

# COMPUTERIZED CURVE FITTING: AN ALTERNATIVE TO GRAPHICAL INTERPRETATION

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**ABSTRACT.** — A comparative study is made of the use of statistical techniques in determining the degree of an empirical polynomial in a problem with experimental error. Each problem requires information on error limits and the magnitude of the dependent and independent variables for establishing a statistical criterion. Data for densities of binary solutions of nitromethane or nitroethane in carbon tetrachloride are used for examples. Concentration, temperature, and excess functions are examined.

The purpose of this paper is to investigate criteria, determining the degree of an empirical polynomial, which appeal to chemists (as well as other scientists whose data contains experimental error). Particular emphasis is placed upon first degree (linear) functions because of their common occurrence in chemical problems.

The availability of high speed computers suggests the feasibility of an alternate to the "eye-ball" graphical techniques long used by chemists in analysis of laboratory data. Graphical analysis involving vagaries such as choice of scale, artistic care, etc., is as much an art as a science while a computer alternative removes the subjective element from the analysis. An ideal criterion has two attributes, *viz* it can be routinely programmed for use on a computer and it is based upon concepts familiar to chemists. Proposed criteria are related to formalized statistical techniques.

The various techniques are applied to density data of binary mixtures of nitromethane and nitroethane which were reported by Gunter, et. al. (1967). These data are neither complete enough nor accurate enough to warrant extensive research treatment but they are sufficient for pedagogical purposes. Consequently, the reader is cautioned that the chemical conclusions are only indicative, not definitive.

## THE QUINTIC CONCENTRATION EQUATION

For each temperature reported by Gunter, et. al. (1967), the best coefficients,  $a_i$ , for density as a function of concentration

$$d = \sum_{i=0}^{i=5} a_i c^i \quad (1)$$

were determined by a least squares procedure (Daniels, et. al., 1962) contained as part of a standard regression program (Purcell, 1965) available at the Data Processing and Computing Center of Southern Illinois University at Carbondale, (Nitromethane at 45°C was not included in this experiment due to insufficient data). Three different representations of concentration were used,  $x_2$ , weight fraction of nitroparaffin, *viz.* mole fraction of nitroparaffin,

$w_2$ , and volume fraction of nitro-paraffin,  $v_2$ . In each case, the nitro-paraffin was assumed to be a monomer. These calculations were performed on an IBM 7044 computer using FORTRAN IV as the computer language.

The choice of a quintic degree was arbitrary but with the expectation that the degree was sufficiently high as to contain terms of no statistical significance. The coefficients are given in Table 1. The value of the mixture density at zero concentration is the carbon tetrachloride density at the specified temperature, irrespective of the concentration representation or the nature of the second solution component. The  $a_0$  values are in close agreement with each

other as well as with experiment except for  $C_2H_5NO_2$  at  $35^\circ C$  which agrees somewhat less well with experiment. The slightly poorer  $35^\circ C$   $C_2H_5NO_2$   $a_0$  value is clearly due to the data, a conclusion which can be verified by an examination of the data and their errors reported by Gunter, et. al. (1967). In Table 1, the values of the mixture density calculated for unit concentration are also listed. These values are the nitroparaffin density values at the specified temperature. The exceptional agreement between sets and between calculated and experimental values indicates that any faults lie with the data near zero concentration. Every value reported in Table 1 has four or five significant figures

TABLE 1. Calculated Constants for Quintic Concentration Equations.

Temp. (°C)	Nitromethane						d(conc=1) (g/ml)
	a <sub>0</sub> (g/ml)	a <sub>1</sub> (g/ml- conc)	a <sub>2</sub> (g/ml- conc <sup>2</sup> )	a <sub>3</sub> (g/ml- conc <sup>3</sup> )	a <sub>4</sub> (g/ml- conc <sup>4</sup> )	a <sub>5</sub> (g/ml- conc <sup>5</sup> )	
d vs. x <sub>2</sub>							
30	1.5749	-0.2624	-0.1400	0.04214	-0.1049	0.007572	1.1173
35	1.5662	-0.2448	-0.2820	0.4054	-0.4713	0.1378	1.1113
45							
d vs. w <sub>2</sub>							
30	1.5750	-0.6757	0.3752	-0.3013	0.2139	-0.06987	1.1172
35	1.5667	-0.6789	0.3613	-0.1868	0.04097	0.007873	1.1112
45							
d vs. v <sub>2</sub>							
30	1.5749	0.4767	0.02663	0.007180	-0.03319	0.01837	1.1172
35	1.5665	-0.4684	-0.07702	0.3432	-0.4280	0.1751	1.1114
45							

