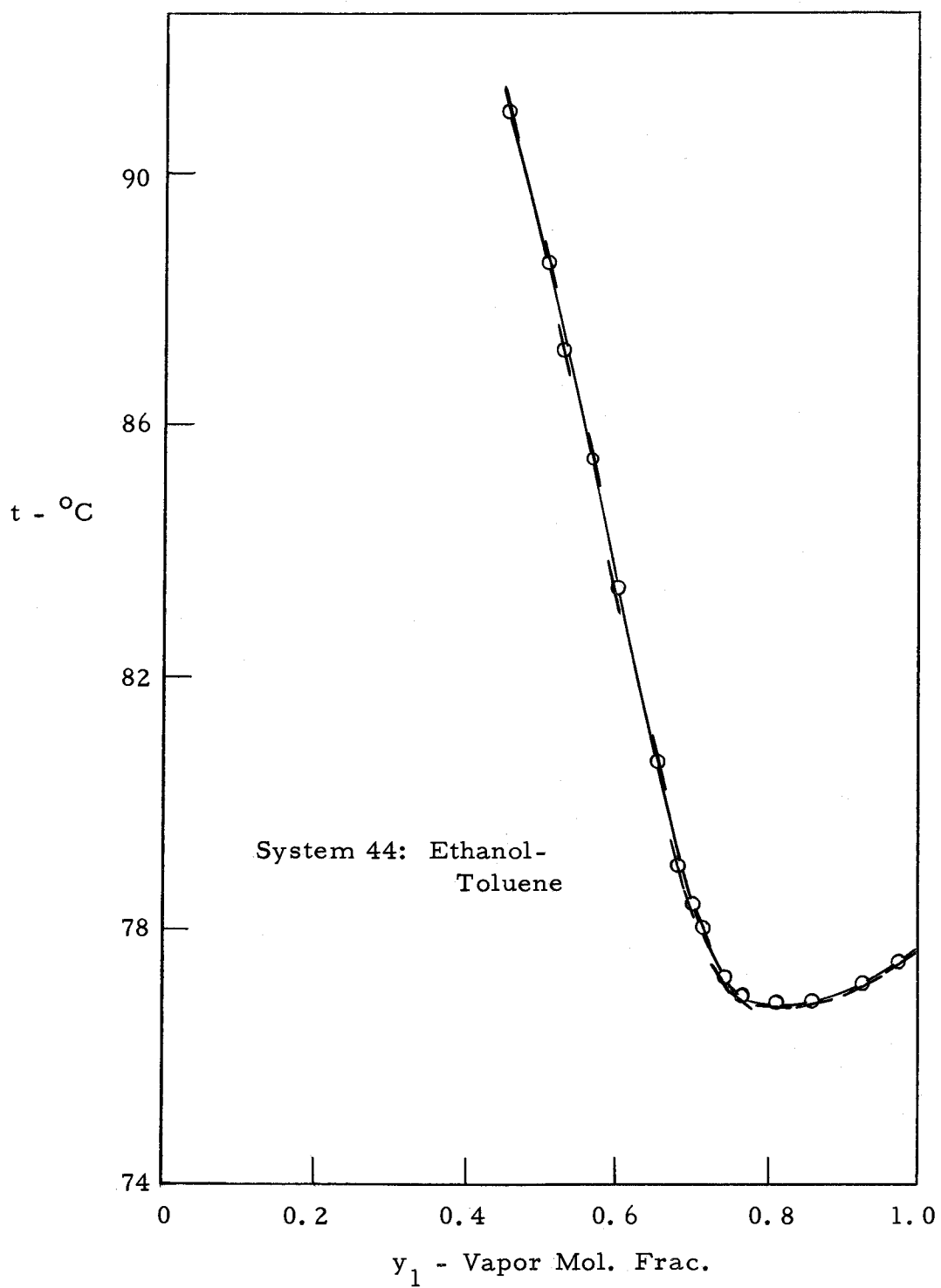
d = .0192

e = -.0071



EVALUATION OF AREA TEST

Figure 5



EXPERIMENTAL DEW POINT CURVE WITH CALCULATED SLOPES

Figure 6

percent of the total area, as well as the magnitude, be considered in evaluating systems. The importance of this becomes obvious when one considers two hypothetical sets of data, A and B, having the same net area of magnitude -0.0100 . Data set A's total area was 0.0100 while data set B's total area was 0.4000 . Due to the relative size of the total areas one can immediately conclude that data set B comes closest to satisfying the area test requirement. Taking as an actual example systems 21 and 32, the magnitude of the areas for these systems are $-.0147$ and $-.0157$ respectively. According to the Redlich - Kister method of rating a system by the area test, system 21 would be rated as better than system 32. This, however, is contrary to the actual situation as indicated by the percentage of the absolute area these magnitudes represent. These percentages are 25.9 and 4.6 respectively indicating that system 32 can be considered more reliable.

Of the two tests for thermodynamic consistency, as suggested by Redlich and Kister, it appears that the slope test is more reliable. The area test is valuable in differentiating between sets of data on the same system. As an example ethanol-benzene has six sets of data available to choose from: sets 30, 31, 32, 33, 34 and 35. According to the slope test set 30 is rated good while the other five are fairly good since they are poorly defined at the azeotropic point. The area

test for these six systems indicates that sets 30, 33 and 35 come the closest to satisfying the requirements of zero net area. As a result of these two tests one immediately can draw the conclusion that set 30 are the most reliable data.

In the case of a system having only one set of data, the natural thing to do is to accept the data as being reliable and proceed to use it. This, however, can lead to erroneous results if the data are inconsistent. As an example system 41 has a poor slope test and an area test of $-.0409$ of which this represents 25.5 percent of the total area. Using these data would lead to results that were definitely unreliable. Before using data even when only one set is available, it is best to at least see how the data appears when using the slope and area tests.

