THE SYSTEM NICOTINE-METHYLETHYLKETONE-WATER

A Thesis
Submitted to
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Master of Science

by
Warren Edgar Falconer
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to my wife

Charlynne

ABSTRACT

The systems nicotine-water, and nicotine-methylethylketone were investigated by thermal analysis. No eutectic points were located, due to the extreme viscosity and supercooling of solutions of high nicotine content.

The densities, viscosities, dispersions, and Hydrogen C and F refractive indices were determined for the nicotine-methylethylketone-water system.

The mutual solubilities of nicotine, methylethylketone, and water were determined over the entire temperature range in which partial solubility exists. Isothermal studies were made at temperatures up to 143.0°C., and eleven isotherms were determined and plotted. Above this temperature the method of Alexejew was used to complete the outline of the heterogeneous volume. A ternary critical point was found at 67.3°C., having a composition of twenty-seven percent nicotine, fourteen percent methylethylketone, and fifty-nine percent water by weight.

In the course of the investigation, the methylethylketone-water and nicotine-water solubility curves were redetermined. The existing data for the former were

confirmed, but considerable deviation from the data of Hudson was obtained in the nicotine-water system. The lower critical temperature for this system was found to be 61.5°C., in good agreement, but the upper critical point was found at 233.0°C., some twenty degrees higher than had been obtained by previous workers. The critical compositions were respectively thirty-six percent and forty percent nicotine by weight.

ACKNOWLEDGEMENTS

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INTRODUCTION

The system nicotine-water, first examined by Hudson (1) in 1904, has always been of interest, for it exhibits both an upper and a lower consolute solution temperature. The system methylethylketone-water, first investigated by Rothmund (2) in 1898, exhibits an upper consolute solution temperature, and the solubility curve can be seen to contract towards what undoubtedly would be the lower consolute solution, except that the curve intersects the ice line before this lower critical temperature can be realized (3). It becomes of interest to study the effect of combining these three components, nicotine, methylethylketone, and water, and to observe the effect of the third component on the individual binary systems. Generally, the introduction of a third component soluble in both members of a binary system will increase the mutual solubility; whereas the introduction of a component soluble in only one of them will decrease the mutual solubility (4).

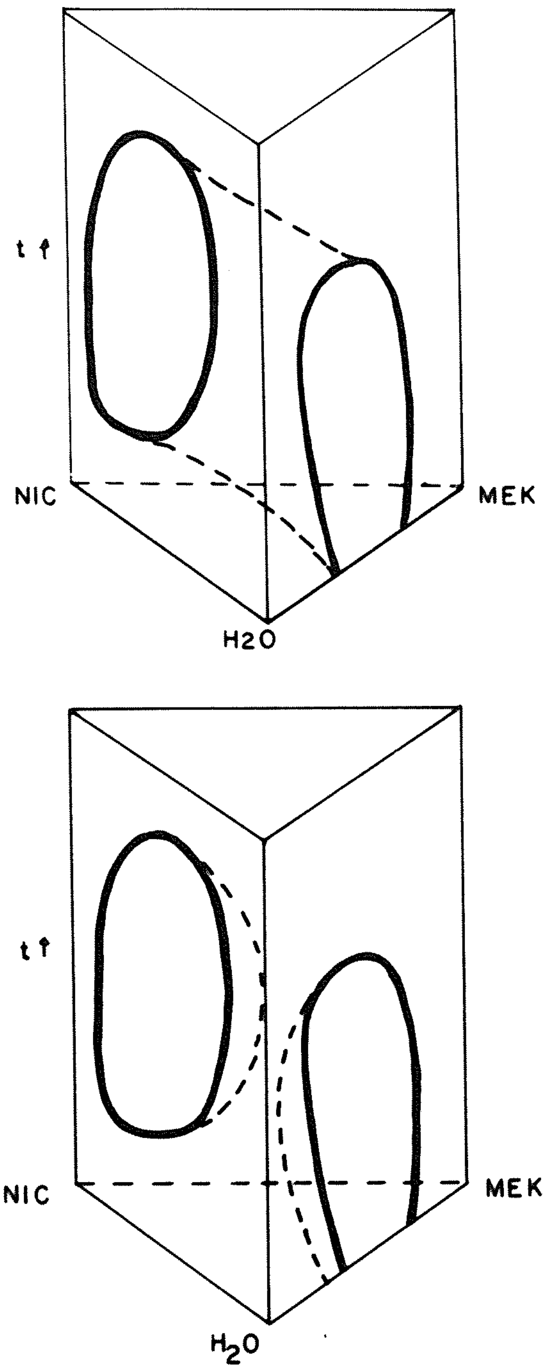
Since methylethylketone is completely soluble in nicotine and partially soluble in water, the introduction of methylethylketone into the nicotine-water system might be expected to increase the mutual solubility of this pair, although this prediction cannot be made with certainty due to the considerable difference in the solubility of the methylethylketone in each member of the binary pair.

Several types of ternary equilibrium diagrams are possible. In this case either a "tunnel" of heterogeneity could form from the completely closed nicotine-water binary system to the partially closed methylethylketone-water binary system, or two hemihedral shells of heterogeneity could form (Figure 1).

It was the purpose of this study to determine which of these forms the equilibrium diagram would take, and to determine exactly the regions of miscibility and immiscibility for the system nicotine-methylethylketone-water at all temperatures.

Freezing point curves were determined as far as was possible by thermal analysis in order to locate the ternary eutectic temperature and to outline the eutectic troughs. The extreme viscosity and supercooling of the solutions with a high nicotine content made a complete study impossible.

Of the methods available for determining the solubility diagram for the entirely liquid system, that of isothermal analysis was preferred and used where possible for two reasons. Firstly, it is the most accurate method, and secondly, it enables tie lines to be plotted between conjugate solutions. This method had to be abandoned when



POSSIBLE SOLUBILITY DIAGRAMS FOR THE SYSTEM NICOTINE - METHYLETHYLKETONE - WATER

FIGURE 1

temperatures, and hence pressures, became so high that sampling of the conjugate layers became impossible. The method of Alexejew (5) was then adopted to complete the solubility study.

In the course of the study the two binary equilibrium diagrams were repeated. The data obtained for the methylethylketone-water binary system were in close agreement with those obtained by the Shell Laboratories (6) but deviated considerably from the original data of Rothmund (2). In the nicotine-water binary system, close agreement with the results of Hudson (1) was obtained in the lower temperature region. Considerable deviation from his results was found in the high temperature region.

THEORETICAL CONSIDERATIONS

1. STATEMENT OF THE PHASE RULE

The phase rule, as enunciated by Willard Gibbs (7) in 1879, is founded upon many years of human experience as presented in the form of the laws of thermodynamics. The phase rule regards a system as having three independent factors--concentration (or volume), pressure, and temperature. It applies, as does thermodynamics, only to macrosystems, and tells one nothing of mechanism or rate of attainment of equilibrium.

Gibbs' phase rule defines the conditions of equilibrium by the following relationship between the number of phases in a system and the number of components:

$$F = C - P + 2$$

P represents the number of phases, or homogeneous, physically unique portions; C represents the least number of components, or least number of constituents capable of independent variation in the various phases; F represents the variance, or the number of variable factors which must be fixed arbitrarily in order to define the state of the system completely; the number 2 arises from the two non-concentration variables, temperature and pressure.

The phase rule makes possible the classification of systems into groups in which the member systems do not outwardly resemble one another. It also defines the conditions under which various substances can exist in equilibrium with their surroundings.

2. TYPES OF SYSTEMS

As this research is concerned with two and three component liquid-solid and liquid-liquid equilibria, these types of systems will be briefly discussed. The effect of small pressure changes on condensed systems is usually small and therefore neglected. In this research the pressure of the system was atmospheric in the low temperature investigations, and the total vapor pressure of the components at the higher temperatures. These later pressures amounted to several atmospheres in some cases, but no account of this pressure was taken in recording the results. The results are comparable to those existing in the literature at present, since it is impossible to attain equilibrium at temperatures above the normal boiling point of a solution unless the pressure is greater than one atmosphere. Previous workers experimenting with the two binary systems to be discussed recorded their results at the total vapor pressure of the system.

Timmermans (8) has shown that an increase in pressure may raise or lower the upper critical solution temperature;

but may only raise the lower critical solution temperature. In the methylethylketone-water system, a pressure of 10 Kg./cm.^{2} lowers the critical solution temperature to 141.0°C. from 142.6°C. As the pressure is increased, a lower critical solution is observed, whose critical solution temperature rises with increasing pressure. The upper and lower critical temperatures coincide at 85°C. at 1100 Kg./cm.^{2} pressure. At all higher pressures, methylethylketone and water are completely miscible in all proportions. Timmermans also lists the nicotine-water system as being of the type exhibiting a complete retraction of the immiscible region with increasing pressure. Above some critical solution pressure, nicotine and water, too, are soluble in all proportions.

A. Systems of Two Components

In the graphical representation of a two component system with pressure regarded as a constant, the composition is plotted on the abscissa, and the ordinate is the temperature axis. The maximum variance of a two component system is three; the temperature, pressure, and composition must all be known to fix the state of a one phase system.

In general the addition of a second component lowers the freezing point of a pure substance. In the system AB, if a little A is added to pure B, the freezing point, or temperature at which liquid and solid coexist, is lowered.