Temp. (°C)	Nitroethane						
	$a_0$ (g/ml)	$a_1$ (g/ml- conc)	$a_2$ (g/ml- conc <sup>2</sup> )	$a_3$ (g/ml- conc <sup>3</sup> )	$a_4$ (g/ml- conc <sup>4</sup> )	$a_5$ (g/ml- conc <sup>5</sup> )	$d(\text{conc}=1)$ (g/ml)
<i>d vs. <math>x_2</math></i>							
30	1.5748	-0.4000	-0.1681	0.2476	-0.3825	0.1628	1.0346
35	1.5670	-0.5201	0.8910	-2.5015	2.4683	-0.8753	1.0294
45	1.5455	-0.4251	0.09944	-0.4724	0.4413	-0.1719	1.0168
<i>d vs. <math>w_2</math></i>							
30	1.5749	-0.8377	0.5220	-0.3867	0.1983	-0.03624	1.0346
35	1.5660	-0.8859	1.3898	-3.4098	4.0286	-1.6599	1.0288
45	1.5452	-0.8286	0.6076	-0.6634	0.5452	-0.1892	1.0168
<i>d vs. <math>v_2</math></i>							
30	1.5749	-0.5471	0.004345	0.1398	-0.2630	0.1344	1.0347
35	1.5673	-0.6922	1.4641	-4.1008	4.5409	-1.7504	1.0289
45	1.5454	-0.5618	0.2168	-0.4943	0.5024	-0.1916	1.0169

depending upon whether the absolute value is less or greater than unity. Gunter, et. al. (1967) indicate an experimental uncertainty in  $x_2$  of  $5 \times 10^{-3}$ , which, for 30°C  $\text{CH}_3\text{NO}_2$ , leads to

$$d = d \pm 10^{-3}(1.31 + 1.40 x_2 - 0.63 x_2^2 + 2.10 x_2^3 - 0.189 x_2^4) \quad (2)$$

where the expression following the  $\pm$  is the error due to the error in  $x_2$ . For  $x_2=0$ , an error of 0.001 results and for  $x_2=-1$ , an error of 0.004 results. The conclusion is that the number of significant figures in Table 1 are useful only to prevent rounding errors during calculation and that all final calculated densities should be rounded to four significant figures. From this view-

point, it is clear that at each temperature all  $a_0$  values are in perfect agreement. In other words, the experimental scientist would not consider the 35°C  $\text{C}_2\text{H}_5\text{NO}_2$  value as slightly poorer but merely a deviation within the range of experimental error. Since, as stated in the introduction a criterion for chemists is sought, the latter viewpoint must prevail.

Many chemists have made little use of statistical tools excepting means and standard deviations. The standard program (Purcell, 1965) produced the variance after the addition of each power of the independent variable. The familiar standard deviation was derived by taking the square root of the variance divided by the degrees of free-

dom (number of observations less the number of constants determined by least squares). These results are presented in Table 2. In both the  $x_2$  and  $w_2$  representations, an error results in the second decimal place if only the linear term is used thereby indicating that the linear term is insufficient. For 30°C  $\text{CH}_3\text{NO}_2$  the use of  $x_2^2$  gives a standard deviation equal to the maximum error due to experimental error in the mole fraction while  $x_2^3$  gives a standard deviation equal to the minimum error. Depending upon the experimenter, either the quadratic or cubic term is sufficient. In either case, it is clear that an individual error analysis is required for each compound, at each temperature. In the present research, the decision to accept the maximum error due to experiment was made. The data in Table 2 indicates that the quadratic term is sufficient in the mole fraction and weight fraction representations and that the linear term is sufficient in the volume fraction representation. Figures 1 through 3 graphically depict the density as a function of volume fraction. Every chemist would agree that both sets of nitroparaffin data are well represented by a linear function thereby verifying the suf-

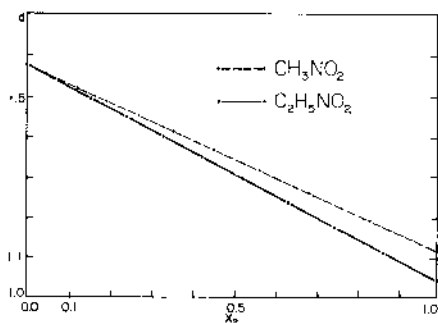


FIGURE 1. Density of Nitroparaffinic Binary Solutions as a Function of Volume Fraction of Nitroparaffins at 30°C.

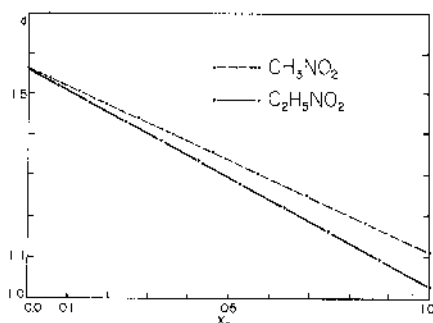


FIGURE 2. Density of Nitroparaffinic Binary Solutions as a Function of Volume Fraction of Nitroparaffins at 35°C.

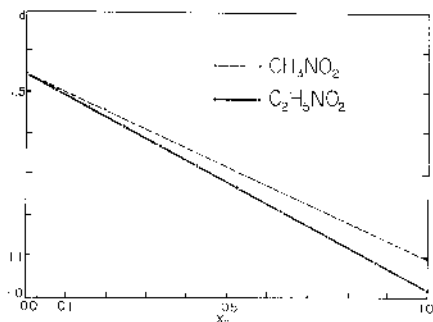


FIGURE 3. Density of Nitroparaffinic Binary Solutions as a Function of Volume Fraction of Nitroparaffins at 45°C.

ficiency of linear terms. The fact that density is a linear function of concentration, expressed in volume units, indicates the solutions are ideal (Weissberger, 1959).

This linearity also substantiates the conclusions of MacFarlane and Wright (1933) that volume fraction is the most suitable independent variable in a density function.

