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THE EVAPORATION OF LEADED METHANOL SOLUTIONS

PURPOSE

To determine the volatility of tetraethyllead (TEL) in anhydrous and in aqueous methanol solutions.

To compare the results of this investigation with similar studies of hydrocarbon-TEL systems, and to consider the hygienic hazard involved in each case.

SUMMARY

A sharp contrast exists between the vapor pressure relationships of hydrocarbon-TEL systems, which are essentially ideal, and methanol or aqueous methanol-TEL systems, which are non-ideal. Evaporation experiments have shown that the degree of non-ideality of anhydrous and aqueous methanol-TEL solutions is so large that the TEL is as much as sixty times as volatile as would be expected from vapor pressure considerations alone. Consequently, the concentrations of TEL in the vapor phase are far higher in the early stages of the evaporation of leaded methanol solutions than in the case of leaded gasolines. Furthermore, the evaporation of leaded methanol solutions leaves a relatively lead-free residue, while leaded gasolines leave a heel which is rich in TEL.

Because of this difference in vapor pressure relationships, the evaporation of methanol solutions of TEL presents a fundamentally new type of health hazard, which cannot be directly evaluated on the basis of available information on the handling of leaded gasolines.

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INTRODUCTION

A new type of fuel, sold under the trade name of Vitol, has recently been introduced to the motoring public. Vitol consists of an emulsion of a methanol-water solution of TEL with a small quantity of Penola oil and kerosene, and is designed to be used as a supplementary fuel, to be injected into the intake system of an automobile during periods of peak octane number requirement. Since Vitol contains 3.0 ml. of TEL per gallon, the health hazard involved in its handling is of sufficient concern to warrant a detailed study of the evaporation characteristics of this material.

The chemical and physical properties of TEL are closely related to those of the paraffin hydrocarbons, TEL is miscible with gasoline, and solutions of the two materials are very nearly ideal (LTD's 44-57 and 46-47). Consequently, the vapor pressure relationships and the evaporation characteristics of leaded gasoline can be approximated by calculations based on vapor pressure data. On the other hand, extreme dissimilarity exists between the chemical and physical properties of TEL and water or methanol. As a result, solutions of TEL in methanol or aqueous methanol do not approach ideality; indeed, aqueous methanol solutions containing a high percentage of water are no longer miscible with TEL.

Since the evaporation characteristics of non-ideal solutions cannot be calculated, the present study of the methanol-water-TEL system was undertaken. A gas stream was contacted with the liquid under substantially equilibrium conditions, and the amounts of TEL and solvent vaporized were determined, giving reproducible data and a direct measure of the non-ideality of the system. These conditions do not, of course, duplicate those of a spilled solution of TEL. Such non-equilibrium evaporation may lead to a different type of distribution pattern. Thus "surface stripping" effects were noted in previous work on leaded heptane, and analogous phenomena can be expected for the evaporation of methanol solutions. Also, commercial Vitol contains a small amount of emulsified oil, and this disperse phase, with which TEL is completely miscible, also greatly complicates the nature of the non-equilibrium evaporation.

EXPERIMENTAL

A. Materials

Three leaded methanol solutions were studied. In each

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case the 3.0 ml. of TEL per gal. of solution were present as 62 Mix fluid. The three solutions were (a) methanol, (b) aqueous methanol containing 82 wt. % (85 vol. %) methanol, and (c) Vitol. The last is a yellow emulsion consisting of 82 wt. % methanol, 18 wt. % water, sufficient 62 Mix fluid to give 3.0 ml. of TEL per gallon, and a small amount of corrosion inhibitor (Penola oil and kerosene). The properties of these solutions are as follows:

TABLE I
PROPERTIES OF LEADED METHANOL SOLUTIONS

<u>Solution</u>	<u>d₄²⁴</u>	<u>TEL content, ml./gal.</u>		
		<u>Input^a</u>	<u>Outgo^b</u>	<u>Average^c</u>
Methanol	0.7905	-	2.66, 3.13	2.94
Aqueous methanol	.8400	3.03	2.97, 3.06	3.02
Vitol	.8400	2.72	2.73, 2.70	2.72

- a. From analysis of original solution.
- b. From lead analyses of iodine scrubbers and final residues of separate runs.
- c. Average used in calculations.

The methanol was C.P., anhydrous, acetone-free material having a density, d_4^{24} , of 0.789₅ (literature: 0.7876, Annual Tables, 1941), obtained from the E. W. Kerr Co. Distilled water was used exclusively. TEL was present as commercial 62 Mix Ethyl Fluid. Vitol was obtained from Thompson Products, Inc., Cleveland, Ohio. It was a lemon-yellow emulsion containing small globules of a dispersed phase which tended to settle on standing. The dispersed portion contained 12% of the TEL, although its bulk was only 0.2% of the material (LTD 48-50). Dry nitrogen (Airco) was used as an inert evaporating medium. This gas was initially saturated with water for those experiments with a water-saturated gas. The 0.1 N iodine solution used to remove the TEL from the effluent gas stream was freshly prepared and stored in a glass bottle shielded from light. Analysis showed that this solution contained no lead.

B. Apparatus and Procedure

The evaporation equipment (Fig. 1) was essentially similar to that used in the previous studies. Dry nitrogen was passed through the solution which was contained in an evaporator, TEL and methanol were then removed in two scrubbers and the gas

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was metered by a wet test meter. In some experiments a water scrubber was used to saturate the nitrogen stream. The evaporator was a 600-ml., 3-in. fritted-disc gas-washing bottle, immersed in a constant temperature water bath. Entrainment of fog-like droplets was prevented by placing a plug of glass wool in the neck of the outlet tube. The evaporator was connected to an U-tube mercury manometer and in series to two 500-ml., 2-in. coarse-frit gas-washing bottles containing the scrubbing solutions. The first, which contained the iodine solution, removed the TEL and some of the methanol from the gas stream. The second scrubber contained distilled water, which removed most of the remaining methanol and the iodine vapor carried over from the first scrubber and also ensured water saturation of the gas stream for accurate measurement in the wet test meter.

In making the measurements, the nitrogen was passed through the solution at 0.5 to 1.5 liter/min., a rate which was sufficiently slow to ensure saturation of the gas with the solution. The evaporator temperature was maintained at $25.0 \pm 0.5^\circ\text{C}$. The evaporation of each solution was done in fractions of 10 to 15%. At the conclusion of each step of the evaporation, the iodine scrubber solution was analyzed for total lead, the change in weight of the evaporator was determined and the density of the residual test solution was obtained by means of a hydrometer. (The results of a test run made with two iodine scrubbers showed that one scrubber was sufficient to remove the TEL from the gas stream.) Finally, at the conclusion of each run, the lead content of the residue was determined by analysis. The pressure above the test solution in the evaporator and the pressure at the wet test meter were recorded at each stage of evaporation. The volume of nitrogen used to evaporate the test solution was obtained by correcting the wet test meter reading for meter calibration and for the water vapor present.

The effect of the small concentration of TEL on the density and volatility characteristics of the water-methanol system was concluded from the characteristics of the evaporation of an unleaded solution of 82 wt. % methanol and 18 wt. % water by both dry and water-saturated nitrogen by the same procedure and in the same apparatus. This test also provided a means for estimating the density and volume of the residues from the first evaporation of a leaded methanol solution on which density determinations were not made.

RESULTS

The results of the evaporation experiments are given below (Tables II-V), together with similar data previously obtained

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on gasoline and hydrocarbon solutions (Tables VI and VII). (The underlying theories and the method of calculation are explained in detail in the appendix.)

A. Evaporation of Unleaded Solutions

The hygroscopic nature of methanol is a complicating factor in the evaporation of methanol solutions: whenever the vapor pressure of water in the air exceeds the partial pressure of water in the methanol solution, water is absorbed into the methanol solution from the air. (Thus the atmospheric humidity is an important factor in considering the evaporation characteristics of Vitol fluid.) Preliminary experiments were made to study this effect and to obtain density-composition and refractive index-composition data on the methanol-water system.

The results of these experiments are shown in Figure 2 in which the methanol concentration of aqueous methanol solutions is plotted against the weight per cent of solution evaporated. The data from the evaporation of an 82 wt. % methanol-18 wt. % water solution with dry nitrogen are shown by the center curve. The more volatile methanol evaporates faster than the water with a resultant decrease in methanol concentration as evaporation proceeds. Evaporation of this same solution with water-saturated nitrogen (bottom curve) results in an accelerated decrease in methanol concentration due to the absorption of water by the solution from the nitrogen stream. The upper curve is a plot of similar data on the evaporation of methanol alone with water-saturated nitrogen. As in the former case, water is progressively absorbed from the nitrogen stream as evaporation proceeds. This phenomenon of water absorption concurrent with the evaporation of methanol has an important bearing on the solubility of TEL in the aging mixtures of methanol and water (see Discussion).