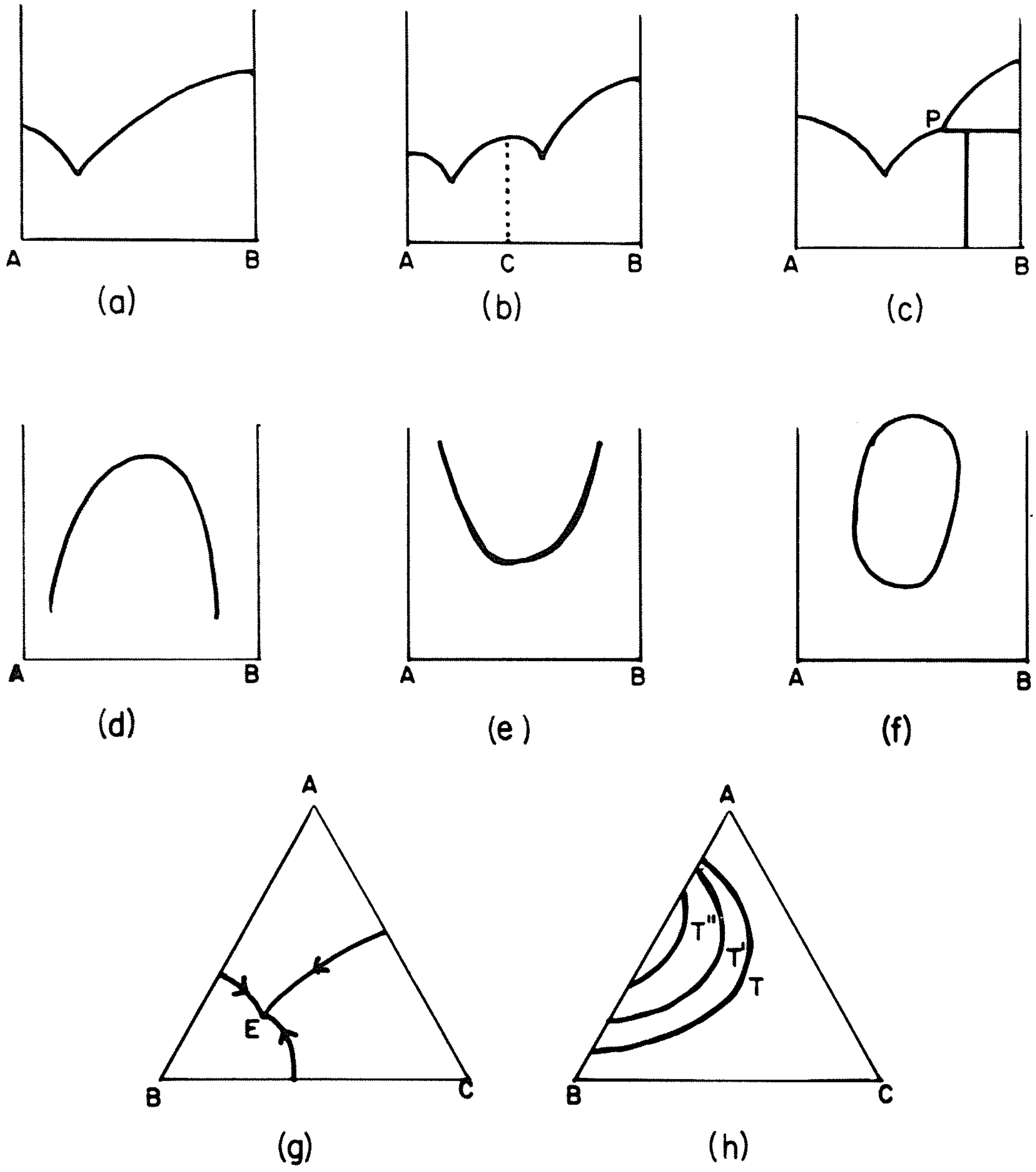
Similarly, adding B to pure A lowers the freezing point. A range of temperature in which liquid and solid are in equilibrium is observed when more than one component is in solution.

It follows that a minimum temperature at which the freezing curves descending from pure A and pure B intersect must exist. Such a point is known as a binary eutectic. If a stable compound forms between A and B, the freezing curves must pass through a maximum, with a eutectic point between each pure component and the stable compound.

Figure 2a is an example of two pure components having a simple freezing curve. Figure 2b shows a congruently melting compound, C, and the two eutectic points.

A third case exists, that of an incongruently melting compound--a solid which decomposes below its own melting point. This gives rise to a peritectic point P on the freezing point diagram (Figure 2c). This solid will decompose into pure solid component and solution at the peritectic temperature.

If two pure liquids are mixed together, they will be either completely miscible, giving rise to a homogeneous solution, or partially miscible, giving rise to two distinct liquid phases in equilibrium with each other. These are known as conjugate solutions, and their composition is a function of temperature and pressure. As the temperature



(a) (b) (c)

(d) (e) (f)

(g) (h)

HYPOTHETICAL EQUILIBRIUM DIAGRAMS

FIGURE 2

changes the composition of the two layers will change and two solubility curves will be formed; one showing the solubility of A in B, the other showing the solubility of B in A. If the two solubility curves merge at a specific temperature, this is known as an upper or lower critical solution (or consolute) temperature, depending upon whether curves merge on raising or lowering the temperature. The composition of the solution at the maximum or minimum point is the critical composition. The region enclosed by the solubility curves is called the heterogeneous region; that outside the curves, the homogeneous region.

Lines joining conjugate solutions are known as tie lines. A line drawn through the midpoints of all the tie lines is a plot of the rectilinear diameter, and if extrapolated will pass through the critical composition. This is analagous to the "law of rectilinear diameters" of Cailletet and Mathias (9).

If both an upper and lower critical solution temperature exist, clearly a completely closed solubility curve will result. It may be mentioned that the closed ends of the curve are continuous, that is to say, the solubility curves merge into one another at a specific temperature and do not intersect at a point.

Examples of a maximum solution temperature, a minimum solution temperature, and a completely closed solubility curve are given in Figures 2d, 2e, and 2f.

B. Systems of Three Components

Three component systems have a maximum variance of four. If one phase only exists, then temperature, pressure, and two composition variables must be fixed to define the system completely. Since the three components investigated behave in much the same manner towards one another, it is advisable to represent the compositions on an equilateral triangle. The method of Roozeboom (10) is the method of graphical representation used in this study. The pure components are represented by the vertices of an equilateral triangle, and the relative amount of each component present in the system is proportional to the vertical distance from the edge opposite to the vertex representing that component. Although the pressure of the system at times was several atmospheres in magnitude, the diagrams have been plotted as if the pressure were constant, as this is the accepted practice. Isothermal sections are represented by planar diagrams, and in order to include the temperature variable, it is customary to employ the equilateral prism, and to represent temperature on the vertical axis.

To represent temperature on a planar diagram it is projected onto the base of an equilateral prism as has been done in Figure 2g, which shows the ternary eutectic point. The ternary eutectic is at a lower temperature than any of the binary eutectics of the three two component systems making up the three component system. Eutectic troughs, indicated by the arrows in Figure 2g, lead from the binary eutectics to the ternary point.

In a three component system, a plot of the freezing points of all solutions, that is, of those temperatures at which liquid and solid are in equilibrium, gives rise to freezing surfaces, rather than freezing curves.

On mixing three liquids at a given temperature two conjugate solutions may again form, and the composition of these solutions will vary with temperature and overall composition, assuming pressure to be constant. Many possibilities exist for the shape of the heterogeneous region, depending at least in part on the behavior of the three binary systems which constitute the ternary system. However, in general one or more heterogeneous volumes will result, each of which is enclosed by a solubility surface, and outside of which is the homogeneous volume of the system. Many types of critical phenomena become possible, but those of particular interest to this study will be considered in the discussion of the experimental results.

A temperature projection of one example in which only two of the components form an immiscible binary pair is shown in Figure 2h.

3. IDEAL AND NON-IDEAL SOLUTIONS

A solution, or a solution region, is any multicomponent phase. Intersolubility of the components depends on the specific properties of the individual chemical species.

Raoult's law states that the escaping tendency of any chemical species is proportional to its mole fraction. A perfect or ideal solution is defined as one which obeys Raoult's law, and the escaping tendency of each chemical species in a perfect solution may be measured by its partial pressure. The essential condition of ideality is that there be no interaction between the chemical species. Since the molecules are very close together in a condensed phase, there is bound to be some interaction. However, it is necessary only that the molecules fail to distinguish between the various species for Raoult's law to be obeyed.

The mixing of two perfect solutions will give no change of volume and no change of heat content, since there will be no change in the mechanical or thermal energies. If the solutions are non-perfect and do not obey Raoult's law, there must be interaction either between the individual atoms, or molecules, or both. The interacting forces are responsible for the behavior of the solutions.

These forces may be classified as balanced, which are non-recognizable, net attractive, or net repulsive. A net attraction brings the molecules closer together, and lowers the vapor pressure below that required by Raoult's law. This is called a negative deviation from Raoult's law, and indicates a tendency towards compound formation. A net repulsion causes a greater separation of the atoms, and a subsequent elevation of the vapor pressure. This is known as a positive deviation from Raoult's law, and indicates a tendency towards incomplete miscibility.

The liquids studied in this investigation; nicotine, methylethylketone, and water; are not completely miscible at all temperatures. Their solutions would then appear to fall into the latter class exhibiting a positive deviation from Raoult's law. They are clearly non-ideal.

4. METHODS USED IN THIS INVESTIGATION TO DETERMINE EQUILIBRIUM DIAGRAMS

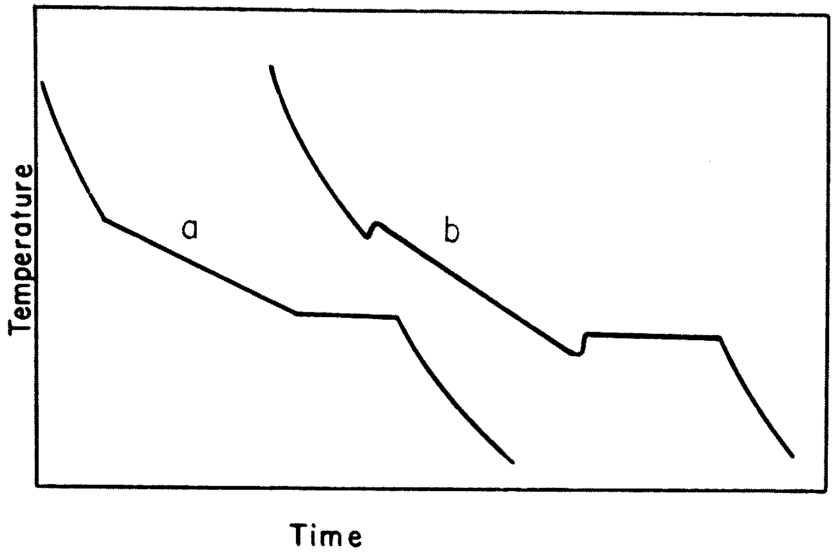
A. Freezing Point Diagrams

The method used to determine the freezing point diagrams was that of thermal analysis of solutions of predetermined concentration. This method may be applied to either two or three component systems, although it lends itself most readily to those of two components. It has the important advantages of speed and simplicity, although the method of isothermal solubility measurement is more accurate particularly where supercooling is pronounced. Extreme supercooling can, at times, be eliminated by inoculating the metastable solution with a crystal of the stable solid phase.