The per cent deviations suggested by Foley, et. al. (1964) were calculated by dividing each entry of Table 2 by the means of all observations of that nitroparaffin at the temperature of that entry. The results

TABLE 2.—The Standard Deviation.<sup>a</sup>

Temperature (°C)	Nitromethane					Nitroethane				
	x	x <sup>2</sup>	x <sup>3</sup>	x <sup>4</sup>	x <sup>5</sup>	x	x <sup>2</sup>	x <sup>3</sup>	x <sup>4</sup>	x <sup>5</sup>
d vs. x <sub>2</sub>										
30.....	0.0244	0.00417	0.000967	0.000764	0.000836	0.0158	0.00172	0.000568	0.000581	0.000520
35.....	0.0238	0.00428	0.00113	0.000617	0.000601	0.0183	0.00407	0.00427	0.00397	0.00389
45.....	0.0351	.....	.....	.....	.....	0.0157	0.00213	0.000580	0.000618	0.000556
d vs. w <sub>2</sub>										
30.....	0.0166	0.00208	0.000775	0.000760	0.000825	0.0220	0.00276	0.000925	0.000506	0.000550
35.....	0.0168	0.00242	0.000769	0.000701	0.000769	0.0204	0.00396	0.00417	0.00451	0.00375
45.....	0.0190	.....	.....	.....	.....	0.0211	0.00308	0.000921	0.000734	0.000717
d vs. v <sub>2</sub>										
30.....	0.00154	0.000755	0.000774	0.000831	0.000900	0.000736	0.000739	0.000750	0.000572	0.000553
35.....	0.00194	0.000862	0.000710	0.000767	0.000759	0.00518	0.00475	0.00488	0.00500	0.00395
45.....	0.00306	.....	.....	.....	.....	0.00107	0.00102	0.000658	0.000673	0.000607

<sup>a</sup> All entries stated in units of g/ml.

given in Table 3 show that the per cent deviations corresponding to terms judged of sufficient degree by the criterion of standard deviation are of  $0(10^{-1}\%)$ . Consequently, an error analysis, as in the case of standard deviation, is used to establish a criterion for judging sufficiency of degree. Another observation is that the percent deviation (or the standard deviation) does not change, perceptibly, if terms of no *statistical* significance are added. For example, with  $30^{\circ}\text{C}$   $\text{CH}_3\text{NO}_2$ , cubic, quatic, and quintic terms in  $x_2$  give a per cent deviation of 0.06% indicating the cubic term is sufficient, but as noted, the use of *experimental* error determined the quadratic term is sufficient. The difference between the experimentalist and non-experimentalist is further emphasized. In the case of  $35^{\circ}\text{C}$   $\text{C}_2\text{H}_5\text{NO}_2$  the two viewpoints merge, indicating a quadratic term in  $x_2$  is sufficient since per cent deviation remains constant at 0.3%, the proper value considering experimental error. Of course, the fact that even the use of a quintic term does not reduce the per cent deviation again shows the difference in quality of this particular set of data.

The standard computer program also yielded the value of  $R^2$ , the square of the multiple correlation coefficient (Baten, 1938) after the addition of each power of the independent variable. These values are given in Table 4. The values of  $R^2$  are also the sum of the proportions of variance through the term being added (Musulin and Musulin, 1967). Consequently a value of 1 indicates that all variance has been accounted for within the number of significant figures yielded by the standard program, i.e. five significant figures for  $R^2$ . An examination of Table 4 indicates that the  $35^{\circ}\text{C}$  nitroethane data is generally not comparable to

the data at  $30^{\circ}\text{C}$  and  $45^{\circ}\text{C}$ , again emphasizing the experimental errors in  $35^{\circ}\text{C}$  data. Excepting this  $35^{\circ}\text{C}$   $\text{C}_2\text{H}_5\text{NO}_2$  data from a statistical viewpoint, the mole fraction representation recovers all the variance with terms through the cubic degree, as is true for the weight fraction representation with nitroethane. For the volume fraction representation, quadratic terms are sufficient for nitromethane and linear terms for nitroethane. Once again, the viewpoint of the experimentalist must be introduced for the use of statistics alone results in equations of greater refinement than can be warranted by experimental error. Figures 1 through 3 show that the requirement of quadratic  $v_2$  terms suggested by statistical methods for the  $\text{CH}_3\text{NO}_2$  data is too stringent.

Foley, et. al. (1964) have suggested that a criterion for linearity, within 6%, is  $|r| \geq 0.995$ . It is proposed to generalize this criterion for use with polynomials of any degree by establishing a lower bound for  $R^2$  (this particular standard program yields  $R^2$  but a lower bound on the absolute value of  $R$  would serve as well). The sum of squared deviations (and hence, the per cent deviation) is proportional to variance of the dependent variable and to  $(1 - R^2)$  (Baten, (1938)). Since the range of the dependent variable is essentially the same for each nitroparaffin, the average criterion  $R^2 \geq 0.998$  can be established for determining the proper polynomial degree to be used in an empirical equation. This criterion provides the same results as were obtained with the standard deviation and the per cent deviation, i.e. quadratic equations are appropriate with  $x_2$  and  $w_2$ , and linear equations with  $v_2$ .

An alternate statistical technique to determine degree of the inde-

TABLE 3.—The Per Cent Deviation.