B. Evaporation of Vitol and Leaded Methanol Solutions.

The evaporation characteristics and the deviation from ideality of the various solutions studied is most easily demonstrated by reference to a graph on a log-log scale of the per cent TEL evaporated against the per cent methanol evaporated. This has been done in Figure 3. The solid red line is a plot of the evaporation of a solution of 3.0 ml. TEL per gallon in anhydrous methanol, and shows that the experimental relative volatility, XRV (see appendix), of TEL to methanol is about 0.19. However, the vapor pressure ratio, VPR, of these materials at this temperature is only 0.0033, about a sixty-fold difference. In other words the TEL is sixty times as volatile in methanol solutions

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as would be anticipated from vapor pressure considerations alone, or we could say that the effective vapor pressure of TEL is sixty times the true vapor pressure. The ideal solution line is so close to the horizontal axis that it would be indistinguishable at the scale used in drawing Figure 3.

The evaporation of a TEL-methanol solution with water-saturated nitrogen (broken red line) introduces the complicating factor discussed in the previous section. As a result of the hygroscopic nature of methanol, the solution dissolves water from the nitrogen stream and as the concentration of water builds up, the solution becomes still less ideal and the XRV of the TEL to the methanol progressively increases. This accelerates the evaporation of TEL to such a degree that 47% is evaporated during the evaporation of 73% of the original solution.

The evaporation of Vitol (green line) demonstrates the effect of 18 wt. % water in augmenting still further the non-ideality of the TEL-methanol system. The XRV has been increased to about 1.6, with the result that almost 80% of the TEL is vaporized during the evaporation of only 50% of the solution. It is interesting to note that in this case a single curve fits the evaporation data for both dry and water-saturated nitrogen. It appears that a slight increase in the water concentration above 18 wt. % has little effect on the effective vapor pressure of TEL. Finally, the blue line shows the characteristics of an 82% methanol - 18% water-TEL system. The slightly greater slope of this curve over that for Vitol is probably due to the presence in Vitol of the kerosene-Penola oil corrosion inhibitor which would act to reduce the XRV by a small amount because of its superior solvent properties for TEL.

Figure 4 is essentially a duplication on a linear scale of the log plot already described. The difference in ideality of the various systems shows up to the same degree in approximately the same manner.

C. Comparison with the Evaporation of Leaded Gasoline.

The striking contrast between the non-ideality of Vitol and other leaded methanol systems and the ideal nature of TEL-gasoline systems is best demonstrated by a comparison of the concentration of TEL in the residual solutions and in the effluent nitrogen as the evaporation of each type of system progresses.

The concentration of TEL in the residual solution during

evaporation is shown in Fig. 5. The TEL-heptane and TEL-gasoline systems (upper green curves) approximate the shape of the curve for an ideal solution: as evaporation proceeds, the less volatile TEL is concentrated in the unevaporated residue. At 90% evaporation the concentration of TEL is approximately 30 ml. per gallon. On the other hand, the considerable non-ideality of the aqueous methanol-TEL system (lower two green curves) results in such a rapid evaporation of TEL that the concentration remaining in the residue is far below that of the original material (3.0 ml./gallon). Evaporation with water-saturated nitrogen (bottom green curve) served only to increase the non-ideality of the system still further by increasing the water concentration of the residual solution.

The anhydrous methanol-TEL system is more ideal than aqueous methanol-TEL systems, but less ideal than hydrocarbon-TEL systems. The rate of TEL evaporation (solid red line) is increased so that the concentration of TEL in the residual solution is considerably lower than for the ideal hydrocarbon solutions in the later stages of the evaporation. Thus when 90% of the solution has evaporated the lead concentration is only 16 ml. per gallon. Water absorbed during evaporation with water-saturated nitrogen (broken red line) increased the non-ideality of this system reducing still further the TEL concentration of the unevaporated material.

Finally it is shown that the ideality of an 82 wt. % methanol-18 wt. % water-TEL system (bottom curve) is even less than that of Vitol due to the absence of the kerosene-Penola oil corrosion inhibitor with its accompanying solvent properties for TEL.

To bring out the significance of these evaporation characteristics from the point of view of health hazard, Figure 6 shows the micrograms of TEL per cubic foot of effluent nitrogen plotted on a log scale against the weight per cent of solution evaporated. The equilibrium evaporation of the nearly ideal solutions of TEL (3 ml. per gal.) in gasoline or *n*-heptane produces an initial concentration of slightly more than 100 micrograms of lead per cubic foot of air. As evaporation proceeds the concentration becomes progressively greater, reaching a value of 10,000 micrograms per cubic foot after 98% evaporation. A similar evaporation of Vitol yields an initial concentration of 10,000 micrograms of lead per cubic foot, a value one hundred times greater than that from leaded gasoline or one-tenth of the concentration which would be obtained from the evaporation of pure TEL. This concentration remains constant until the bulk of the

TEL has evaporated, and then falls rapidly to zero at the end of evaporation. The two curves cross at approximately 85% evaporation. The curve for leaded anhydrous methanol solutions has its origin midway between the gasoline and Vitol curves, at a concentration of 1,000 micrograms of lead per cubic foot, and increases gradually as evaporation progresses. The toxic limit allowable for continuous human exposure, 4 micrograms per cubic foot, is shown for purposes of comparison.

DISCUSSION

A solution of TEL in light hydrocarbons of the gasoline boiling range is entirely analogous in evaporation characteristics to a solution of a heavy hydrocarbon of the same volatility as TEL in the light hydrocarbon mixture. The chemical and physical properties of TEL make it almost as compatible with hydrocarbons as the hydrocarbons are with each other. Consequently, equilibrium evaporation of leaded gasoline results in the vaporization of a very small amount of TEL until almost all of the gasoline has evaporated, just as simple distillation would concentrate the less volatile TEL or other hydrocarbons in the undistilled residue.

The mode of evaporation of Vitol is quite the opposite. Here the equilibrium evaporation is analogous not to a simple distillation of a hydrocarbon mixture, but rather to the steam distillation of immiscible liquids. The properties of TEL contrast so sharply with those of methanol and water that the vapor pressure characteristics of the system approach those of a system of mutually insoluble liquids. The TEL concentration in the evaporating medium approximates that which would be present if TEL alone were being evaporated. Furthermore, the TEL concentration in the vapor remains constant until the bulk of the TEL has evaporated (50% of the solution evaporated) after which it rapidly falls to a very low level. The presence of the kerosene-Penola oil corrosion inhibitor with its favorable solvent properties for TEL is probably responsible for the fact that the TEL concentration in the effluent vapor does not remain constant until all the TEL has evaporated. During the evaporation of the first 50% of the solution the concentration of TEL in the vapor from Vitol is approximately 100 times greater than from leaded gasoline. After 50% solution evaporation, the concentration of TEL in the vapor from the evaporation of Vitol decreases and that from leaded gasoline increases until at 85% evaporation the two curves cross (Fig. 6). Only during the last 15% of the evaporation is the TEL concentration greater from the evaporation of leaded gasoline than from Vitol.

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In practical cases of the hygienic hazard from storage, handling and spillage of solutions such as Vitol, conditions of equilibrium evaporation may or may not exist. Consequently, the effect of non-equilibrium conditions of evaporation must also be considered. Lack of effective stirring and intimate vapor-liquid contact existing during the evaporation of spilled Vitol would result in non-equilibrium effects such as surface stripping, thermal gradients within the solution, and non-saturation of the atmosphere above the spill. Such conditions are non-reproducible and a separate study would be necessary to determine the hazards of each specific set of conditions.

On the other hand, the hazard involved in storage areas can be evaluated to a certain degree by the equilibrium evaporation data of this study. For example, the air above the liquid in a partially filled tank of Vitol will be saturated (equilibrium conditions) and will contain approximately one-hundred times as much TEL as the air above leaded gasoline in a similar situation.

CONCLUSION

The health hazard involved in handling Vitol is radically different from that of leaded gasoline. The presence of the same concentration of TEL in the two materials has no bearing on the concentration of TEL in the atmosphere in contact with these liquids. The equilibrium concentration of TEL in the vapor state from Vitol is approximately one hundred times that from leaded gasoline due to the non-ideality of aqueous methanol as a solvent for TEL. In order to produce the vapor concentration of TEL obtained from Vitol during the first 50% evaporation, a gasoline solution would have to contain approximately 194 ml. of TEL per gallon.

Finally, it must be emphasized that the results of this study give data on equilibrium conditions only. In actual practice equilibrium conditions would, of course, not always be obtained. However, equilibrium conditions were chosen as the only means of obtaining an exactly definable and reproducible set of conditions.

The evaporation of Vitol is such a complex problem, and so different from that of gasoline, that a complete experimental re-evaluation will be necessary to determine the nature of the hygienic hazard present under each specific set of non-equilibrium evaporation conditions.

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APPENDIX

A. Vapor Pressure Relationships of Ideal and Non-ideal Systems

Theoretical considerations. - The natural laws governing the volatility of pure compounds are very simple, but those for mixtures of two or more components are quite complex. If a liquid evaporates more readily than another under the same circumstances, we think of it as being more volatile. Thus, if a current of air is passed over some methanol at room temperature (25°C.) and the same amount of air over some water, 5.1 times as much methanol as water will be evaporated. It is therefore natural to think of the methanol as being 5.1 times "as volatile" as the water. Methanol has a vapor pressure of 122.3 mm. of mercury at 25°C., and water a vapor pressure of 23.8 mm. at the same temperature and the vapor pressure ratio (VPR), 5.1, is a measure of the "relative volatility" of the methanol and water when each is evaporated separately.