The method involves cooling a solution uniformly, and observing the change in temperature with time. When a phase change takes place, the rate of temperature change is reduced due to the latent heat effect, and a discontinuity in the cooling curve will result. If temperature is plotted against time, an exponentially decreasing curve will result in accordance with Newton's law of cooling. If the system is two component, a more or less sharp change of slope will result when a new phase appears, followed by a horizontal line of constant temperature at an invariant point. At an invariant point one phase disappears completely at a constant temperature.

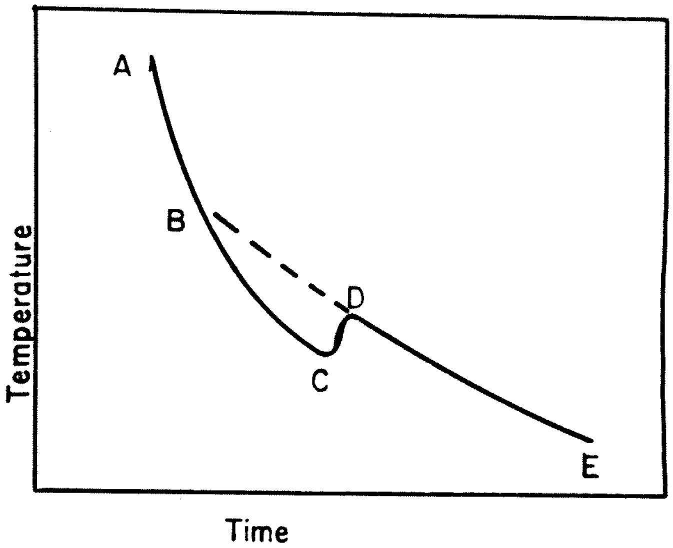
In actual practice, the cooling curve generally falls below the true freezing point, and then rises sharply as crystals form and heat is evolved from the phase change. Figure 3a shows an idealized cooling curve. Figure 3b shows the same cooling curve, but with supercooling occurring before crystalization begins, and again at the invariant point.

If the freezing point is not an invariant point, the cooling curve will not rise to the proper freezing point, but to some lower temperature. The deviation of this



TYPICAL COOLING CURVES

FIGURE 3



AN EXAMPLE OF FREEZING POINT DETERMINATION BY EXTRAPOLATION

FIGURE 4

temperature from the freezing point will depend on the degree of supercooling and on the rate of crystallization. Weissberger (11) and Andrews et al (12) discuss the precise determination of the freezing point in such a case. Figure 4, page 16, demonstrates the method followed in this investigation to obtain the true freezing point from a cooling curve exhibiting supercooling. ABCDE is a portion of the plot of the actual cooling curve. ABC represents the cooling of the liquid, C is the point at which crystallization begins, and DE represents concurrent cooling and crystallization. If DE, that portion of the cooling curve immediately succeeding the maximum which follows supercooling, is extrapolated back to the point B at which it intersects the curve ABC for the cooling of the unfrozen solution, then the temperature of B may be taken as an approximation of the true temperature of freezing. The deviation of this value from the true freezing point will be small if the supercooling is not excessive.

If the freezing point is an invariant, the curve will usually rise to the true invariant temperature, and remain at this point for a period of time, exhibiting a horizontal on the freezing curve.

The method of thermal analysis was not applied to the ternary system because the eutectic points in the nicotine-water and nicotine-methylethylketone systems could not be reached due to the high viscosities and extreme supercooling of the liquids, and also because the methylethylketone-water eutectic composition found by Randall and McKenna (3) is so close to pure water.

B. Isothermal Solubility Diagrams

The isothermal method may be used for both liquid-solid and liquid-liquid solubility curves; in this study it was used only for the liquid-liquid determinations. The overall composition of the mixture was made such that when equilibrium was attained, the two conjugate liquid layers were present in approximately equal volumes. The liquid was stirred at constant temperature for a period of time sufficient for the attainment of equilibrium, and then allowed to settle into two layers. A sample of each layer was taken and analysed.

For a two component system, the compositions of the two layers are functions of the temperature, and a plot of the equilibrium compositions against temperature will give the complete solubility curve. In a three component system, the compositions of the congruent solutions are functions of both temperature and overall composition. Therefore, if at a fixed temperature the overall composition is altered, an isothermal solubility curve is obtained. If the temperature is now altered, the form of the isothermal solubility curve will be changed. A three dimensional temperature-composition plot of the conjugate solution compositions will define the solubility surfaces which divide the homogeneous and the heterogeneous regions.

C. The Alexejew Method

When the temperatures, and hence the pressures, of the solutions became so great that the conjugate solutions could not be sampled satisfactorily, the method of isothermal analysis had to be abandoned in favour of the method of Alexejew (5). Mixtures of known composition were heated in completely closed cells, and were agitated by rotating the cells. The temperature at which the two conjugate solutions first became completely miscible was averaged with that at which the homogeneous solution first became heterogeneous. This point of known temperature and composition was a point on the solubility surface (or, in the case of only two components, it was a point on the solubility curve). This method does not have the accuracy of the method of isothermal analysis, nor does it yield tie lines between conjugate solutions. On the other hand, it has the advantages of being more rapid, and it can be used up to the temperature at which the liquids attack the glass of the cell, or at which the pressure of the contents is sufficient to burst the cell.

REVIEW OF THE LITERATURE

1. THE METHYLETHYLKETONE - WATER SYSTEM

Rothmund (2), Marshall (13), the Shell Chemical Company (6), and Randall and McKenna (3) have made solubility measurements in this system.

The first measurements were made by Rothmund using the method of Alexjew (5). He found the appearance of a minimum solubility temperature in the liquid-liquid equilibrium. He determined the upper critical solution temperature and composition, but he was unable to find a lower critical solution because of crystallization of the liquids. Marshall determined a few points above zero degrees Centigrade for this system, and found the solubilities to be greater than those originally found by Rothmund. The Shell Chemical Company investigated the system above zero degrees Centigrade in greater detail, and found the solubility curve to be in close agreement with that proposed by Marshall.

Randall and McKenna have determined the freezing curves for the system. The eutectic point was found to be $-88.88^{\circ}C.$ and 99.91 weight percent methylethylketone. The material solubilities were determined between $0^{\circ}C.$ and $-18.51^{\circ}C.$ by the method of isothermal analysis.

2. THE NICOTINE-WATER SYSTEM

This system was first investigated by Hudson (1) in 1904. He was unable to crystallize nicotine, since, on cooling, it formed an amorphous solid. Using the method of Alexejew, with solutions sealed in one millimetre capillary tubing, and heating in an air bath, Hudson determined the solubility curve for the nicotine-water system and found it to be completely closed. He found both critical compositions to be the same, 32.2 percent nicotine by weight. He found the lower critical solution temperature to be 61.0°C. and the upper to be 210°C.

Tsakalotos (14) repeated the work of Hudson in 1909 and found the saturation temperatures to be one to five degrees lower than those of Hudson. He found the upper and lower critical temperatures to be 208°C. and 60.8°C. respectively, and the critical composition for both to be thirty-four percent nicotine by weight. He found that the form of the curve was not influenced greatly by the use of an extremely pure sample.

Leone (15) in 1926 reconstructed the curve of the binary system nicotine-water, which, apart from small variations of less than two degrees, was identical to that found by Hudson. He used the method of Alexejew, placing his samples in Jena glass tubes which were sealed and placed in a double bath of paraffin oil. He found the upper critical temperature to be 213°C.

PURITY OF MATERIALS

The water used in this investigation was distilled from a Barnsted still with an all tin condenser. It was characterized by the following properties:

$n_C^{25^\circ}$ 1.33066

$n_F^{25^\circ}$ 1.33663

Specific Conductance ..... less than 5×10^{-6} mhos/cm.

The methylethylketone was Fischer Reagent grade, and was used without further purification. It was characterized by the following properties:

$d_{4^\circ}^{25^\circ}$ 0.79979

$n_C^{25^\circ}$ 1.37450

$n_F^{25^\circ}$ 1.38115

Relative Viscosity 0.4244

The nicotine was obtained from the Eastman-Kodak Company, who prepare the pure substance as follows:

> Our material is obtained from a commercial tobacco nicotine that we purify. This is done by making the material a salt and extracting the nonsalt materials from it. We then convert back to a base and distill.