The results obtained for the area test by drawing a smooth curve through the experimental points and measuring the area with the planimeter, agreed quite well in most instances with the values calculated from the smooth data as indicated by the coefficient "a" in the Legendre polynomial. In some systems where little data were available at either the low or high concentration ranges, it was very difficult to draw an accurate curve in this region. For systems where the data were scattered, a curve which was felt to represent the

points in general was drawn. This, however, tends to introduce some uncertainty as to the reliability of the curve. In the case of the computer all points are considered equal and in general a curve more representative of the data was obtained.

CONCLUSIONS

1. Reliable sets of experimental vapor-liquid equilibrium data satisfy the slope test. The same reliable set may fail to satisfy the requirements of zero net area in the Redlich and Kister area test due to $\frac{\Delta H}{RT^2} \cdot \frac{dt}{dx}$ being neglected.
2. Data that fail to satisfy both the area and slope tests, cannot be classified as thermodynamically consistent or inconsistent without additional knowledge of the $\frac{\Delta H}{RT^2} \cdot dt/dx$ term.
3. When systems have more than one set of data available, the best set of data can generally be obtained by evaluating both the slope and area tests, using the area test with the $\frac{\Delta H}{RT^2} \cdot \frac{dt}{dx}$ term, to differentiate between sets to obtain the most reliable.
4. In order to test vapor-liquid equilibrium data accurately, for constant pressure processes, the rigorous form of the Duhem equation should be used when evaluating the area test. This will require both vapor-liquid data and heats of mixing information.

RECOMMENDATIONS

1. It is recommended that work be continued on evaluating binary vapor-liquid equilibrium data using experimental vapor-liquid equilibrium data and heat of mixing data.
2. The author suggests that in future evaluations some statistical method be employed to eliminate data points which are inconsistent.
3. In the future in evaluating the magnitude as a percentage of the total area, it is suggested that an algorithmic method be employed using some numerical method.