The amount of one component which is vaporized from a mixture or solution of two or more components is a much more complicated matter. Even though methanol is 5.1 times "as volatile" as water, it is impossible to remove all of the methanol from an aqueous solution by either evaporation or simple distillation. The volatility of the methanol compared with water is thus much less in a mixture of the two materials than would be predicted on the basis of the evaporation of the substances separately. The ratio in which two or more compounds present in a mixture or solution will be volatilized or evaporated depends on the molecular nature of the compounds, the temperature, and the concentration of the solution; the pressure has a relatively minor effect.

If two components of a solution are so similar that the intermolecular forces between the unlike molecules are equal to the intermolecular forces between the like molecules, then the solution is said to be ideal, and the ratio in which the components are volatilized from a solution containing equal molar concentrations is the same as if the compounds were being evaporated separately. Mathematically, the partial pressure of each component in an ideal solution is equal to the product of the vapor pressure of the pure substance and its molar concentration in the solution. Thus, in the special case cited above, in which the components are present in equal molecular concentration, the ratio in which they are evaporated would equal the VPR, although the actual quantity of each component volatilized would be considerably greater if each were evaporated separately. Although ideal conditions are never completely realized, many solutions of similar compounds are very nearly ideal. Solutions of paraffin hydrocarbons such as hexane and heptane, for example, are usually essentially ideal.

When the constituents of a solution are different in chemical nature, and especially when the molecules are shaped very differently or contain strongly polar groups, the intermolecular forces between the unlike molecules vary widely from those between the like molecules, and become of greater importance. In such cases the laws of ideal solutions do not hold, and the ratio in which the components evaporate can no longer be calculated from solution concentration and VPR. Such solutions are non-ideal and constitute the great majority of all liquid systems. In place of the true VPR, we must substitute a new concept, that of experimental relative volatility, KRV, which expresses the equilibrium between the quantity of each of the components in the liquid and vapor state. Since the simple laws governing ideal solution behavior are no longer valid, it is necessary to determine the KRV experimentally. A mixture of two essentially immiscible liquids such as water and TEL is an extreme sample of non-ideality. The relative rate of vaporization of the components of immiscible mixtures is entirely independent of concentration and is dependent only on the vapor pressure of the components. Consequently, in an extreme case such as this, the quantities evaporated are identical whether evaporated separately or as a mixture. For example, a given quantity of air bubbled through a mixture of water and TEL under equilibrium conditions would evaporate identically the same amount of TEL as it would if TEL alone were present. (This discussion neglects the slight solubility of water in TEL and TEL in water.)

Many true solutions - miscible liquid mixtures having homogeneous physical and chemical properties - deviate so far from ideal conditions that their vapor pressure characteristics approach those of immiscible liquids. Solutions of TEL in aqueous methanol are examples of this case. A condition of "borderline immiscibility" exists which increases the effective vapor pressure of the TEL to a value approximately one hundred times greater than that in an ideal solution.

A simple diagram is helpful in summarizing the difference between the vapor pressure of ideal and non-ideal systems at constant temperature. In Figure 7 the abscissa represents molar concentration and the ordinate vapor pressure. Point a is the vapor pressure of component A, and b that of component B. Then, in an ideal system, lines Ab and Ba represent the partial pressures (p_B , p_A) of components B and A, respectively, and the sum of these components, line ab, is the total vapor pressure (π) of the system. Any deviation from solution ideality will give other than straight lines through points A and B for the partial pressure curves Ab and Ba. A typical example of non-ideality is

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shown in the lower part of the figure. In the extreme case of immiscibility, the p_A and p_B curves do not even pass through A and B but are horizontal, and the total vapor pressure of the mixture is equal to the sum of the partial pressures, a value entirely independent of concentration.

Effective vapor pressure of TEL. - If the solutions were ideal, the amount of each component evaporated at constant temperature under equilibrium conditions could be computed from the Rayleigh equation (see Perry, Chemical Engineers' Handbook, 2nd ed., p. 1384) by the relation:

$$\frac{2 - \log (100 - T)}{P_T} = \frac{2 - \log (100 - M)}{P_M} = \frac{2 - \log (100 - W)}{P_W}$$

where T, M, W represent the percentages of TEL, methanol and water evaporated and P_T , P_M , P_W are the vapor pressures of the pure compounds. For any two components, such as methanol and TEL, the relation can be written:

$$\frac{2 - \log (100 - M)}{2 - \log (100 - T)} = \text{VPR}$$

where, in this case, VPR is the vapor pressure ratio of methanol to TEL, that is:

$$\text{VPR} = P_M/P_T.$$

Even if the solution is not ideal, the equations have the same form but the fraction is no longer equal to the VPR but to another constant, which we have termed the experimental relative volatility (XRV). That is:

$$\frac{2 - \log (100 - M)}{2 - \log (100 - T)} = \text{XRV}.$$

The ratio of XRV to VPR thus provides a measure of the non-ideality of the solution.

B. Sample Calculation of Experimental Data

The results obtained are summarized in Tables II to V. Instead of detailing the data which led to these results, the complete calculations for a single step in one of the evaporations are shown. The example chosen is the first step of the evaporation

of Vitol by water-saturated nitrogen (Run 6, Tables II and III).

The weight per cent of the original solution remaining after the evaporation of the first fraction was equal to the weight of the residue (neglecting the relatively small weight of water absorbed from the water-saturated nitrogen stream), divided by the original solution weight, W_0 :

$$\frac{W_1}{W_0} = \frac{273.71}{337.08} \cdot 100 = 81.2 \text{ wt. \% left}$$

The volume, V_1 , and volume per cent of the residual solution were calculated from the weight and density of the original, W_0 , d_0 , and residual solutions, W_1 , d_1 :

$$V_1 = \frac{W_1}{d_1} = \frac{273.71}{0.8535} = 321 \text{ ml. of residual solution}$$

and

$$\frac{V_1}{V_0} \cdot 100 = \frac{321}{402} \cdot 100 = 80.3 \text{ vol. \% left.}$$

The concentration of methanol, C_1 , in the residual solution was calculated from the density of the solution (corrected for the presence of TEL) and Fig. 8, a plot of the density-composition relationship of the methanol-water system (International Critical Tables, Vol. 3, p. 115).^{*} Thus, the residue remaining after the evaporation of the first fraction contained 76.2 wt. % methanol and 23.8% water. The weight and weight per cent of the original methanol remaining were then calculated from the weight of the residue and the methanol concentration:

$$\frac{W_1 C_1}{100} = \frac{(273.71)(76.2)}{100} = 208.6 \text{ g. of methanol in residue}$$

and

$$\frac{W_1 C_1}{W_0 C_0} \cdot 100 = \frac{(208.6)(100)}{277.1} = 75.3 \text{ wt. \% of original methanol in residue}$$

The calculation of the TEL content (as lead) of the

* Experimental data obtained in this study, which are also shown on Fig. 8, are in excellent agreement with the values from the International Critical Tables.

residual solution, R_1 , was based on the weight of TEL evaporated, E_1 (analysis of iodine scrubber), and the weight of TEL originally present, R_0 (analysis of original solution):

$$R_0 - E_1 = R_1: \quad 335.4 - 133.6 = 201.8 \text{ mg. Pb}$$

Finally, the weight per cent of the original TEL remaining in the residue and the concentration in milliliters per gallon were calculated from the above data, the volume per cent of the residue, and the original concentration of TEL in milliliters per gallon. (Since the TEL concentration of the test solutions varied from 2.72 to 3.02 ml. per gallon, all of the figures pertaining to TEL were corrected to an original concentration of 3.0 ml. per gallon to make the data on the various runs strictly comparable.)

$$\frac{R_1}{R_0} = \frac{201.8}{335.4} = 60.2 \text{ wt. \% of original TEL in residue}$$

and

$$\frac{60.2}{80.3} \cdot 3.0 = 2.26 \text{ ml. TEL/gal. in residue}$$

The TEL analyses also provide a convenient check on the precision of the test procedure. Table I lists the TEL concentration of the test solutions calculated from both the analyses of the original solutions and the analyses of the evaporated fractions and final residues. The sum of the latter, calculated for both the dry and water-saturated nitrogen runs, deviated from the analysis of the original by a maximum of only 0.06 ml. per gallon or 2.0%. The accuracy of these material balances is remarkable in view of the numerous analyses involved and the handling losses incurred during the density determinations.