It became yellow after exposure to the atmosphere, and was periodically distilled in an inert atmosphere under reduced pressure to give a clear, colorless product. During the investigation nicotine was recovered from methylethylketone and water solutions by vacuum distillation, and then redistilled as before to give the desired purity of product. The nicotine was characterized by the following properties:

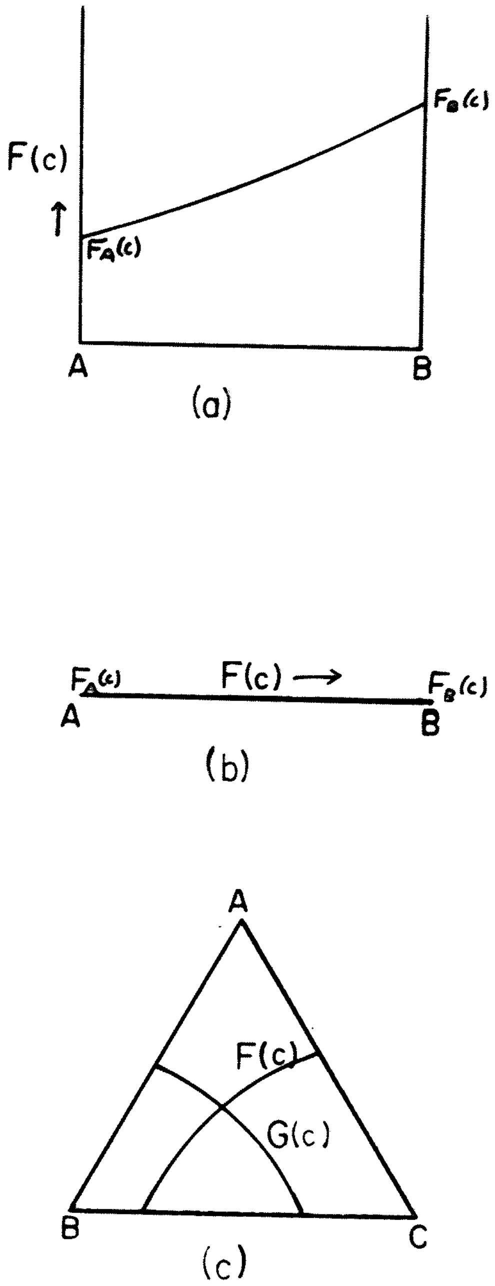
$d_{4^\circ}^{25^\circ}$	1.00677
$n_C^{25^\circ}$	1.52127
$n_F^{25^\circ}$	1.53606
Relative Viscosity	4.285

EXPERIMENTAL PROCEDURE AND APPARATUS

1. METHOD OF ANALYSIS

The method chosen to analyse the samples of the equilibrium layers was based on the physical properties of the solutions. If a particular property varies more or less linearly with composition between the two pure components of a solution, then fixing the value of that property will fix the composition of the solution. The accuracy of this method of analysis depends upon the accuracy with which the property can be measured, and upon the difference of the value of this property between one pure component and the other. Graphically, the property F(c) is plotted against composition C, as in Figure 5a. If the values of the property F(c) are projected on the base of the graph, 5a, then the plot is reduced to a linear one, and each point represents a particular composition and the corresponding value of the physical property (Figure 5b).

Physical analysis can be used for solutions of three components if the value of the physical property is sufficiently different for any two of the three pure components. For each solution there will be a fixed value for any given physical property. However, for any value



(a)

(b)

(c)

PHYSICAL PROPERTY PLOTS

FIGURE 5

of this property there will be an infinite number of solutions, and the locus of the compositions of these solutions will be a continuous curve on the composition-property diagram. If the property F(c) is projected onto the base of an equilateral prism, it will appear as a line superimposed on the composition; passing through a continuous series of compositions. If a second property G(c) is similarly projected onto this same planar diagram, it will appear as a second line passing through another series of compositions.

If these properties are independent, they should not form parallel lines on the projection, and will therefore intersect at a point. Since a point on the composition curve fixes the composition, then a determination of two independent properties will fix the composition. Figure 5c shows the intersection of one value of each of two physical properties superimposed on the three component composition diagram. The accuracy of the analysis depends upon the accuracy with which the properties can be measured, the difference between the values of the properties for the two pure components having the greatest difference, and upon the angle at which the plots of the two properties intersect. The accuracy is greatest if the two curves intersect orthogonally.

In order to choose a suitable pair of properties for the analysis of the nicotine-methylethylketone-water system, the density, viscosity, dispersion, and refractive indices for both hydrogen C (λ = 6563Å) and hydrogen F (λ = 4861Å) light were determined for various compositions. The results of the determinations are presented in Table I, page 55.

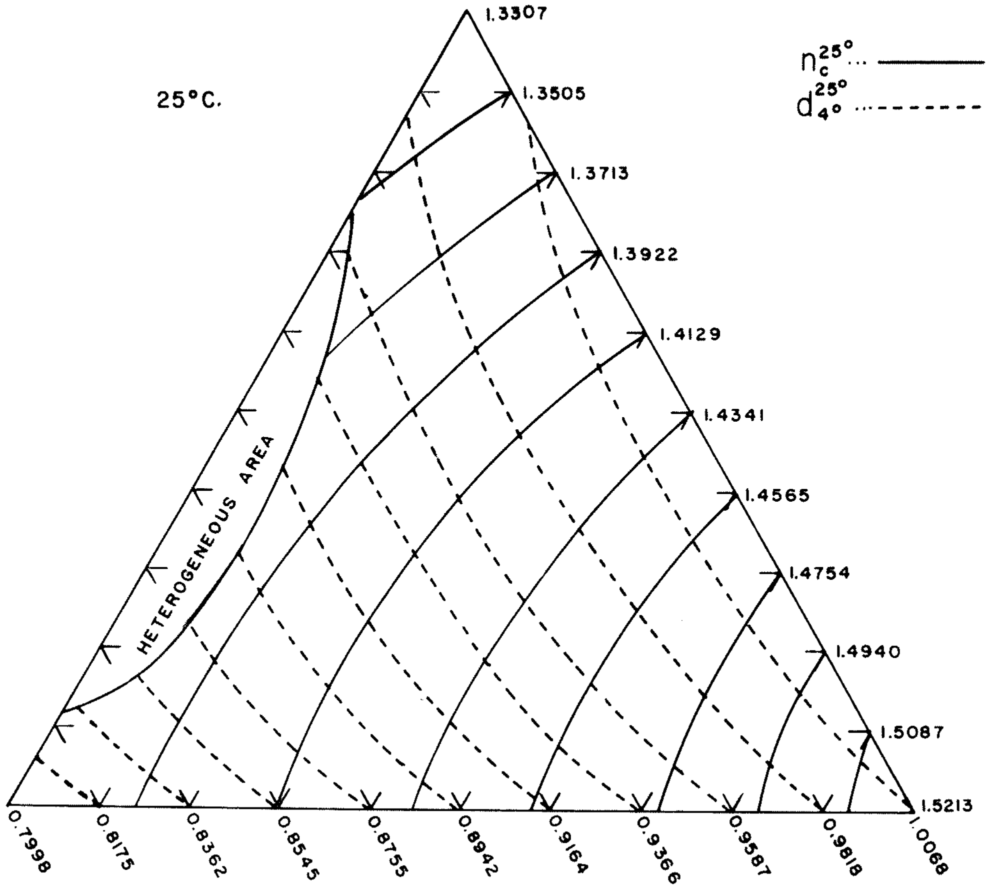
The refractive index for hydrogen red light (λ = 6563Å) and the density were chosen as the analytical properties. The plot of these properties on the composition diagram is shown in Figure 6.

Data have been published on the densities and viscosities of nicotine-water solutions at various temperatures (14), (16), (17), but this system was repeated in order that the values used be consistent with the method used in the rest of the study.

The density of a sample could be determined within ±0.0002 gm./cm.^{3}. The refractive index was accurate within ±0.0002 units. The greatest analytical error was in the extrapolation between determined points on the density and refractive index plots. The over all accuracy of the analysis was better than ± 0.5 percent by weight.

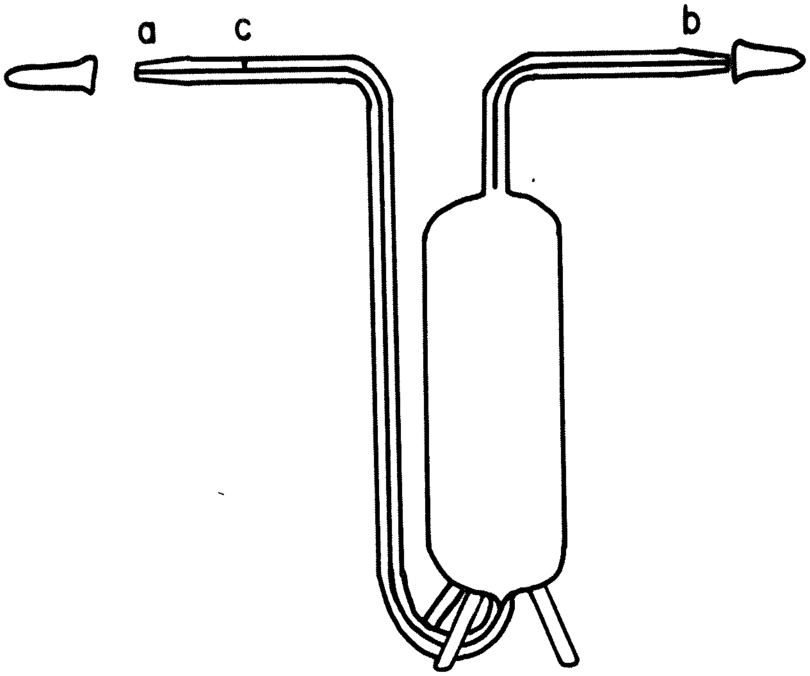
To check the method of analysis, a solution of known composition was analysed. The analysis of this solution was within the limits of experimental error.

The densities were determined using density bottles



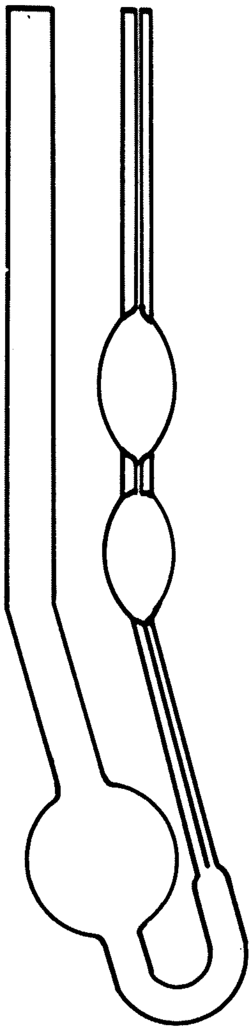
DENSITY AND REFRACTIVE INDEX PLOTTED ON A THREE COMPONENT COMPOSITION DIAGRAM

FIGURE 6



DENSITY BOTTLE

FIGURE 7



VISCOMETER

FIGURE 8

determinations. Three of these viscometers were calibrated using distilled water as a standard. The run times observed in the calibrations agreed within ± 0.2 seconds. The viscometers had run times of approximately one, two, and six minutes for water. Each viscometer was used with different solutions in order that a convenient run time could be obtained.