Temp. (°C)	Nitromethane					Nitroethane				
	x	x <sup>2</sup>	x <sup>3</sup>	x <sup>4</sup>	x <sup>5</sup>	x	x <sup>2</sup>	x <sup>3</sup>	x <sup>4</sup>	x <sup>5</sup>
d vs. x <sub>2</sub>										
30	1.76	0.301	0.0698	0.0551	0.0603	1.19	0.129	0.0427	0.0437	0.0391
35	1.73	0.311	0.0821	0.0448	0.0437	1.38	0.307	0.323	0.300	0.294
45	2.57	.....	.....	.....	.....	1.20	0.163	0.0444	0.0474	0.0426
d vs. w <sub>2</sub>										
30	1.20	0.150	0.0559	0.0549	0.0596	1.66	0.208	0.0696	0.0381	0.0414
35	1.22	0.176	0.0559	0.0510	0.0559	1.54	0.299	0.315	0.341	0.283
45	1.39	.....	.....	.....	.....	1.62	0.236	0.0706	0.0562	0.0549
d vs. v <sub>2</sub>										
30	0.111	0.0545	0.0559	0.0600	0.0656	0.0554	0.0556	0.0564	0.0430	0.0416
35	0.141	0.0627	0.0516	0.0558	0.0552	0.391	0.359	0.369	0.378	0.298
45	0.224	.....	.....	.....	.....	0.0820	0.0782	0.0504	0.0516	0.0465
V <sub>M</sub> vs. x <sub>2</sub>										
30	0.0975	0.0474	0.0505	0.0546	0.0593	0.0424	0.0450	0.0410	0.0366	0.0303
35	0.127	0.0514	0.0542	0.0527	0.0482	0.333	0.301	0.319	0.294	0.286
45	0.220	.....	.....	.....	.....	0.0691	0.0714	0.0447	0.0462	0.0410
V <sub>M</sub> vs. w <sub>2</sub>										
30	4.96	1.24	0.294	0.0831	0.0610	2.06	0.406	0.0484	0.0312	0.0328
35	4.93	1.21	0.290	0.0951	0.0686	2.23	0.621	0.315	0.322	0.272
45	6.16	.....	.....	.....	.....	2.10	0.378	0.0703	0.0498	0.0516
V <sub>M</sub> vs. v <sub>2</sub>										
30	3.12	0.490	0.0855	0.0541	0.0577	0.866	0.0616	0.0361	0.0302	0.0288
35	3.09	0.472	0.0876	0.0561	0.0549	1.04	0.298	0.274	0.280	0.226
45	4.29	.....	.....	.....	.....	0.890	0.0539	0.0470	0.0482	0.0472

TABLE 4.—The Multiple Correlation Coefficient.

Temp. (°C)	Nitromethane					Nitroethane				
	$x$	$x^2$	$x^3$	$x^4$	$x^5$	$x$	$x^2$	$x^3$	$x^4$	$x^5$
d vs. $x_2$										
30	0.9763	0.9994	1.0000	1.0000	1.0000	0.9930	0.9999	1.0000	1.0000	1.0000
35	0.9771	0.9993	1.0000	1.0000	1.0000	0.9905	0.9996	0.9996	0.9997	0.9998
45	0.9890	1.0000	.....	.....	.....	0.9927	0.9999	1.0000	1.0000	1.0000
d vs. $w_2$										
30	0.9890	0.9998	1.0000	1.0000	1.0000	0.9864	0.9998	1.0000	1.0000	1.0000
35	0.9886	0.9998	1.0000	1.0000	1.0000	0.9882	0.9996	0.9996	0.9996	0.9998
45	0.9968	1.0000	.....	.....	.....	0.9868	0.9997	1.0000	1.0000	1.0000
d vs. $v_2$										
30	0.9999	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
35	0.9998	1.0000	1.0000	1.0000	1.0000	0.9992	0.9994	0.9995	0.9995	0.9998
45	0.9999	1.0000	.....	.....	.....	1.0000	1.0000	1.0000	1.0000	1.0000
$V_M$ vs. $x_2$										
30	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
35	1.0000	1.0000	1.0000	1.0000	1.0000	0.9990	0.9993	0.9993	0.9995	0.9996
45	1.0000	1.0000	.....	.....	.....	1.0000	1.0000	1.0000	1.0000	1.0000
$V_M$ vs. $w_2$										
30	0.9371	0.9965	0.9998	1.0000	1.0000	0.9600	0.9986	1.0000	1.0000	1.0000
35	0.9377	0.9966	0.9998	1.0000	1.0000	0.9534	0.9968	0.9993	0.9994	0.9996
45	0.9758	1.0000	.....	.....	.....	0.9594	0.9988	1.0000	1.0000	1.0000
$V_M$ vs. $v_2$										
30	0.9750	0.9994	1.0000	1.0000	1.0000	0.9930	1.0000	1.0000	1.0000	1.0000
35	0.9753	0.9995	1.0000	1.0000	1.0000	0.9899	0.9993	0.9995	0.9995	0.9997
45	0.9883	1.0000	.....	.....	.....	0.9927	1.0000	1.0000	1.0000	1.0000

pendent variable which is required in the empirical equation is the Analysis of Variance (Bennett and Franklin (1954)). In order to confirm the statistical conclusions drawn from Table 2, an analysis of variance was performed on the 30°C  $\text{CH}_3\text{NO}_2$  data. At the 1% level, the F-ratio test indicated  $x_2^2$ ,  $w_2^2$ , and  $v_2^2$  were significant. This information is identical to that derived from Table 4. Statistically the analysis of variance is equivalent to the use of  $R^2$  made in this study but insertion of the experimentalists viewpoint would require redefining F-ratio test values at the various levels of significance.