The data for the evaporated fractions are tabulated in Table III. The weight of solution evaporated was determined by correcting the weight loss of the evaporator, $W_0 - W_1$, for the weight of water absorbed from the water-saturated nitrogen by the evaporating solution. Thus, $W_0 - W_1$, plus the weight loss of the water saturator, S_1 , gave the weight of solution evaporated.

$$W_0 - W_1 + S_1 = 337.08 - 273.71 + 7.6 = 71.0 \text{ g. of solution evaporated}$$

Division of this value by the volume of effluent nitrogen (corrected to standard conditions of temperature and pressure) gave the weight of solution evaporated per liter of nitrogen.

$$71.0/371.9 = 0.191 \text{ g./liter nitrogen}$$

The weight of methanol evaporated and the grams of methanol per liter of nitrogen were found from the difference between the weight of methanol in the original, M_0 , and residual solutions, M_1 , and the quotient of this value divided by the volume of nitrogen.

$$M_0 - M_1 = 277 - 209 = 68 \text{ g. of methanol evaporated}$$

and

$$68/371.9 = 0.183 \text{ grams of methanol/liter nitrogen.}$$

The weight of water evaporated and its concentration in the nitrogen stream were found in an analogous manner.

Finally, the cumulative weight per cent of TEL evaporated and its concentration in milligrams per cubic foot in the effluent nitrogen were calculated from the weight of TEL evaporated, E_1 , the original weight of TEL present, R_0 , and the volume of nitrogen, N_1 .

$$\frac{E_1}{R_0} = \frac{133.6}{335.4} = 39.8\% \text{ TEL evaporated.}$$

and

$$\frac{E_1}{N_1} = \frac{133.6}{13.14} = 10.17 \text{ mg./cu. ft.}$$

The only exception to the procedure described above was the measurement of the density values of the residual solutions for the original evaporation (Run 4). The nature of the problem was not completely understood at that time and density measurements were not made. Consequently, these values were calculated from the weight of the residual solution and Figures 2 and 8.

C. Gasoline-TEL and Heptane-TEL Data

The data on the hydrocarbon-TEL systems (LTDs 44-59 and 46-47) necessary for comparison with the present study are given in Tables VI and VII.

TABLE II - Evaporation of Loaded Methanol Solutions: Residual Solutions

	Solution				Methanol				TFL (b)		Water absorbed from saturator, lb.
	Height, ft.	% of original	Density, d_{25}^4	Volume, ml.	% of original	Concn., Wt. %	Weight, lb.	Wt. % of original	mg. lb	Wt. % of original	ml./gal.
Run 1. Loaded methanol; dry nitrogen											
Fraction 0	317.35	100	0.7905	401.5	100	100	see	see	336.4	--	3.00
1	274.67	86.5	--	347.5	86.7	100	column	column	329.0	97.8	3.39
2	251.45	79.2	--	318.1	79.2	100	column	column	326.2	96.8	3.67
3	207.50	65.4	--	262.5	65.4	100	1	2	322.3	95.8	4.40
4	177.22	55.8	0.7915	224.0	55.8	100	1	2	318.9	94.8	5.09
5	114.87	36.2	--	145.3	36.2	100	1	2	283.3	84.2	6.98
6	66.12	20.8	0.7956	83.1	20.7	100	1	2	245.3	73.0	10.58
Run 2. Loaded methanol; wet nitrogen											
Fraction 0	273.47	100.0	0.7895	346	--	100.0	275	--	289.7	--	3.00
1	217.02	79.4	.7950	273	78.9	99	215	78.2	272.4	94.0	3.58
2	183.67	67.2	.8005	229	66.2	98	180	65.4	256.2	88.4	4.00
3	133.15	48.7	.8085	165	47.7	96	130	47.3	221.7	76.5	4.83
4	121.62	44.5	.8140	149	43.1	93	110	40.0	210.2	72.6	5.03
5	87.96	32.2	.8330	106	30.6	85	75	27.3	151.1	53.2	5.24
Run 3. Loaded aqueous methanol; dry nitrogen											
Fraction 0	330.43	100.0	0.8400	354	--	81.8	270.3	--	328.8	--	3.00
1	313.16	94.8	.8420	372	94.4	81.0	253.7	93.8	290.0	88.2	2.80
2	299.02	90.5	.8435	355	90.1	80.4	240.4	88.9	258.4	78.6	2.61
3	279.84	84.7	.8460	331	84.0	79.5	222.5	82.3	212.7	64.7	2.30
4	242.98	73.5	.8510	286	72.6	77.3	187.8	69.5	127.5	38.8	1.60
Run 4. Loaded aqueous methanol; dry nitrogen (same as Run 3)											
Fraction 0	334.64	100.0	0.8400	359	--	81.8	273.7	--	333.0	--	3.00
1	157.63	47.1	.8723 (a)	181	45.4	68.7	108.3	36.6	9.4	2.8	0.19
2	57.31	17.1	.93- (a)	62	16	41	23.5	8.6	4.7	1.4	0.28
3	24.53	7.3	.97- (a)	25	6	16	3.9	1.4	4.1	1.2	0.58
Run 5. Vitrol; dry nitrogen											
Fraction 0	331.64	100.0	0.8400	395	--	81.8	271.3	--	330.0	--	3.00
1	312.54	94.2	.8425	371	93.9	80.9	252.8	93.2	294.9	89.4	2.85
2	279.09	83.0	.8465	325	82.3	79.2	217.9	80.3	225.1	68.2	2.48
3	243.65	73.5	.8510	286	72.4	77.3	188.3	69.4	166.3	50.4	2.09
4	87.69	26.4	.904	97	25	--	--	--	28.8	8.7	1.07
Run 6. Vitrol; wet nitrogen											
Fraction 0	337.66	100.0	0.8390	402	--	82.2	277.1	--	335.4	--	3.00
1	273.71	81.2	.8535	321	80.3	76.2	208.6	75.3	201.8	60.2	2.26
2	240.73	71.4	.8625	279	69.8	72.2	173.8	62.7	129.0	38.5	1.66
3	206.03	61.1	.8760	235	58.8	66.6	137.2	49.5	68.7	20.5	1.05
4	61.72	18.3	.9690	63.8	16.0	16.0	9.9	3.6	15.4	4.6	0.87

(a) values calculated from % residue and Figs. 2 and 3.

(b) corrected to an original concentration of 3.0 ml./gallon

TABLE III - Evaporation of Loaded Methanol Solutions: Evaporated Fraction

	Nitrogen		Solution		Methanol		Water		TPE	
	Volume, cu. ft.	Pressure, mm. Hg.	Weight, g.	g./l. of nitrogen	Weight, g.	g./l. of nitrogen	Weight, g.	g./l. of nitrogen	Evaporated, g.	Cumulative, g. in nitrogen
Run 1. Loaded methanol; dry nitrogen										
Fraction 1	158.4	5.35	861	42.72	see	see	--	--	7.4	2.2
2	65.6	3.02	806	23.22	column	column			2.8	3.2
3	167.0	5.50	812	43.95	column	column			3.9	4.2
4	113.3	4.00	813	30.28	4	5			3.4	5.2
5	231.0	8.16	813	61.47					34.1	15.8
6	186.5	6.55	807	48.75					37.8	27.0
Run 2. Loaded methanol; wet nitrogen										
Fraction 1	256.6	8.36	815	60	see	see	(c)	(c)	17.3	6.0
2	133.5	4.71	801	35	column	column			14.3	11.6
3	217.9	7.70	806	50	column	column			32.8	23.5
4	51.7	1.83	806	10					10.6	27.4
5	165.8	5.85	810	35	4	5			54.0	46.8
Run 3. Loaded aqueous methanol; dry nitrogen										
Fraction 1	88.1	3.11	825	17.27	0.196	0.189	0.7	0.007	38.8	11.8
2	72.5	2.56	823	14.14	.195	.183	0.8	.012	31.6	21.4
3	99.9	3.53	825	19.18	.192	.180	1.3	.012	45.7	35.3
4	198.2	7.00	817	36.86	.186	.175	2.2	.011	85.2	61.2
Run 4. Loaded aqueous methanol; dry nitrogen										
Fraction 1	972.9	34.36	830	177.01	0.182	0.170	11.5	0.012	323.6	97.2
2	870.1	30.73	820	100.32	.115	.097	15.5	.018	4.7	98.6
3	543.7	19.20	824	32.78	.060	.056	13.2	.024	0.6	98.8
Run 5. Vitcol; dry nitrogen										
Fraction 1	56.2	3.40	817	19.10	0.199	0.192	0.7	0.007	35.1	10.6
2	151.8	6.77	816	37.45	.195	.182	2.5	.013	69.8	31.8
3	161.5	5.70	808	31.44	.195	.183	1.9	.012	58.8	49.6
4	520.7	32.52	819	153.86	.167	--	--	--	136.2	91.3
Run 6. Vitcol; wet nitrogen										
Fraction 1	371.5	13.14	810	71.0	0.191	0.183	3.0	0.008	133.6	39.8
2	205.4	7.23	830	36.5	.178	.166	2.5	.012	72.4	61.5
3	220.7	7.79	818	38.1	.173	.164	2.0	.009	59.7	79.5
4	1050.3	37.09	811	165.1	--	--	37.8	--	53.1	95.4

(a) at 760 mm., 0°C.
 (b) pressure at 25°C. in evaporator
 (c) beyond accuracy limits of apparatus