Five runs agreeing within ± 0.2 seconds were obtained for each sample. The relative viscosity was determined from the following relationship:

$$\text{Relative Viscosity} = \frac{t_x \cdot d^{25°}_{4°\,x}}{t_{H_2O} \cdot d^{25°}_{4°\,H_2O}}$$

where t = run time

$d^{25°}_{4°}$ = density

x = sample

H_2O = water standard

The refractive indices were determined on a Zeiss model Pulfrich refractometer, using the C and F lines of a hydrogen discharge tube. The zero point of the instrument was found by the method described in Findlay (18). The thermometer of the instrument was calibrated in the 25°C. thermostat. Temperature was controlled in the refractometer by circulating water at 25.0°C. from a reservoir through the jacket of the instrument. Control was better than ±0.05°C. over the short period of time required to determine the refractive index of a sample.

The instrument was standardized against distilled water that had been passed through an ion exchange column, and the operational error was found to be negligible. The literature values for water could be reproduced to better than 0.0001 units, or within plus or minus one minute on the instrument.

The dispersions were also determined using this instrument. The difference between the index of refraction of any substance for any two wave lengths is a measure of the dispersion for these wave lengths, called the coefficient of dispersion. The dispersions were found between hydrogen C and hydrogen F wave lengths. These were tabulated relative to the dispersion of water which was arbitrarily given a value of unity.

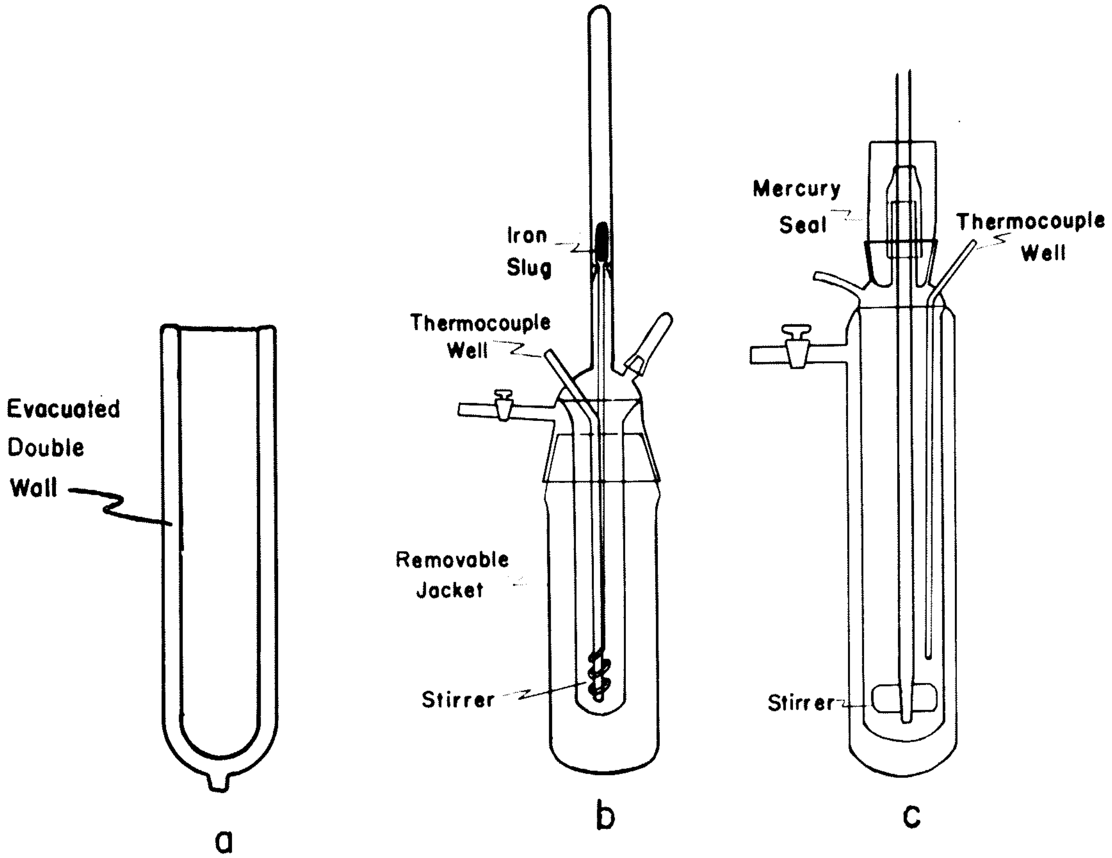
2. FREEZING POINT DIAGRAMS BY THERMAL ANALYSIS

The freezing points of the pure components and of all the solutions to be investigated lay at or below the freezing point of water, 0°C. The actual freezing temperatures were determined by the method of thermal analysis. The liquids were stirred in a cell which was immersed in a Dewar flask filled with either liquid nitrogen or a dry ice-acetone mixture; the change of temperature of the liquid with time was observed.

It was found necessary to use three types of cells in this investigation. These are shown in Figure 9. These cells differ primarily in the method of stirring the freezing liquid. In each case the liquid was enclosed in an evacuated jacket which insulated it from the coolant, and reduced the rate of cooling.

In the simplest of the three, and unsilvered Dewar flask (Figure 9a), the liquid was stirred manually by raising and lowering the glass loop about a Beckmann thermometer or a thermocouple well. This cell was used for those solutions in the binary system nicotine-water having compositions ranging from pure water to forty percent nicotine; sixty percent water. These solutions all crystallized at temperatures above $-4^{\circ}C$. The Beckmann thermometer was calibrated at the ice point of distilled water before and after the experimental runs. The calibrations agreed within $\pm 0.001^{\circ}C$. (The water used was distilled from a Barnsted still with a tin condenser. It had a specific conductance of not more than 5×10^{-6} mhos/cm.)

The cell was immersed in a Dewar flask containing crushed dry ice and acetone. A liquid sample of known composition was placed in the cell and stirred vigorously. Temperature readings were made periodically, and the



CELLS FOR THERMAL ANALYSIS

FIGURE 9

temperature was plotted against time to give the cooling curve of the liquid mixture. Several trials were made for each liquid, and the freezing points were read from the cooling curves in the manner described previously. No eutectic halts were observed in the cooling curves, because the liquid became so viscous that crystallization did not occur.

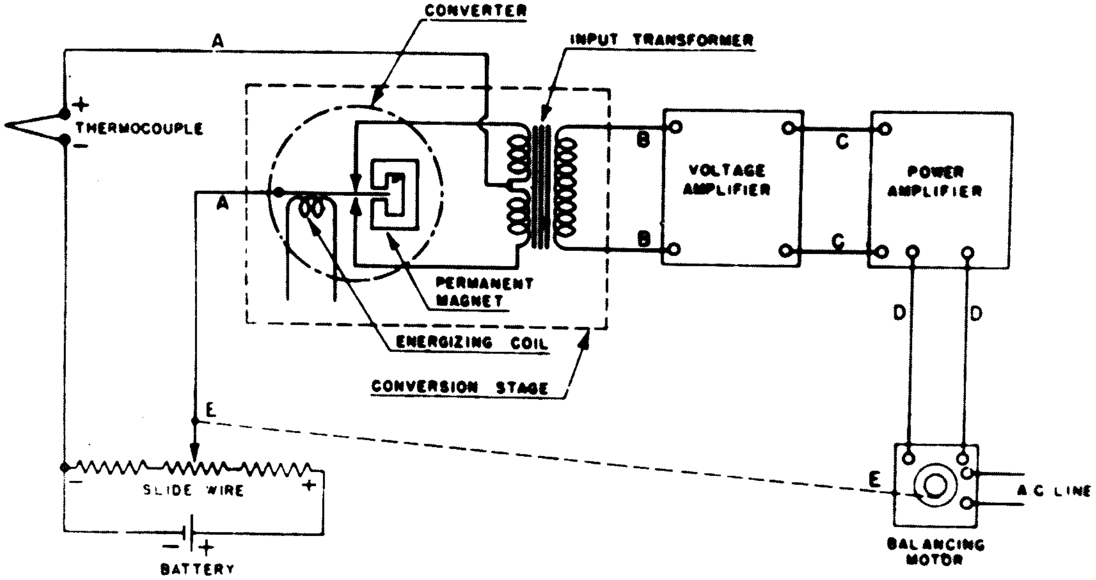
The freezing points of all other liquids investigated were more remote from zero degrees. The freezing points of solutions of nicotine in water having compositions of fifty, sixty, and sixty-five percent nicotine by weight were determined in the same type of cell, using hand stirring, but a thermocouple was used to measure the temperature in these cases. Hand stirring was required for these solutions because they became extremely viscous as the freezing points were approached.

To obtain the cooling curves of these solutions a two-junction copper-constantan thermocouple (19) was used in conjunction with a Brown recording potentiometer. The reference junctions of the thermocouple were placed in a six millimetre glass tube, sealed at one end, and immersed in a Dewar flask of crushed ice and water.

The thermocouple and the recording potentiometer were calibrated together at low temperatures from the freezing points of redistilled mercury (-38.87°C.), refractive index grade acetone (-94.6°C.), ethylbromide (-119°C.), and ethylene dichloride (-35.3°C.), and the eutectic point of reagent grade chloroform and carbon tetrachloride (-81.4°C.). These points are all well known, and the liquids could all be obtained in a state of high purity and exhibited little tendency towards extreme supercooling.

A schematic diagram of the Brown recording potentiometer is shown in Figure 10. This instrument operates as a basic potentiometer, but is self-balancing; the recorder plots a continuous E. M. F. versus time curve. Since the E. M. F. of the thermocouple is a direct function of the temperature, this is the equivalent of a temperature versus time plot, or cooling curve.