NOMENCLATURE

<u>Symbol</u>	<u>Description</u>	<u>Units</u>
<u>A, B, C</u>	constants of Antoine equation	none
A, B, C, D, E	coefficients of the power series	none
a, b, c, d, e	coefficients of the Legendre polynomial	none
P^o	vapor pressure of pure components	mmHg.
$P_o(x_1)$	function = 1	none
$P_1(x_1)$	function = 1 - 2x	none
$P_2(x_1)$	function = 1 - 6x + 6x ²	none
$P_3(x_1)$	function = 1 - 12x + 30x ² - 20x ³	none
$P_4(x_1)$	function = 1 - 20x + 90x ² - 140x ³ + 70x ⁴	none
Q	excess free energy function	none
t	temperature	°C
x	mole fraction in liquid phase	none
y	mole fraction in vapor phase	none
γ	activity coefficient	none
π	total pressure	mmHg.
1	subscript denoting more volatile component	none
2	subscript denoting less volatile component	none

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APPENDIX

```

C   Evaluation of binary vapor-liquid equilibrium data
    Dimension X(35), Y(35), T(35), P(2, 35), A(2), B(2), C(2)
11  Read 10, M, D, N
    Print 14, N
    DO 1 I=1, M
      1  Read 2, X(1), Y(1), T(1)
        DO 6 I=1, 2
          6  Read 3, A(1), B(1), C(1)
            DO 8 J=1, 2
              DO 4 I=1, M
                E=(A(J)-(B(J)/(C(J)+T(1))))
                4  P(J, I)=EXP (2. 303*E)
              8  Continue
            17  DO 5 I=1, M
              V=(Y(I)*D)/(X(I)*P(1, I))
              V=(LOG(V))/2. 303
              W=((1. -Y(I))*D)/((1. -X(I))*P(2, I))
              W=(LOG(W))/2. 303
              Z=V-W
              G=B(1)/((C(1)+T(I))**2.)
              H=B(2)/((C(2)+T(I))**2.)
              R=(0.4343*(X(I)-Y(I)))/((Y(I)*(1. -Y(I)))*((X(I)*G)+((1. -X(I))*H)))
              Print 9, X(I), Y(I), T(I), V, W, Z, R
              Punch 13, Y(I), T(I)
            5  Punch 12, X(I), Z
          10  Format (I3, 4X, F6. 0, 4X, I4)
          2  Format (F6. 0, F6. 0, F8. 0)
          3  Format (F10. 0, F10. 0, F10. 0)
          9  Format (2X, F6. 4, 2X, F6. 4, 2X, F7. 2, F7. 4, 2X, F7. 4, 2X, F7. 4,
                2X, F10. 4)
          12  Format (4X, F6. 4, 4X, F8. 5)
          13  Format (4X, F6. 4, 4X, F7. 2)
          14  Format (31X, 6H Table, 2X, I4)
            Go to 11
        End
    End

```

```

C   Calculation of the coefficients of a polynomial by the method of
    least squares
    Dimension S(5, 6), X(35), Y(35), P(9), C(5)
16  Read 3, N, M
    Print 5, M
    DO 1 I=1, N
1   Read 2, X(I), Y(I)
    S(1, 6)=0.
    S(2, 6)=0.
    S(3, 6)=0.
    S(4, 6)=0.
    S(5, 6)=0.
    P(1)=N
    P(2)=0.
    P(3)=0.
    P(4)=0.
    P(5)=0.
    P(6)=0.
    P(7)=0.
    P(8)=0.
    P(9)=0.
    DO 4 I=1, N
    Z2=X(I)**2.
    Z3=X(I)**3.
    Z4=X(I)**4.
    Z5=X(I)**5.
    Z6=X(I)**6.
    Z7=X(I)**7.
    Z8=X(I)**8.
    P(2)=X(I)+P(2)
    P(3)=Z2+P(3)
    P(4)=Z3+P(4)
    P(5)=Z4+P(5)
    P(6)=Z5+P(6)
    P(7)=Z6+P(7)
    P(8)=Z7+P(8)
    P(9)=Z8+P(9)
    S(1, 6)=Y(I)+S(1, 6)
    S(2, 6)=(Y(I)*X(I))+S(2, 6)
    S(3, 6)=(Y(I)*Z2)+S(3, 6)
    S(4, 6)=(Y(I)*Z3)+S(4, 6)
4   S(5, 6)=(Y(I)*Z4)+S(5, 6)
    K=5
    L=1