Run	Fraction	Solution			Methanol		Water unabsorbed from saturated, g.	
		Weight, g. of original	Density, d_{4}^{25}	Volume, ml.	% of original	Weight, g.		Wt. % of original
Run 2. Aqueous methanol; dry nitrogen								
Fraction 0	0	100.0	0.8410	401	100.0	273.6	100.0	
1	1	306.44	.8445	363	50.5	243.5	89.2	
2	2	271.40	.8485	320	75.8	211.4	77.5	
3	3	253.52	.8510	298	74.4	199.5	71.5	
4	4	197.98	.8636	229	72.2	142.9	52.2	
5	5	170.15	.8705	195	48.6	69.0	42.5	
6	6	131.51	.8850	149	37.2	82.6	30.2	
7	7	59.19	.9015	110	27.4	55.6	20.3	
8	8	76.35	.9195	83.0	20.7	35.9	12.1	
Run 3. Aqueous methanol; wet nitrogen								
Fraction 0	0	100.0	0.8410	398	100.0	271.1	100.0	
1	1	315.11	.8445	373	53.7	251.1	92.6	2.25
2	2	271.78	81.2	318	79.5	205.7	75.9	7.23
3	3	210.15	62.8	240	60.3	140.4	51.8	7.72
4	4	157.48	47.0	175	44.0	57.1	33.2	7.11
5	5	119.59	35.7	129	32.4	43.9	15.4	6.34
6	6	82.09	24.5	84.6	21.3	13.1	4.8	11.15

TABLE V - EVAPORATION OF AQUEOUS METHANOL: EVAPORATED FRACTIONS

Run	Fraction	Aqueous methanol; wet nitrogen	Nitrogen		Solution		Methanol		Water			
			Volume (a) liters	Rate, l./min.	Pressure (b) mm. Hg.	Wt. %	E./l.	Wt. %	E./l.	Wt. % in vapor	Wt. %	E./l.
Run 7. Aqueous methanol; dry nitrogen												
	Fraction 1		156.7	0.83	782	31.31	0.200	29.7	0.189	55	1.6	0.011
2			175.9	.79	798	33.96	.193	31.5	.179	93	2.5	.014
3			89.4	.68	799	16.73	.187	15.3	.171	92	1.4	.016
4			313.7	.71	809	55.23	.176	52.1	.166	94	3.1	.010
5			151.6	.39	809	26.28	.173	24.7	.163	94	1.6	.010
6			228.9	.51	797	36.87	.161	34.1	.149	92	2.8	.012
7			203.5	.55	805	30.00	.147	26.3	.129	88	3.7	.018
8			162.0	.60	802	21.54	.131	19.6	.116	90	2.3	.015
Run 8. Aqueous methanol; wet nitrogen												
	Fraction 1		102.6	0.72	773	21.9	0.214	20.0	0.195	91	1.9	0.019
2			246.1	.80	769	49.7	.202	44.7	.182	50	5.0	.020
3			367.3	.81	767	68.4	.177	64.5	.167	94	3.9	.010
4			372.7	.91	783	57.6	.154	49.0	.131	85	8.6	.023
5			328.8	.72	772	43.4	.132	36.8	.112	85	6.6	.020
6			558.8	.62	777	47.9	.089	39.1	.073	82	8.8	.016

(a) at 760 mm. and 0°C.

(b) at 25°C. at evaporator

TABLE VI - Evaporation of Leaded Hydrocarbon Solutions:
Evaporated Fractions

These data are calculated from LTDs 44-57 and 46-47

<u>Fraction</u>	<u>Cumulative % Fuel Evaporated</u>		<u>Wt. of fuel per liter of air, g.</u>	<u>TEL</u>	
	<u>Vol. %</u>	<u>Wt. %</u>		<u>mg. Pb/cu. ft.</u>	<u>Cum. wt. % evaporated</u>
<u>Gasoline</u>					
1	10	9	1.76	0.155	0.023
2	20	18	0.76	.102	.060
3	30	27	.39	.076	.115
4	70	68	.10	.127	.96
5	90	89	.07	.325	3.61
6	100	100	--	1.274	100.00
<u>Heptane</u>					
1	10	10	--	--	0.07
2	20	20	--	--	.16
3	35	35	0.20	0.084	.31
4	70	70	.19	.100	.85
5	90	90	--	.150	1.66

RE 0020770

TABLE VII - Evaporation of Leaded Hydrocarbon Solutions:
Residual Solutions

These data are calculated from LTDs 44-57 and 46-47

<u>Fraction</u>	<u>Residual Fuel</u>		<u>TEL</u>
	<u>Vol. %</u>	<u>Wt. %</u>	<u>conc., ml./gal.</u>
	<u>Gasoline</u>		
0	100	100	3.00
1	90	91	3.53
2	80	82	3.75
3	70	73	4.28
4	60	63	4.99
5	50	53	5.98
6	30	32	9.90
7	20	22	14.75
8	10	11	28.92
	<u>Heptane</u>		
0	100	100	3.00
1	90	90	--
2	80	80	--
3	65	65	4.60
4	30	30	10.26
5	10	10	29.50

KE 0020771

Distribution:

G. W. Beste (2)
G. Edgar
✓ R. A. Kehoe (3)
R. Champlin

References: 1360XP29-38

Work by: Report by:

T. McDyer	T. McDyer
H. R. Neal	J. B. Hinkamp
	G. W. Thomson

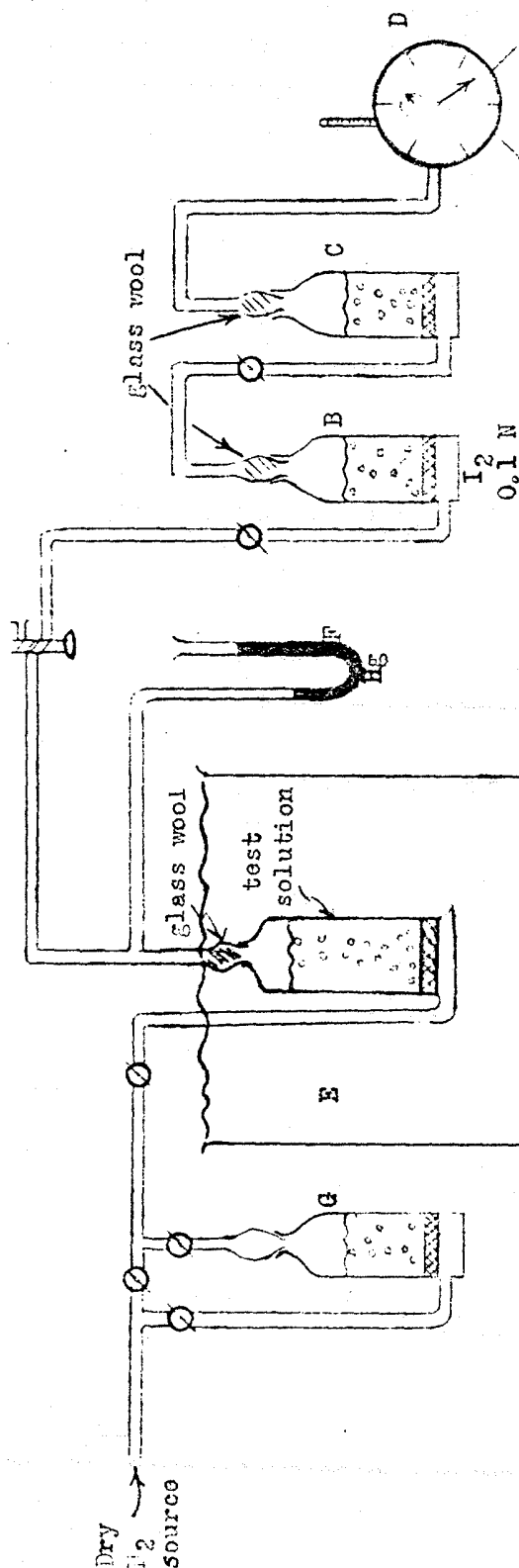
Supervisor:

J. B. Hinkamp
J. B. Hinkamp

Approved:

TMD,JBH,GWT:ld

KE 0020772



- A Evaporator
 B Iodine scrubber solution
 C Water scrubber solution
 D Wet test meter
 E Constant-temperature water bath
 F Open-end U-tube manometer
 G Water-saturator for nitrogen stream

Fig. 1 - Evaporation Apparatus

(100% Saturation)