In a potentiometer, a known E. M. F. is varied by varying resistance until it is equal and opposite to the unknown E. M. F. which in this case arises from the thermocouple. At all points on the slide wire a potential difference exists between the known E. M. F. from the battery and the unknown E. M. F. from the thermocouple, except at the balance point. A d. c. voltage will appear across AA in the direction of unbalance. The "conversion stage" converts this d. c. voltage to an a. c. voltage at BB which passes through the "voltage amplifier." This a. c. voltage controls the "power amplifier" output which in turn drives the "balancing motor" which moves the slide wire contact



SCHEMATIC CIRCUIT DIAGRAM OF THE BROWN RECORDING POTENTIOMETER

FIGURE 10

and the recording pen. The battery is frequently standardized, automatically or manually, against a standard cell.

The recorder used has a range of zero to ten millivolts, and the chart can be read to ± 0.05 millivolt. The two-junction couple has a temperature coefficient of about 0.08 millivolt per degree. This enables the temperature to be obtained within ± 0.5°C. The range of the potentiometer with the two-junction thermocouple is from zero to about -130°C.

As before, the cell was immersed in a dry ice-acetone coolant, the sample of known composition was introduced into the cell, and was stirred vigorously as it cooled. A continuous temperature versus time plot was obtained, and from this the freezing temperature of the sample was determined. No eutectic halts were observed.

The sixty-five percent nicotine-thirty-five percent water solution became very viscous at the freezing temperature (-22.1°C.), and at -26°C. stirring became impossible. The seventy percent nicotine-thirty percent water solution became too viscous to permit stirring at -30°C., and crystallization of this solution could not be attained.

A magnetic stirring device was used in the second cell, Figure 9b (20). Two horseshoe magnets are driven up and down along a vertical track by a six volt windshield wiper motor, and they in turn raise and lower a glass spiral which has a piece of soft iron rod enclosed in glass affixed to its upper end. The glass stirring coil slides up and down around the thermocouple well. The sample is introduced through a ground glass joint, which is then capped to prevent condensation from the atmosphere. The cell was enclosed by an outer jacket which was evacuated to a greater or lesser extent to control the rate of cooling. The cell and jacket were immersed in a Dewar flask of liquid nitrogen, and the temperature versus time curve was obtained as before using the two-junction copper-constantan thermocouple and the Brown recording potentiometer.

This apparatus was used for those solutions of the methylethylketone-nicotine binary system which solidified without a great increase in the viscosity of the liquids; that is, those solutions having a nicotine content of fifty percent or less by weight.

The third cell, Figure 19c (20) differed from the second only in the manner of stirring. This last cell was fitted with a mercury seal and a motor-driven paddle stirrer. This mechanical stirrer could be used with liquids of a much greater viscosity than was possible with the relatively weak magnetic stirring device.

An attempt was made to crystallize pure nicotine, using this cell in a Dewar flask of liquid nitrogen. The nicotine solidified without crystallizing at about -60°C., or at least it became so viscous at this temperature that it broke the glass thermocouple well. By -100°C. to -120°C. it had become a solid glassy mass. A smooth cooling curve was obtained with no irregularities or breaks. In the attempt to crystallize nicotine, slow and rapid cooling, with and without stirring were used with both pure nicotine, and samples containing trace amounts of either water or methylethylketone. Crystallization of the nicotine could not be obtained.

All solutions of water-nicotine containing more than sixty-five percent nicotine by weight solidified without crystallization. Those solutions of methylethylketone-nicotine containing more than fifty percent nicotine by weight solidified without crystallization. No eutectics were obtained for these binary systems.

The freezing curve of the methylethylketone-water binary system had been determined previously (3) and was not repeated.

No attempts to locate the ternary eutectic were made, since the binary eutectic points were unattainable.

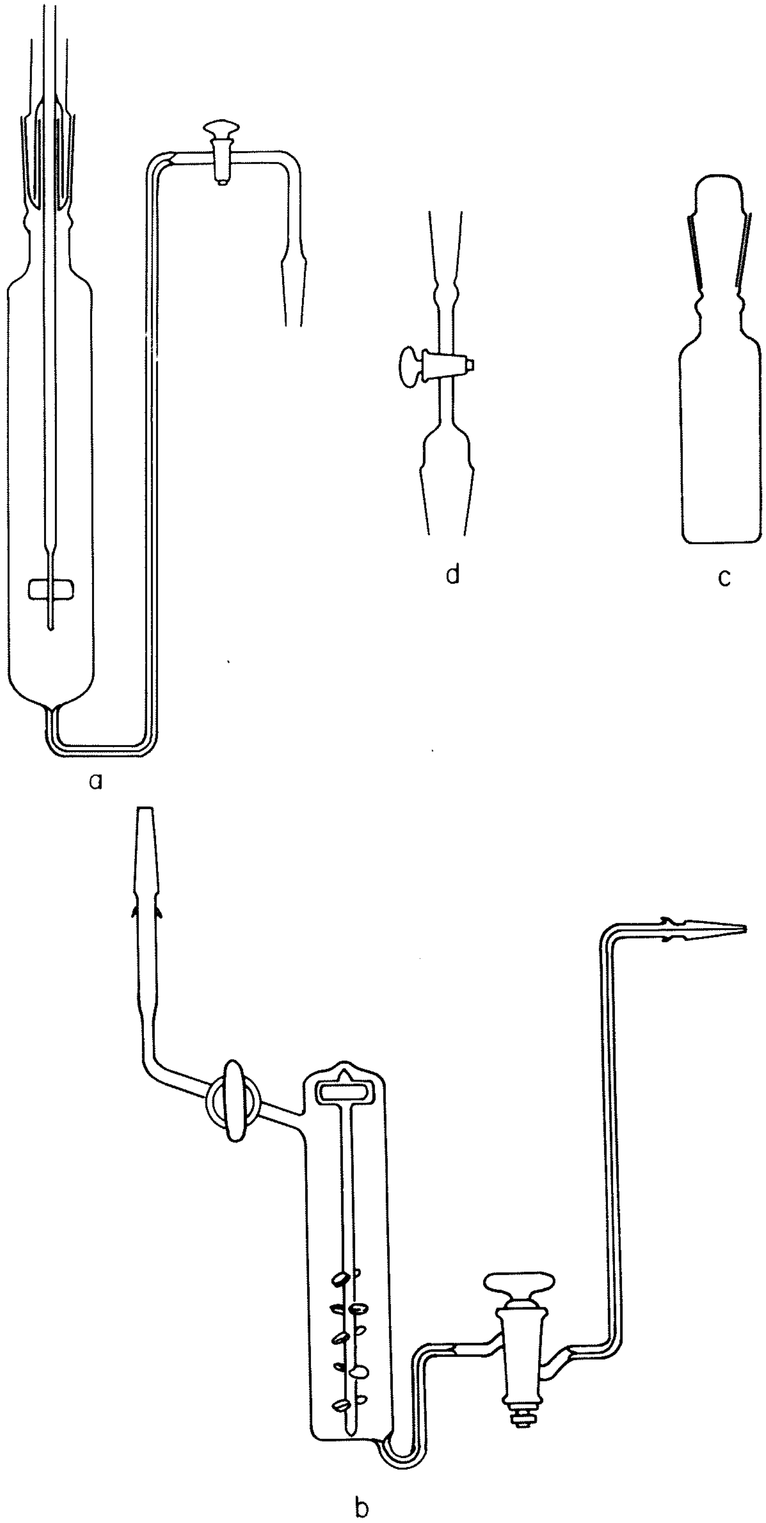
The freezing curves are plotted in Figure 12 and Figure 13, pages 64 and 65 respectively, and the data are presented in Table II, and Table III, page 57.

3. ISOTHERMAL SOLUBILITY DIAGRAMS

The two types of equilibrium cells used for isothermal solubility measurements are shown in Figure 11. The first of these, Figure 11a, was used with liquid mixtures whose total vapor pressure was below atmospheric pressure. The mixtures were made up to approximately known overall compositions such that two equilibrium layers of more or less equal volumes would form at the temperature in question. A sufficient number of conjugate pairs were examined such that the isotherms studied were completely outlined.

Three thermostats were used during the isothermal investigations.

For the -11.4°C. and the 5°C. isotherms, cooling of the bath was effected by circulating cooled kerosene through a copper coil immersed in a metal vessel containing five gallons of kerosene and wrapped with felt. The bath was stirred at all times by two paddle stirrers. Temperature was controlled by a mercury bulb thermoregulator which activated a two way relay. This relay operated either a forty watt light bulb if the bath temperature became too low or a circulating pump which circulated kerosene through the coil if the bath temperature became too high. The kerosene was cooled by circulation through a second coil immersed in a Dewar flask filled with a dry ice-acetone cooling mixture. This mixture was stirred when the pump was in operation to



CELLS FOR ISOTHERMAL ANALYSIS

FIGURE 11

prevent the acetone mixture from boiling over. The thermostat was controlled to within ±0.3°C.

The second thermostat was used for the density and viscosity measurements, and the 25.0°C. isotherm. It maintained a constant temperature of 25°C. ±0.01°C.

The third thermostat was used for all temperatures above 25.0°C. It was a vessel insulated with felt and filled with a suitable oil. A heating coil was placed in the bath. This coil was controlled by an electronic relay activated by a mercury bulb thermoregulator immersed in the oil bath. The power, drawn by the heater, was controlled by a powerstat in series with the coil. The bath was stirred by two paddle-type motor-driven stirrers at all times. Temperatures in the thermostat could be maintained within ±0.2°C.