```



```

J=0
7 DO 6 I=L, K
  J=J+1
6 S(L, J)=P(I)
  J=0
  L=L+1
  K=K+1
  If (K-9)7, 7, 8
8 Continue
  DO 9 I=2, 6
9 S(1, I)=S(1, I)/S(1, 1)
  DO 10 I=2, 5
10 S(I, 2)=S(I, 2)-S(1, 2)*S(I, 1)
  DO 11 I=3, 5
11 S(2, I)=S(I, 2)/S(2, 2)
  DO 12 I=3, 5
12 S(I, 3)=S(I, 3)-(S(1, 3)*S(I, 1)+S(2, 3)*S(I, 2))
  DO 13 I=4, 5
13 S(3, I)=S(I, 3)/S(3, 3)
  DO 14 I=4, 5
14 S(I, 4)=S(I, 4)-(S(1, 4)*S(I, 1)+S(2, 4)*S(I, 2)+S(3, 4)*S(I, 3))
  S(4, 5)=S(5, 4)/S(4, 4)
  S(5, 5)=S(5, 5)-(S(1, 5)*S(5, 1)+S(2, 5)*S(5, 2)+S(3, 5)*S(5, 3))
  S(5, 5)=S(5, 5)
  S(5, 5)=S(5, 5)-S(4, 5)*S(5, 4)
  S(2, 6)=(S(2, 6)-S(1, 6)*S(2, 1))/S(2, 2)
  S(3, 6)=(S(3, 6)-S(1, 6)*S(3, 1)-S(2, 6)*S(3, 2))/S(3, 3)
  S(4, 6)=(S(4, 6)-S(1, 6)*S(4, 1)-S(2, 6)*S(4, 2)-S(3, 6)*S(4, 3))/S(4, 4)
  S(5, 6)=S(5, 6)-S(1, 6)*S(5, 1)-S(2, 6)*S(5, 2)-S(3, 6)*S(5, 3)
  S(5, 6)=S(5, 6)-S(4, 6)*S(5, 4)
  C(5)=S(5, 6)/S(5, 5)
  C(4)=S(4, 6)-S(4, 5)*C(5)
  C(3)=S(3, 6)-S(3, 5)*C(5)-S(3, 4)*C(4)
  C(2)=S(2, 6)-S(2, 5)*C(5)-S(2, 4)*C(4)-S(2, 3)*C(3)
  C(1)=S(1, 6)-S(1, 5)*C(5)-S(1, 4)*C(4)-S(1, 3)*C(3)-S(1, 2)*C(2)
  DO 15 I=1, 5
15 Print 17, C(I)
  C(1)=C(1)+0.50*C(2)+0.3333*C(3)+0.25*C(4)+C(5)*0.20
  C(2)=0.5*C(2)+0.5*C(3)+0.45*C(4)+0.40*C(5)
  C(2)=0.0-C(2)
  C(3)=(C(3)/30.+C(4)/20.+(2.*C(5))/35.)*5
  C(4)=(C(4)/140.+C(5)/70.)*7.
  C(4)=0.0-C(4)
  C(5)=C(5)/70.

```

```
DO 23 I=1, 5
23 Print 17, C(I)
   Go to 16
   3 Format (I3, 14X, I4)
   5 Format (7H System, 2X, I4)
   2 Format (4X, F6. 4, 4X, F8. 5)
17 Format (4X, F10. 6)
   End
```