In an ideal mixture, the molar volume,  $V_M$ , is a linear function of the mole fraction of the solute,  $x_2$ , (Rowlinson, 1959). The plots of  $V_M$  vs.  $x_2$ , Figures 4 through 6, are linear. In order to verify the validity of the criteria which have been suggested, the experiment of substituting  $V_M$  for the dependent variable in Equation (1) was performed. The per cent deviation and the values of  $R^2$  are given in Tables 3 and 4, respectively. An error analysis for 30°C  $\text{CH}_3\text{NO}_2$  indicates  $0.39\% \geq$  per cent deviation  $\geq 0.23\%$  for  $0 \leq x_2 \leq 1$ . Thus the maximum per

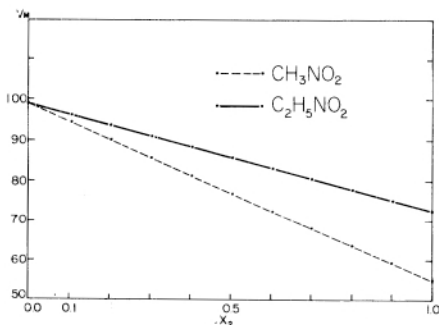


FIGURE 4. Molar Volume of Nitroparaffinic Binary Solutions as a Function of Mole Fraction of Nitroparaffins at 30°C.

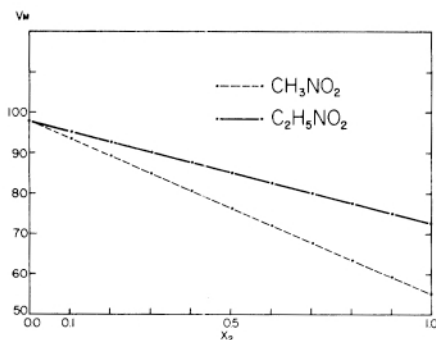


FIGURE 5. Molar Volume of Nitroparaffinic Binary Solutions as a Function of Mole Fraction of Nitroparaffins at 35°C.

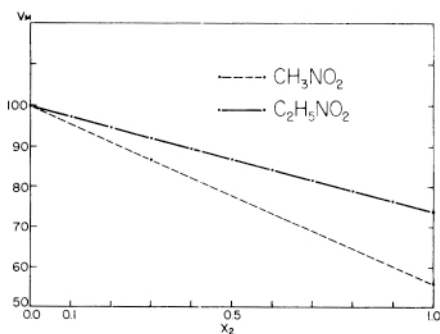


FIGURE 6. Molar Volume of Nitroparaffinic Binary Solutions as a Function of Mole Fraction of Nitroparaffins at 45°C.

cent deviation is approximately the same as the maximum per cent deviation for density even though the values of  $V_M$  are approximately 50 times greater than the values of  $d$  reaffirming the contention of Foley, et. al. (1964) with regards to per cent deviation.

From the per cent deviation, linear equations are appropriate if  $x_2$  is the independent variable and quadratic equations are appropriate (barely so for  $\text{CH}_3\text{NO}_2$ ) if  $v_2$  is the independent variable. With  $w_2$  as the independent variable, the per cent deviation indicates quadratic equations with nitroethane and cubic

equations with nitromethane. As usual, 35°C  $C_2H_5NO_2$  is slightly poorer than the other data. For this choice of dependent variable the range of the dependent variable is rather different for the two nitro-paraffins resulting in a standard deviation for nitromethane  $1\frac{3}{4}$  times larger than the standard deviation of nitroethane. The difference in standard deviation leads to two different exact criteria, *viz.*  $R^2 \geq 0.999$  ( $CH_3NO_2$ ) and  $R^2 \geq 0.998$  ( $C_2H_5NO_2$ ). These separate criteria reproduce exactly the information given by per cent deviation.

An exact analysis of variance for 30°C nitromethane indicates that quadratic terms in the  $x_2$  representation, quartic terms in the  $w_2$  representation, and cubic terms in the  $v_2$  representation are required. As with the density data, terms of degree one higher are required by the use of pure statistics than are required by an experimentalist desiring correctness within the experimental error defined by Gunter, et. al. (1967).

#### FINAL CONCENTRATION EQUATIONS

The least squares procedure was repeated with the density and molar volume data, the degree of each empirical polynomial being that degree determined by the criteria established in this work. The coefficients which result are slightly different than those presented in Table 1 since the minimization is accomplished with less variables. The new coefficients are given in Table 5. The values of the standard deviation, per cent deviation, and  $R^2$  given in Tables 2, 3, and 4 for each degree of freedom are invariant and desired information of this type may be read directly from the appropriate col-

umn of the suitable table. Entries have been made in Tables 2, 3, and 4 from the quadratic and linear fits of the three point 45°C  $CH_3NO_2$ . The  $R^2$  value does not have the same significance as adjudged by the Student t-test (Baten (1938)). Of course, the resulting minimization yields predicted values which are not as good, mathematically, as those obtained by the quintic equations but the range of  $a_0$  values and the values of the functions at unit concentration (also listed in Table 5) are within the appropriate tolerance ranges.