The cell shown in Figure 11a was filled with about one hundred grams of sample through the opening at the top with the stopcock closed. The opening was fitted with a mercury seal, and the liquid mixture was stirred in a thermostat for not less than one hour in order that thermal and chemical equilibrium be attained. Then the seal was removed and replaced by a ground glass stopper. The liquid mixture was allowed to settle into two distinct layers. This pair of equilibrium solutions was the conjugate pair for the particular overall composition chosen at that given temperature. To withdraw samples of these layers, a glass container of the type shown in Figure 11c was fitted with the stopcock and ground glass fitting, Figure 11d, and evacuated. The stopcock was closed and the fitting attached to the cell. The stopcock on the cell was opened fully, and that on the fitting was opened gradually to allow liquid to flow from the cell, through the capillary tubing, and into the glass container.

A little of the liquid was first washed through and discarded, so that the first sample would be representative of the bottom layer. The liquid in the vicinity of the inter-liquid boundary was also washed through and discarded. A sample of the upper layer was taken, and the last portion of the liquid was discarded. The samples were retained in the glass containers which were fitted with ground glass stoppers. All sampling was done while the cell remained in the thermostat.

The sample was allowed to come to room temperature. If it was homogeneous at this temperature and was over fifty millilitres in volume, it was analysed directly by a density and refractive index determination. If it became heterogeneous at 25°C., or if it was of less than fifty millilitres volume, as was generally the case, it was weighed. A known mass of one of the three components of the system was then added to the sample to give the required volume or to render the mixture homogeneous. This sample was then analysed as before, and the original composition was calculated.

This cell and method sampling was used for the following isothermal solubility determinations:

-11.4°C. isotherm. This study was carried out in the refrigerated kerosene bath. Temperature was controlled to ± 0.3°C., and was measured with a toluene in glass thermometer (graduated in degrees Centigrade) which had been calibrated at four points; the 25.00 ± 0.01°C. thermostat; the freezing point of distilled water; the freezing point of mercury; a dry ice-acetone mixture.

5.0°C. isotherm. This study was carried out in the refrigerated kerosene bath. Temperature was controlled to ± 0.3°C., and was measured with a mercury in glass thermometer (graduated in one-tenths of a degree Centigrade) which had been calibrated against freezing distilled water and the 25.00 ± 0.01°C. thermostat.

25.0°C. isotherm. This study was carried out in the 25.00 ± 0.01°C. thermostat. The temperature was measured with a Beckmann thermometer, which had been calibrated against a platinum resistance thermometer.

50.0°C., 65.0°C., 67.5°C., 70.0°C., and 85.0°C. isotherms. These isotherms were determined in the oil bath with the immersed heating coil. Temperature was controlled to ± 0.2°C. and was measured with a mercury in glass thermometer (graduated in one-tenths of a degree Centigrade).

This had been calibrated against a total immersion thermometer which had in turn been calibrated at ten degree intervals against a platinum resistance thermometer. The calibration of the thermometer used thus included the correction for exposed stem.

The cell shown in Figure 11b was constructed of heavy-walled glass and was used for solutions whose total vapor pressure was greater than one atmosphere. Its total volume was somewhat less than that used for the lower pressures, and about eighty millilitres of sample were introduced through the neck of the cell. This opening was closed by the high pressure stopcock after filling. The capillary arm for withdrawing samples was also closed with a high pressure stopcock. The sample was stirred by the glass propellers on the glass rod when a motor driven horseshoe magnet was rotated above the iron slug in the cell. The cell was completely immersed in the thermostat, except for the end of the delivery tube, which was isolated from the contents of the cell by the high pressure stopcock. When samples were required, the stopcock on the capillary delivery tube was turned while immersed in the oil in the bath by means of a slotted hardwood rod. Some difficulty was encountered due to the stopcock leaving its seat when it was turned, particularly at the higher pressures. This was partially overcome by employing a more powerful spring to hold the stopcock in place, and by the use of the minimum amount of stopcock grease.

Due to the danger of explosion at higher pressures, the entire thermostat was enclosed in a large box made of seven-ply plywood. A small opening was provided for the manipulation of equipment in the box. A plate glass window, reinforced with wire, was provided in order that the behavior of the liquids in the cell could be observed. The lower half of the front of the box was hinged to allow free access to the thermostat at safe pressures. A preliminary trial showed that the cell would withstand pressures up to twenty atmospheres.

The method of sampling was similar to that used for cell A. An extension of the delivery arm was connected to the ground glass fitting D which was in turn connected to the collecting vessel C. This vessel was surrounded by an ice water mixture to cool the liquids quickly so as to prevent composition changes by evaporation. The container C was evacuated only for samples at 115°C. There was sufficient pressure at the other temperatures to drive the samples from the cell without evacuation of the receiver. For these isotherms (other than 115°C.) an extension of the delivery arm of the cell was run to the bottom of the receiving bottle C, and sampling was done very slowly to allow the samples to condense and cool, and thus prevent evaporation losses.

The samples taken were treated as before. They were first diluted to provide a homogeneous solution of the required volume, then analysed, and their composition determined.

Isotherms were determined at 115.0°C., 140.0°C., and 143.0°C. using this cell and method. The nicotine-water binary conjugate pair at 150.0°C. was also determined, but samples could not be taken of three component mixtures at this temperature because the stopcock could not be turned without it leaving its seat.

Temperature was controlled to ± 0.2°C., and was measured as before by a mercury in glass thermometer (graduated in one-tenths of a degree Centigrade), calibrated against a total immersion thermometer which had in turn been calibrated against a platinum resistance thermometer.

The data for the solubility measurements are listed in Table IV, page 58 and sketches of the isothermal solubility diagrams are shown in Figure 14, page 66.

4. THE ALEXEJEW METHOD

The method of isothermal analysis was abandoned due to difficulties in sampling at high temperatures and pressures. To complete the solubility studies in the ternary system at temperatures above 143.0°C. the method of Alexejew was used to outline the region of incomplete miscibility.

Samples of known composition by weight were placed in heavy-walled glass cells eight millimetres in cross-section and twelve centimetres in length. These cells were filled to approximately two-thirds capacity, and then sealed with a torch, care being taken that the sample was kept cool to prevent composition changes due to evaporation. The cells were placed, one by one, into a variable temperature bath, filled with silicone oil. The temperature at which homogeneity occurred on heating was noted, and also the temperature at which heterogeneity occurred on cooling. The mean of these two observed temperatures was taken to be the solution temperature for the composition in question.

The bath was a glass vessel with a capacity of about three gallons. It was partially filled with two gallons of silicone oil. Heating was effected by two knife edge heaters, one of five hundred watts, and the other of two hundred and fifty watts. A bimetal thermoregulator was placed in series with the smaller heater, so that the temperature of the bath could be held constant if desired, and also so that the rate of heating or cooling the bath could be controlled. It was found that a temperature gradient of one degree per five minutes was most satisfactory in the region of the solution temperature.

The cells were held in the bath by two spring clips on a rectangular metal plate. The plate was affixed to a sprocket mounted on an angle iron bar. A metal frame encased the glass bath, and held it in position. The angle iron bar was attached to this frame, and reached nearly to the bottom of the liquid. A motor which drove a second sprocket was supported on the frame. A drive chain connected the two sprockets, so that the cell could be rotated. The motor was connected in series to a powerstat, so that the rate of rotation could be varied from zero to seventy revolutions per minute. The contents of the cells were stirred thoroughly by rotation in the bath. However, at higher rates of rotation, the centrifugal force prevented the liquids in the cells from flowing freely from end to end of the cells, and thus inhibited thorough mixing. The rotation of the cell, plate, sprocket, and chain also provided adequate agitation of the bath liquid.

An uncalibrated mercury in glass thermometer was placed in the bath to indicate the approximate bath temperature, but the temperature of homogeneity or heterogeneity were measured with a single-junction copper-constantan thermocouple. This thermocouple was calibrated against the freezing points of extremely pure indium (156.5°C.), tin (231.9°C.), and lead (327.3°C.). Temperatures could be measured to better than ± 0.5°C. using the bath and thermocouple described. The calibration was repeated after the experimental observations had been made, and the results agreed within the experimental error with the original calibration. As a further check on the reliability of the temperature measurements of phase changes within the glass cells, a sample of pure tin was placed in a glass cell of the type described, and its melting and freezing points were determined using the conditions of the experiments. The mean of these two temperatures agreed within the experimental error with the calibration value.

Most of the compositions studied formed homogeneous solutions at room temperature. For these, ten grams of solution were made up to a known composition, and an aliquot sample was taken for observation. The remaining compositions, which were heterogeneous at room temperature, were made up by weighing the components directly into the cells.

The cells were illuminated for observation by a photospot light, mounted outside the bath, and turned on only as required. No difficulty was encountered in observing the state of the samples in the cells using this form of illumination.

The data for these observations are listed in Table V, page 61. Figure 15, page 68, shows temperature versus composition plots for fixed percentages of methylethylketone.

To check the upper critical solution temperature approximately, an aliquot of a few drops of the nicotine-water upper critical solution composition was sealed in a one inch piece of heavy-walled, one millimetre capillary tubing. This was placed in an electrically heated melting point apparatus, and viewed through a magnifying lens. The thermocouple was placed in the opening with the small cell, and the top of the opening was plugged with asbestos wool to prevent heat loss. The total volume of the air space into which the cell was placed was between three and four cubic centimetres. Using this apparatus, the upper critical solution temperature was found to be 234 ± 2°C.

EXPERIMENTAL RESULTS

The tables of experimental results, and the graphs of some of these data, are set forth in the following pages. The significance of these results has been explained in the outline of the experimental procedure, and is discussed further under Discussion of Results.

TABLE I

PHYSICAL PROPERTIES OF SOLUTIONS OF NICOTINE, METHYLETHYLKETONE AND WATER AT 25°C.