KE 0020773

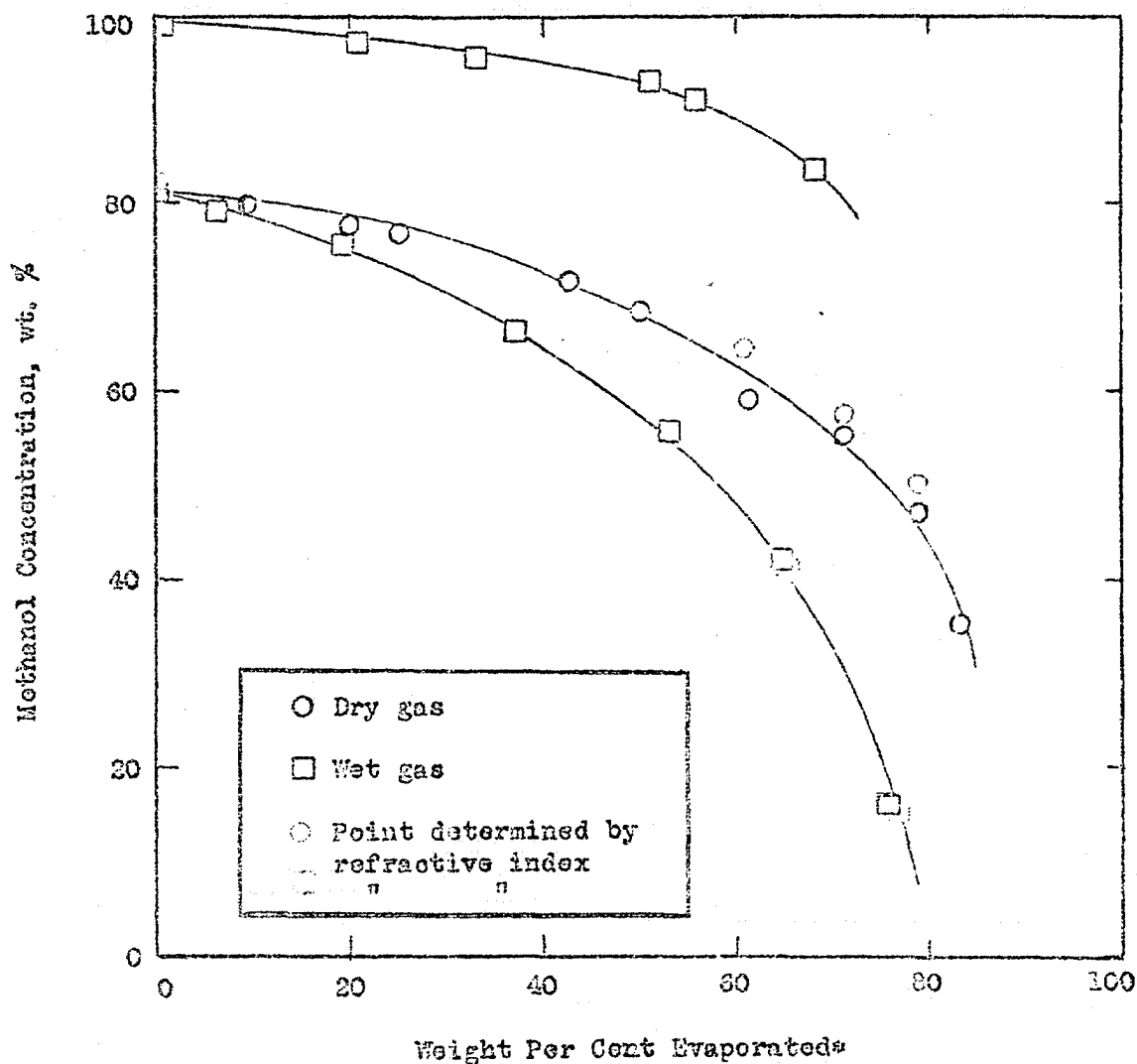


Fig. 2 - Methanol Concentration of Evaporating Water-Methanol Solutions

* These values were computed from the weight per cent of original solution remaining at each stage of evaporation. The error in the plotted values due to water absorption from the wet gas stream (see text) is negligible.