In those cases where quadratic coefficients are listed, the value of  $a_2$  indicates the amount of curvature, i.e. the lack of linearity. Further, extrema of the quadratic functions lie outside the region of physical significance, i.e.  $0 \leq \text{conc.} \leq 1$ . For density as a function of  $v_2$ , the second derivative of a quadratic fit, in every case, is positive which indicates the curvature of each plot is convex downward. It should be noted that the magnitude of the second derivative also shows that the amount of such curvature is very small. In such plots, Usol'tseva (1960) attributes a curvature which is convex downward to an associated compound dissociating into another component. Usol'tseva's conclusion is in accord with the concept of a nitroparaffin dimer dissociating, slightly, into a monomer.

#### TEMPERATURE FUNCTIONS

For each mole fraction of each solution, the density was fitted, by a least squares procedure, to a linear function of temperature (Equation (1) with the temperature,  $t$ , as the independent variable and the upper limit  $i = 1$ ). The linear form was chosen for two reasons; the tem-

TABLE 5.—Calculated Constants for Final Concentration Equations.

Temperature (°C)	Nitromethane				Nitroethane				
	$a_0$ (g/ml)	$-a_1$ (g/ml-conc)	$a_2$ (g/ml-conc <sup>2</sup> )	d(Conc =1)	$a_0$ (g/ml)	$-a_1$ (g/ml-conc)	$a_2$ (g/ml-conc <sup>2</sup> )	Per Cent d(conc =1)	
d vs. $x_2$									
25 <sup>a</sup>	1.5796	0.1977	-0.2447	1.1372	.....	.....	.....	.....	
30	1.5702	0.2009	-0.2462	1.1231	1.5727	0.3755	-0.1608	1.0364	
35	1.5619	0.2042	-0.2404	1.1173	1.5629	0.3504	-0.1829	1.0296	
45	1.5456	0.2378	-0.2101	1.0977	1.5426	0.3637	-0.1592	1.0197	
<sup>a</sup> Brown & Smith (1955)									
d vs. $w_2$									
30	1.5723	0.6217	0.1686	1.1192	1.5709	0.7572	0.2236	1.0373	
35	1.5636	0.6207	0.1706	1.1135	1.5628	0.7378	0.2053	1.0303	
45	1.5456	0.6504	0.2025	1.0977	1.5407	0.7346	0.2140	1.0201	
d vs. $V_2$									
30	1.5728	0.4577	.....	1.1151	1.5746	0.5398	.....	1.0348	
35	1.5637	0.4549	.....	1.1088	1.5687	0.5370	.....	1.0317	
45	1.5437	0.4465	.....	1.0972	1.5446	0.5259	.....	1.0187	
Temp. (°C)	Nitromethane					Nitroethane			
	$a_0$ (ml/g)	$-a_1$ (ml/g-conc)	$a_2$ (ml/g-conc <sup>2</sup> )	$-a_3$ (ml/g-conc <sup>3</sup> )	$V_M$ (Conc =1)	$a_0$ (ml/g)	$-a_1$ (ml/g-conc)	$a_2$ (ml/g-conc <sup>2</sup> )	$V_M$ (Conc =1)
$V_M$ vs. $x_2$									
30	97.776	43.049	.....	.....	54.727	97.697	25.175	.....	72.522
35	98.332	43.290	.....	.....	55.042	98.097	25.327	.....	72.770
45	99.625	43.990	.....	.....	55.635	99.599	25.894	.....	73.705
$V_M$ vs. $w_2$									
30	97.395	96.548	87.748	34.071	54.524	97.210	42.034	17.734	72.910
35	97.911	96.533	86.927	33.482	54.824	97.712	43.236	18.909	73.385
45	99.527	96.850	52.916	.....	55.593	99.117	43.393	18.413	74.137
$V_M$ vs. $V_2$									
30	97.153	66.252	24.135	55.036	.....	97.624	32.549	7.536	72.611
35	97.685	66.478	24.111	55.318	.....	98.192	33.872	8.766	73.086
45	99.527	72.811	28.877	55.593	.....	99.533	33.592	7.889	73.830

perature range used was narrow and the maximum of three temperature points would allow for compensation of experimental error. The results are given in Table 6. The per cent deviation is also tabulated. Where only two temperature points were available, no error per cent is given. These and succeeding calculations were performed on an IBM 1620 computer with 40K storage using an IBM PR 025 monitor. The programs were written in FORTRAN II (IBM, 1962).

Except for 0.4 and 0.5 nitroethane, all per cent deviations are  $0(10^{-2})$ . This order of magnitude indicates a better fit than is warranted by the data. It further substantiates the validity of choice of linear form. Although the exceptional data have per cent deviations appropriate to this study, these two sets are not of the same quality. Combining this information with the information from the concentration data, the two slightly poorer data points are 0.4 and 0.5  $35^{\circ}\text{C}$   $\text{C}_2\text{H}_5\text{NO}_2$ . Various literature values are presented in Table 8. Intercepts and

slopes calculated from several sets of density data in the literature have been included in Table 8.

#### EXCESS FUNCTIONS

Scatchard (1949) has found that the excess molar volume of mixing,  $V^E$ , can be fitted to a series,

$$V^E = \sum_{i=0}^{i=n} a_i x_1 x_2 (x_1 - x_2)^i \quad (3)$$

where the  $a_i$  are constants. The  $V^E$  values calculated by Gunter, et. al. (1967) were fitted by a least squares procedure to a two-term equation of the form given in Equation (3) ( $i = 0$  to  $1$ ). Least squares fits were also made of single term equations ( $i = 0$  and  $i = 1$ , corresponding to quadratic and cubic equations, respectively, in  $x_2$ ). A discard criterion (Worthing and Gaffner, 1943) was applied in the fitting procedures. The coefficients for each case are summarized in Table 7.

The per cent deviation is also

TABLE 6.—Calculated Constants for Linear Temperature Equations.

Mole Fraction (RNO <sub>2</sub> )	Nitromethane			Nitroethane		
	$a_0$ (g/ml)	$-a_1 \times 10^4$ (g/ml-°C)	Per Cent Deviation	$a_0$ (g/ml)	$-a_1 \times 10^3$ (g/ml-°C)	Per Cent Deviation
0.0	1.6344	1.9686	0.03	1.6344	1.9686	0.03
0.1	1.5943	1.5740	.....	1.5939	2.0073	0.03
0.2	1.5679	1.6940	.....	1.5476	1.9096	0.05
0.3	1.5424	1.9333	0.02	1.4971	1.7567	0.06
0.4	1.4980	1.7180	.....	1.4553	1.8293	0.37
0.5	1.4661	1.9180	.....	1.4030	1.7731	0.41
0.6	1.4067	1.4580	.....	1.3378	1.5503	0.01
0.7	1.3585	1.5220	.....	1.2743	1.3794	0.01
0.8	1.2989	1.4160	.....	1.2096	1.2877	0.03
0.9	1.2296	1.2620	.....	1.1410	1.1885	0.09
1.0	1.1566	1.3066	0.02	1.0703	1.1841	0.01

TABLE 7.—Calculated Constants for Volume of Mixing Equations.

Temp. (°C)	Nitromethane			Nitroethane		
	$a_0$ (ml/mole- (mole fraction) <sup>2</sup> )	$-a_1$ (ml/mole- (mole fraction) <sup>2</sup> )	Error Per Cent	$a_0$ (ml/mole- (mole fraction) <sup>2</sup> )	$-a_1$ (ml/mole- (mole fraction) <sup>2</sup> )	Error Per Cent
Two Term Equation						
30	0.6715	0.009510	30.3	0.01983	0.3995	86.5
35	0.8251	-0.04203	30.2	0.1183	0.5076	109
45	.....	.....	.....	0.08515	1.0004	55.2
Quadratic Term Only						
30	0.6715	0.0000	28.6	0.01983	0.0000	142
35	0.8251	0.0000	28.5	0.1457	0.0000	144
45	1.0502	0.0000	.....	0.08515	0.0000	141
Cubic Term Only						
30	0.0000	0.009510	131	0.0000	0.3995	82.7
35	0.0000	-0.04203	136	0.0000	0.5378	114
45	0.0000	-2.6255	.....	0.0000	1.0004	59.8

given for each fitted equation in Table 7. A slight modification was necessary in calculating the per cent deviation for nitroethane binary solutions. At all temperatures, the mean value of  $V^E$  for each of these solutions was approximately zero. For tabulation purposes, and to eliminate anomalous values due to sign cancellation, the per cent deviation was calculated using the mean of the absolute values of  $V^E$ .

The error columns of Table 7 verify the conclusions drawn by Gunter, et. al. (1967) that the  $V^E$  values of nitromethane are of the quadratic form obtained by discard of all but the leading term of Equation (3) and the  $V^E$  values of nitroethane are of the cubic form ob-

tained by discard of all but the second term of Equation (3). For nitromethane, the two-term fit reduces the error by a minimal amount compared to the use of only the quadratic term. In a like-manner, for nitroethane, the two-term fit is only slightly better than the use of only a cubic term. In every case, the relative smallness of one coefficient in the two-term fit also indicates the validity of a single term fit. (The magnitude of the  $V^E$  values also changes the base used to calculate the error per cent which, in turn, explains the differences in magnitude of that quantity in Table 7.) The fact that  $\text{CH}_3\text{NO}_2\text{-CCl}_4$  solutions are less nearly ideal than  $\text{C}_2\text{H}_5\text{NO}_2\text{-CCl}_4$  solutions is also sub-

TABLE 8.—Summary of Literature Coefficients for Temperature Equations.