KE 0020774

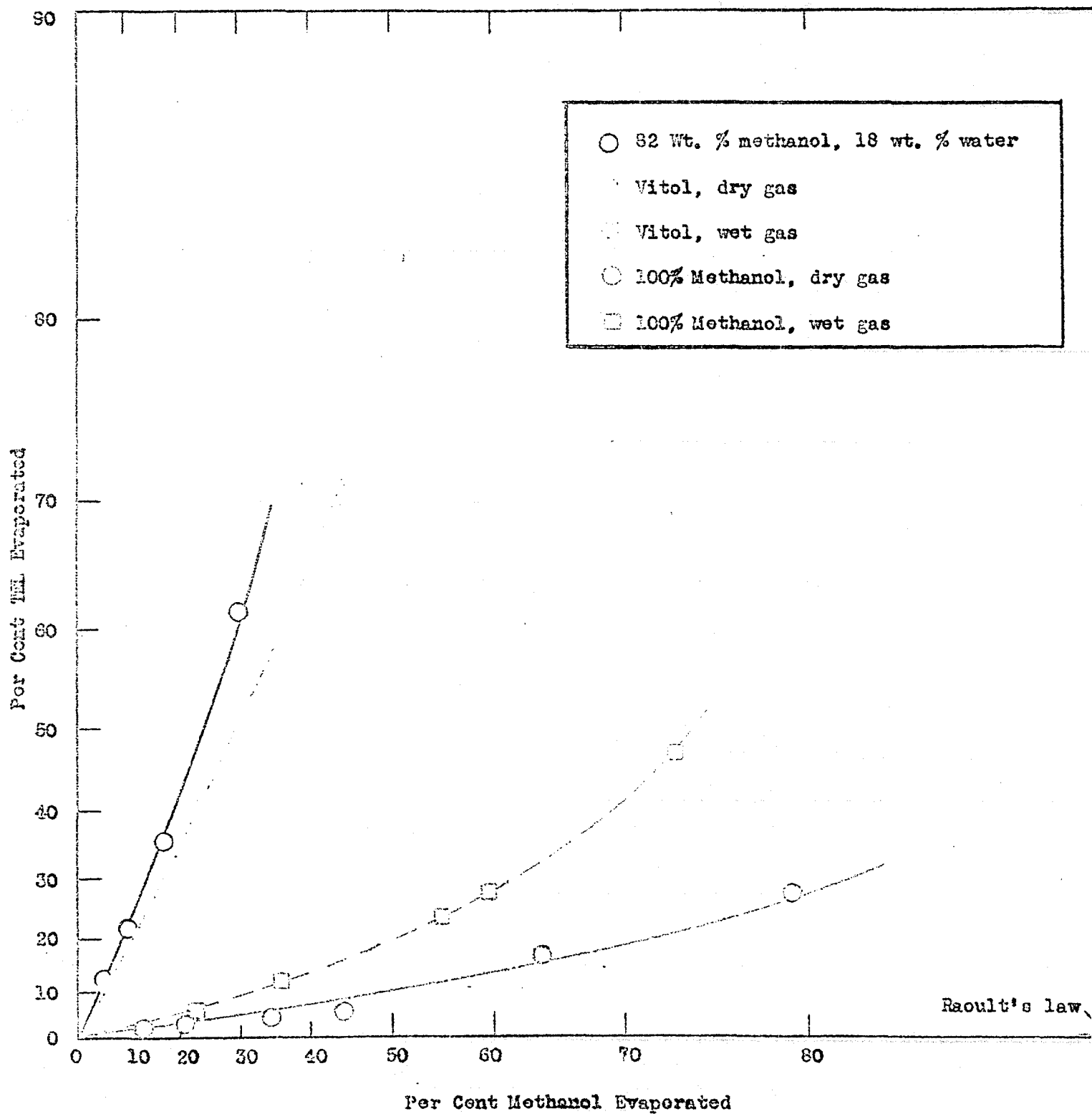


Fig. 3 - Volatility of TEL in Methanol and Aqueous Methanol Solutions

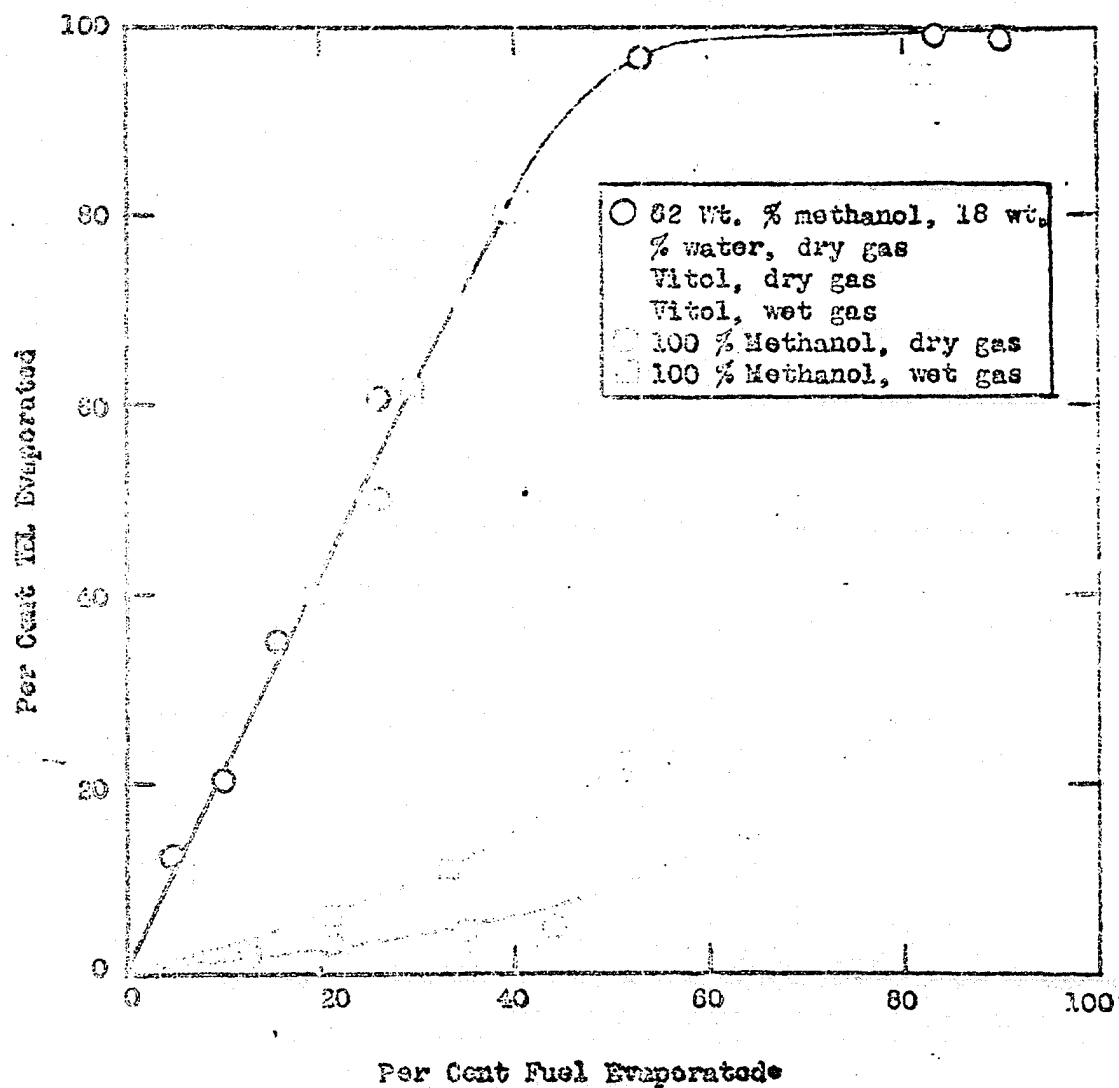


Fig. 4 - Volatility of TEL in Methanol and Aqueous Methanol Solutions

* See note, Fig. 2.

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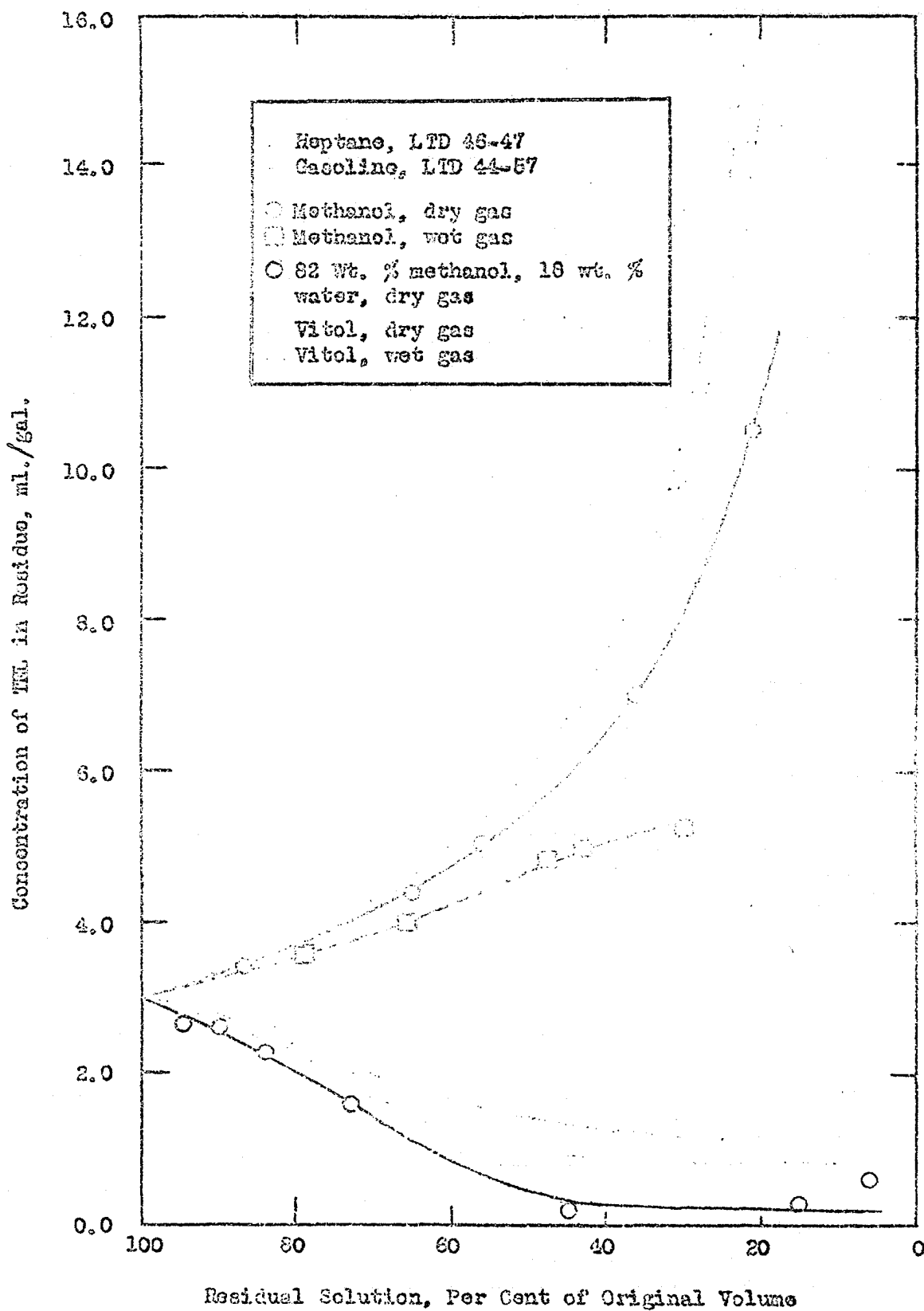