$a_0$ (g/ml)	$-a_1 \times 10^3$ (g/ml-°C)	$a_2 \times 10^6$ (g/ml-(°C) <sup>2</sup> )	Temperature Range (°C)
Nitromethane			
1.1574	1.356	-1.15	20-25 <sup>6</sup>
1.1637	1.346		0-45.1 <sup>32</sup>
1.1639	1.340		0-25 <sup>24</sup>
1.1639	1.342		0-50 <sup>23</sup>
1.1642	1.323		0-50 <sup>27</sup>
1.1643	1.361		17.3-60.9 <sup>14</sup>
1.16448	1.351		20-30 <sup>6</sup>
1.1645	1.337		0-100 <sup>1</sup>
1.1646	1.377		16.4-96.3 <sup>26</sup>
1.1648	1.366		25-45 <sup>16</sup>
1.1649	1.346		0-30 <sup>25</sup>
1.1652	1.384		20-50 <sup>29</sup>
1.1657	1.341		0-85 <sup>30</sup>
1.1657	1.377		20-30 <sup>7</sup>
1.1657	1.744	-4.94	-21.5-101.4 <sup>3</sup>
1.16576	1.383	-5.49	25-60 <sup>2</sup>
1.1668	1.358	-0.55	20-101 <sup>4</sup>
Nitroethane			
1.06823	1.202		25-60 <sup>2</sup>
1.0707	1.210		18.6-108.5 <sup>26</sup>
1.0724	1.170		20.2-87.3 <sup>14</sup>
1.0743	1.187		20-30 <sup>7</sup>
1.0743	1.207		20-50 <sup>29</sup>
1.0750	1.206		16.6-79.6 <sup>17</sup>
Carbon Tetrachloride			
1.5239	-0.4607	-11.2	20-283 <sup>31</sup>
1.6287	1.763	-2.09	..... <sup>8</sup>
1.6296	1.956	-1.26	24.2-54.0 <sup>10</sup>
1.6306	1.949		11.8-78.0 <sup>28</sup>
1.6314	1.870		20.1-59.8 <sup>14</sup>
1.6321	1.877		..... <sup>21</sup>
1.6325	1.920		0-40 <sup>11</sup>
1.63255	1.9110		0-40 <sup>1</sup>
1.6326	1.920		20-25 <sup>12</sup>
1.6327	1.936		20-25 <sup>6</sup>
1.6329	1.927		15-75 <sup>22</sup>
1.6329	1.927		0.563
1.6331	1.945	0.392	15-75 <sup>20</sup>
1.6334	1.961	0.705	11.8-68.0 <sup>9</sup>
1.6335	1.955		15-75 <sup>19</sup>
1.6337	1.960		19.35-58.2 <sup>13</sup>
1.6347	2.006		25-45 <sup>16</sup>
1.6468	2.759		15-44 <sup>15</sup>

1. Washburn (1928)
2. Boyd & Copeland (1942)
3. Jaeger & Kohn (1915)
4. Williams (1925)
5. Thompson, Coleman, & Helm (1954)
6. Dreisbach & Martin (1949)
7. Toops (1956)
8. Pugachevich, Nisef'son, Sokolova, & Anurov (1963)
9. Renard & Guye (1907)
10. Morgan & Higgins (1908)
11. Cowley and Partington (1936)
12. Mumford and Phillips (1950)
13. Patterson & Thomson (1908)
14. Vogel (1948)
15. Soucek (1938)
16. Brown & Smith (1962)
17. Ramsay & Shields (1893a)
18. Washington & Battino (1968)
19. Wood & Brusie (1943)
20. Wood & Gray (1952)
21. Fried and Schmeier (1968)
22. Gibson & Loeffler (1941)
23. Walden (1909)
24. Walden (1906)
25. Timmermans & Hennaut-Roland (1932)
26. Friend & Hargreaves (1943)
27. Walden & Birr (1933)
28. Ramsay & Aston (1894)
29. Geiseler & Kessler (1964)
30. Philip & Oakley (1924)
31. Ramsey & Shields (1893b)
32. Morgan & Stone (1913)

stantiated by the tests for linearity given in Tables 3 and 4.

Nitromethane at 45° does not fit into the pattern of these calculations. The data which was obtained at 45° is such that the system of equations in the least squares procedure degenerates into a single equation. The result is that only the single constant, shown in Table 7, is derivable. In all other cases except one, the coefficient of the single term equation is the same as the corresponding term of the two-term equation. This identity results from the facts that the terms occurring in the least squares procedure are symmetric in  $x_1$  and  $x_2$  and that the input data of the independent variables are symmetric in  $x_1$  and  $x_2$ . The single exception occurs when two data points are rejected, by the usual criterion (Worthing and Geffner, 1943), which destroys the symmetry of the input data.

Prigogine (1957) provides a theoretical basis for Equation (3) through the use of the average potential model. The coefficients of Equation (3) can be estimated from the critical constants of the components of the binary solution. The critical constants of nitromethane (Weissberger, 1955) were used to make an estimate which could be

compared with the results in Table 7. Since the method depends upon which component of the solution is taken as the reference substance, the calculation was made in both frames of reference. The results are

$$V^E - x_1x_2 [1.2898 + 0.001876(x_1 - x_2)] \text{ CH}_3\text{NO}_2 \text{ as reference}$$

$$V^E - x_1x_2 [2.0960 + 0.003416(x_1 - x_2)] \text{ CCl}_4 \text{ as reference}$$

Both estimates clearly show the same behavior as the results in Table 7, i.e. the quadratic term completely dominates the cubic term. Further, the order of magnitude of the quadratic coefficient is the same as those obtained in Table 7 (the estimation process is temperature independent). Insufficient critical data for nitromethane prevented a similar estimation.

#### ACKNOWLEDGMENT

This research was supported by a grant from the Petroleum Research Fund (602-B) administered by the American Chemical Society. The authors gratefully acknowledge the use of the Data Processing and Computing Center of Southern Illinois University. Thanks are also accorded to the Cartographic Laboratories for the drafting work. In accordance with the obligation assumed with the use of the

Choleski program, the authors wish to thank Eugene Fitzpatrick for permission to use, without fee, the subroutine for the calculation of the Student's *t*-ratio in this "not for profit, scholarly research".

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