Fig. 5 - Concentration of TEL in the Residual Solution

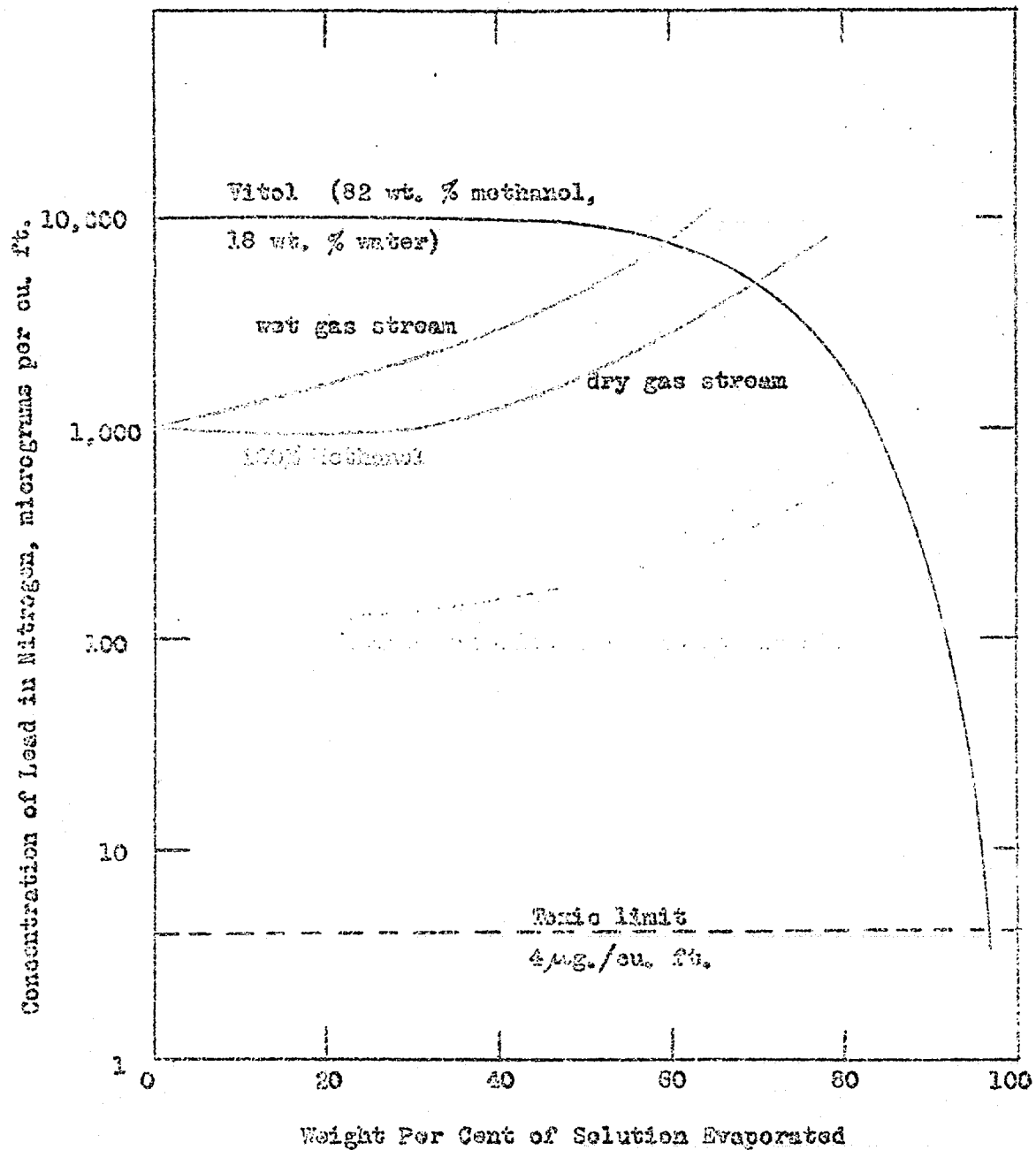
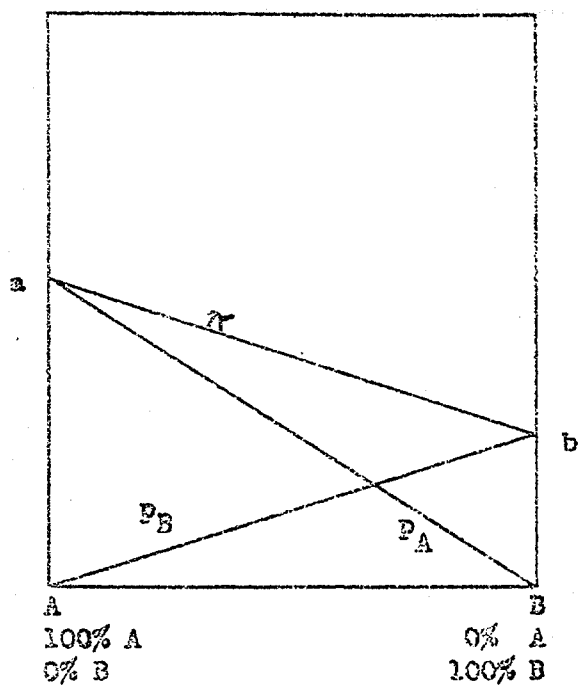
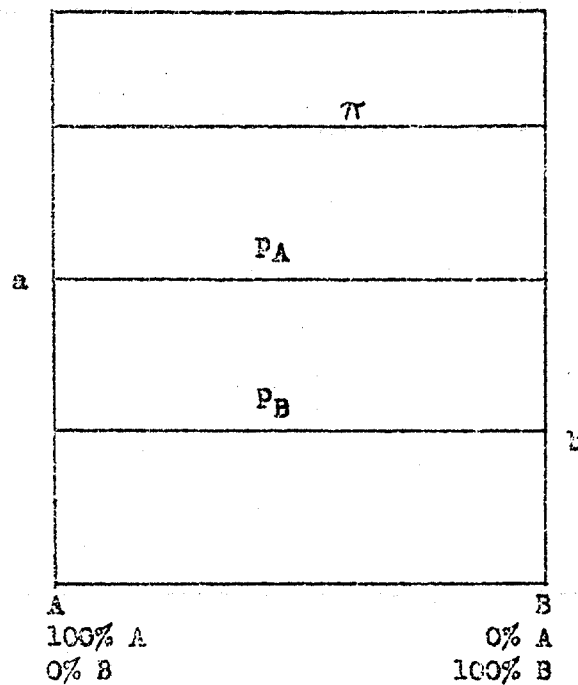


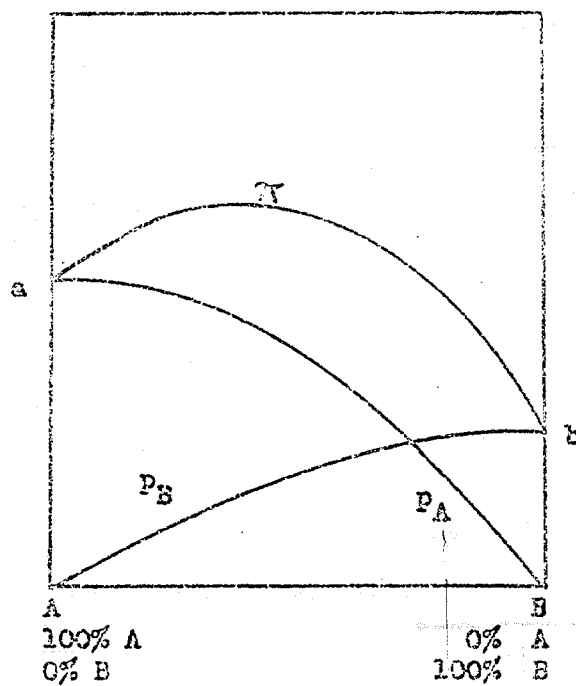
Fig. 6 - Concentration of TEL (as Lead) in Fuel-saturated Nitrogen



Ideal



Immiscible



Non-ideal

Fig. 7 - Solution Ideality and Non-ideality

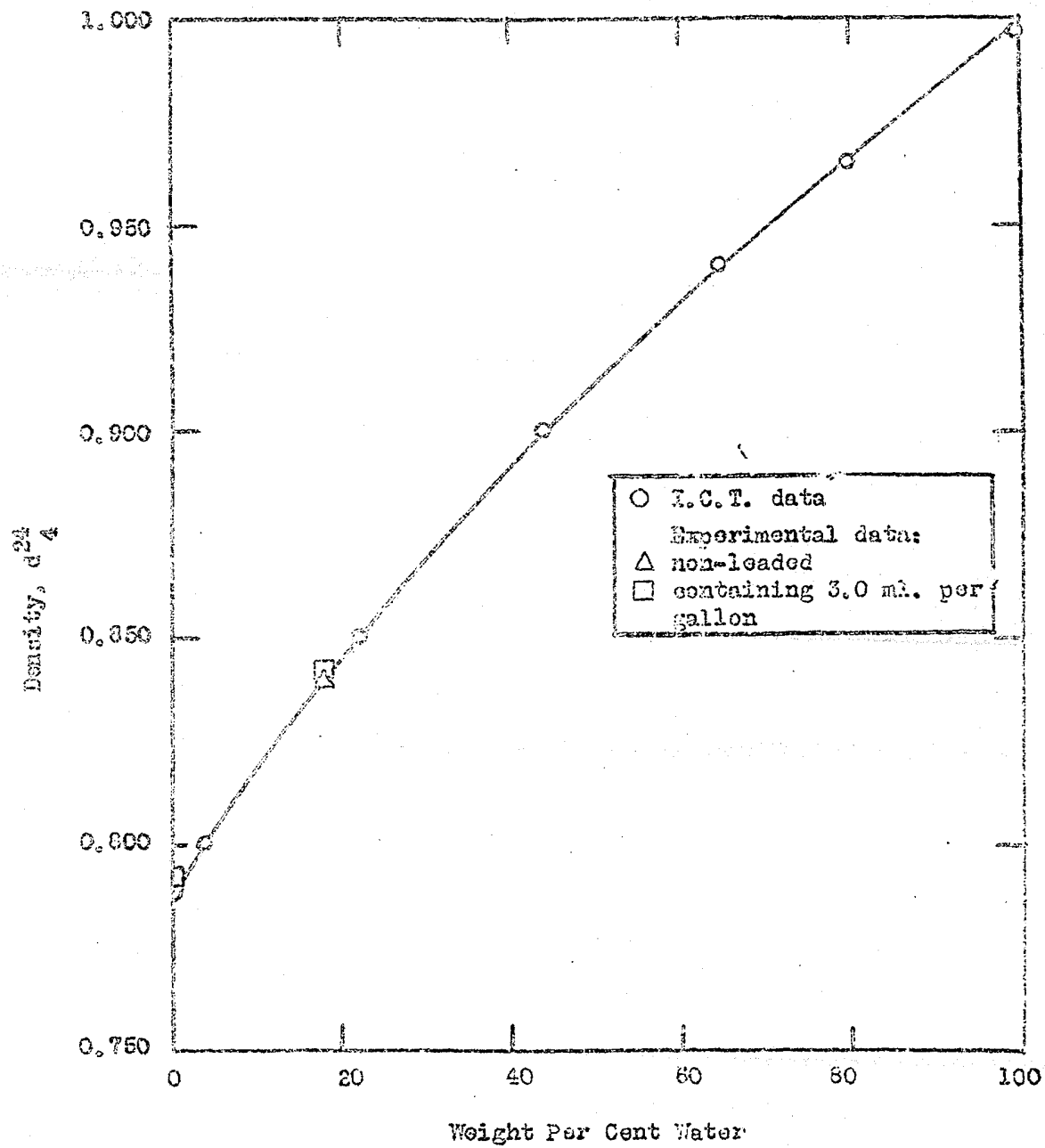


Fig. 8 - Density of Aqueous Methanol Solutions