Composition Weight Percent			Density gm./cm.^{3}	Relative Viscosity	Relative Dispersion	Refractive Index	
Water	Nicotine	MEK				C λ = 6563Å	F λ = 4861Å
100	-	-	0.99706	1.0000	1.000	1.33066	1.33663
90	10	-	1.00351	1.457	0.824	1.35046	1.35722
80	20	-	1.01046	2.285	0.718	1.37127	1.37853
70	30	-	1.01718	3.693	0.617	1.39217	1.40036
60	40	-	1.02369	5.973	0.520	1.41290	1.42247
50	50	-	1.02921	9.884	0.468	1.43407	1.44428
40	60	-	1.03409	16.020	0.401	1.45649	1.46768
30	70	-	1.03525	23.376	0.345	1.47536	1.48751
25	75	-	1.03500	26.128	-	-	-
20	80	-	1.03169	25.819	0.292	1.49397	1.50705
10	90	-	1.02173	14.369	0.242	1.50867	1.52267
-	100	-	1.00677	4.285	0.192	1.52127	1.53606
90	-	10	0.98416	1.260	0.934	1.33888	1.34491
80	-	20	0.97095	1.517	0.932	1.34763	1.35287
8	-	92	0.82085	0.5570	0.735	1.37632	1.38307
-	-	100	0.79979	0.4244	0.746	1.37450	1.38115
-	10	90	0.81750	0.4777	0.681	1.38670	1.39392
-	20	80	0.83619	0.5487	0.642	1.40019	1.40775
-	30	70	0.85454	0.6326	0.579	1.41310	1.42140
-	40	60	0.87549	0.7560	0.502	1.42882	1.43842
-	50	50	0.89421	0.9089	0.449	1.44173	1.45225
-	60	40	0.91636	1.129	0.390	1.46147	1.47290
-	70	30	0.93655	1.412	0.336	1.47242	1.48479

TABLE I (continued)

Composition Weight Percent			Density gm./cm.^{3}	Relative Viscosity	Relative Dispersion	Refractive Index	
Water	Nicotine	MEK				C λ= 6563Å	F λ= 4861Å
-	80	20	0.95868	1.882	0.300	1.48752	1.50071
-	90	10	0.98181	2.696	0.239	1.50475	1.51875
60	10	30	0.95658	2.141	0.723	1.37411	1.38307
50	10	40	0.93580	2.043	0.708	1.37854	1.38565
40	10	50	0.91412	1.824	0.698	1.38298	1.38999
30	10	60	0.89191	1.460	0.698	1.38590	1.39289
20	10	70	0.86943	1.050	0.689	1.38844	1.39542
10	20	70	0.86477	0.8782	0.642	1.40218	1.40968
70	20	10	0.99595	2.669	0.684	1.37971	1.38721
20	30	50	0.91234	1.769	0.568	1.41622	1.42474
50	30	20	0.98251	3.792	0.588	1.40588	1.41434
20	50	30	0.95795	3.740	0.462	1.44546	1.45564
10	80	10	0.99742	7.293	0.307	1.49284	1.50563

TABLE II

FREEZING POINT DATA FOR THE BINARY SYSTEM NICOTINE-WATER

Composition Weight Percent		Freezing Point °C.
Water	Nicotine	
100	-	0.00
90	10	-0.854 ± 0.003
80	20	-1.455 ± 0.010
70	30	-2.270 ± 0.010
60	40	-3.642 ± 0.013
50	50	-5.9 ± 0.5
40	60	-12.7 ± 0.5
35	65	-22.1 ± 0.5

TABLE III

FREEZING POINT DATA FOR THE SYSTEM NICOTINE-METHYLETHYLKETONE

Composition Weight Percent		Freezing Point °C.
MEK	Nicotine	
100	-	-87.0 ± 0.5
90	10	-88.3 ± 0.5
80	20	-89.7 ± 0.5
70	30	-91.8 ± 0.5
60	40	-94.0 ± 0.5
50	50	-99 ± 3

TABLE IV

DATA FOR THE ISOTHERMAL SOLUBILITY MEASUREMENTS

Composition of Top Layer			Composition of Bottom Layer		
Wt.% H_2O	Wt.% Nic.	Wt.% MEK	Wt.% H_2O	Wt.% Nic.	Wt. % MEK
-11.4°C. Isotherm					
13.2	-	86.8	56.2	-	43.8
19.5	1.0	79.5	47.0	1.6	51.4
23.2	1.6	75.2	40.2	2.5	57.3
Plait Point (extrapolated)			30.8	2.5	66.7
5.0°C. Isotherm					
13.0	-	87.0	65.7	-	34.3
15.0	2.0	83.0	59.5	2.2	38.3
24.1	5.7	70.2	44.4	6.0	49.6
Plait Point (extrapolated)			33.0	7.0	60.0
25.0°C. Isotherm					
11.6	-	88.4	74.5	-	25.5
15.3	5.8	78.9	68.6	2.8	28.6
21.4	8.8	69.8	62.0	5.0	33.0
29.9	9.2	60.9	53.2	6.5	40.3
Plait Point (extrapolated)			41.0	8.6	50.4
50.0°C. Isotherm					
12.9	-	87.1	79.4	-	20.6
17.6	8.8	73.6	76.2	2.4	21.4
25.4	16.0	58.6	70.6	5.8	23.6
36.8	17.9	45.3	62.3	9.6	28.1
Plait Point (extrapolated)			49.3	14.6	36.1

TABLE IV (continued)

Composition of Top Layer			Composition of Bottom Layer		
Wt.% H_2O	Wt.% Nic.	Wt.% MEK	Wt.% H_2O	Wt.% Nic.	Wt.% MEK
65.0°C. Isotherm					
14.2	-	85.8	81.7	-	18.3
18.4	9.5	72.1	79.4	1.8	18.8
21.9	17.9	60.2	77.5	3.9	18.6
29.6	25.0	45.4	74.7	7.4	17.9
45.0	27.5	27.5	64.4	16.2	19.4
Plait Point (extrapolated)			55.3	22.6	22.1
82.4	17.6	-	43.4	56.6	-
70.4	26.0	3.6	53.0	44.3	2.7
Plait Point (extrapolated)			61.6	34.7	3.7
67.5°C. Isotherm					
26.5	22.3	51.2	76.1	6.6	17.3
43.4	32.8	23.8	70.0	16.0	14.0
53.6	32.1	14.3	65.4	22.8	11.8
54.1	35.4	10.5	68.0	23.2	8.8
45.7	50.5	3.8	78.4	18.9	2.7
70.0°C. Isotherm					
27.0	27.3	45.7	77.5	6.5	16.0
38.3	33.7	28.0	75.7	11.7	12.6
42.6	40.2	17.2	73.8	15.2	11.0
43.0	49.4	7.6	77.1	15.6	7.3
87.2	12.8	-	35.7	64.3	-
85.0°C. Isotherm					
16.1	-	83.9	81.4	-	18.6
20.9	18.2	60.9	81.9	2.6	15.5
24.0	33.7	42.3	80.4	6.4	13.2
27.5	48.7	23.8	82.9	7.2	9.9
28.2	50.5	22.3	85.0	7.0	8.0
30.3	58.7	11.0	86.6	7.7	5.7
28.0	67.0	5.0	88.6	8.0	3.4
90.5	9.5	-	25.0	75.0	-

TABLE IV (continued)

Composition of Top Layer			Composition of Bottom Layer		
Wt.% H_2O	Wt.% Nic.	Wt.% MEK	Wt.% H_2O	Wt.% Nic.	Wt. % MEK
115.0°C. Isotherm					
23.1	-	76.9	78.9	-	21.1
26.5	29.3	44.2	81.5	4.5	14.0
24.2	44.9	30.9	84.6	5.6	9.8
20.7	64.9	14.4	88.8	5.5	5.7
19.3	80.7	-	96.8	3.2	-
140°C. Isotherm					
40.2	-	59.8	68.3	-	31.7
37.6	12.1	50.3	73.0	3.2	23.8
34.2	25.0	40.8	77.5	5.5	17.0
27.3	45.6	27.1	85.3	5.9	8.8
21.8	60.6	17.5	87.2	6.8	6.0
17.0	83.0	-	93.7	6.3	-
143°C. Isotherm					
27.6	42.5	29.9	82.6	6.0	11.4
36.8	19.6	43.6	76.3	5.7	18.0
49.1	4.9	46.0	64.0	3.7	32.3
Plait Point (extrapolated)			56.0	1.7	42.3
Nicotine-Water at 62.0°C.					
70.0	30.0	-	57.1	42.9	-
Nicotine-Water at 150.0°C.					
16.8	83.2	-	94.0	6.0	-

TABLE V

DATA FOR THE ALEXEJEW MEASUREMENTS

Composition			Upper Temperature Limit of Heterogeneous Volume °C.
Wt. % MEK	Wt. % H_2O	Wt. % Nic.	
-	20.0	80.0	183.0 ± 0.5
-	25.0	75.0	203.5
-	32.0	68.0	219.5
-	43.0	57.0	231.0
-	54.0	46.0	232.5
-	62.0	38.0	233.0
-	68.0	32.0	232.5
-	73.0	27.0	231.5
-	85.0	15.0	218.0
-	90.0	10.0	200.0
10.0	25.0	65.0	180.0
10.0	40.0	50.0	205.5
10.0	48.0	42.0	207.0
10.0	55.0	35.0	205.5
10.0	59.0	31.0	205.0
10.0	63.0	27.0	202.0
10.0	70.0	20.0	196.0
10.0	80.0	10.0	171.0
20.0	29.0	51.0	168.5
20.0	40.0	40.0	182.5
20.0	45.0	35.0	183.0
20.0	50.0	30.0	181.0
20.0	55.0	25.0	178.0
20.0	63.0	17.0	169.5
20.0	70.0	10.0	156.0
30.0	35.0	35.0	159.5
30.0	45.0	25.0	163.0
30.0	52.0	18.0	157.0
30.0	63.0	7.0	146.0
40.0	37.0	23.0	146.5
40.0	45.0	15.0	147.5
40.0	50.0	10.0	145.5
* 40.0	55.0	5.0	143.5
45.0	42.0	13.0	143.5
* 45.0	47.0	8.0	144.5

* These samples were made up by direct weighing, as they were heterogeneous at room temperature.

TABLE VI

DATA FOR THE MUTUAL SOLUBILITIES OF THE METHYLETHYLKETONE-WATER SYSTEM

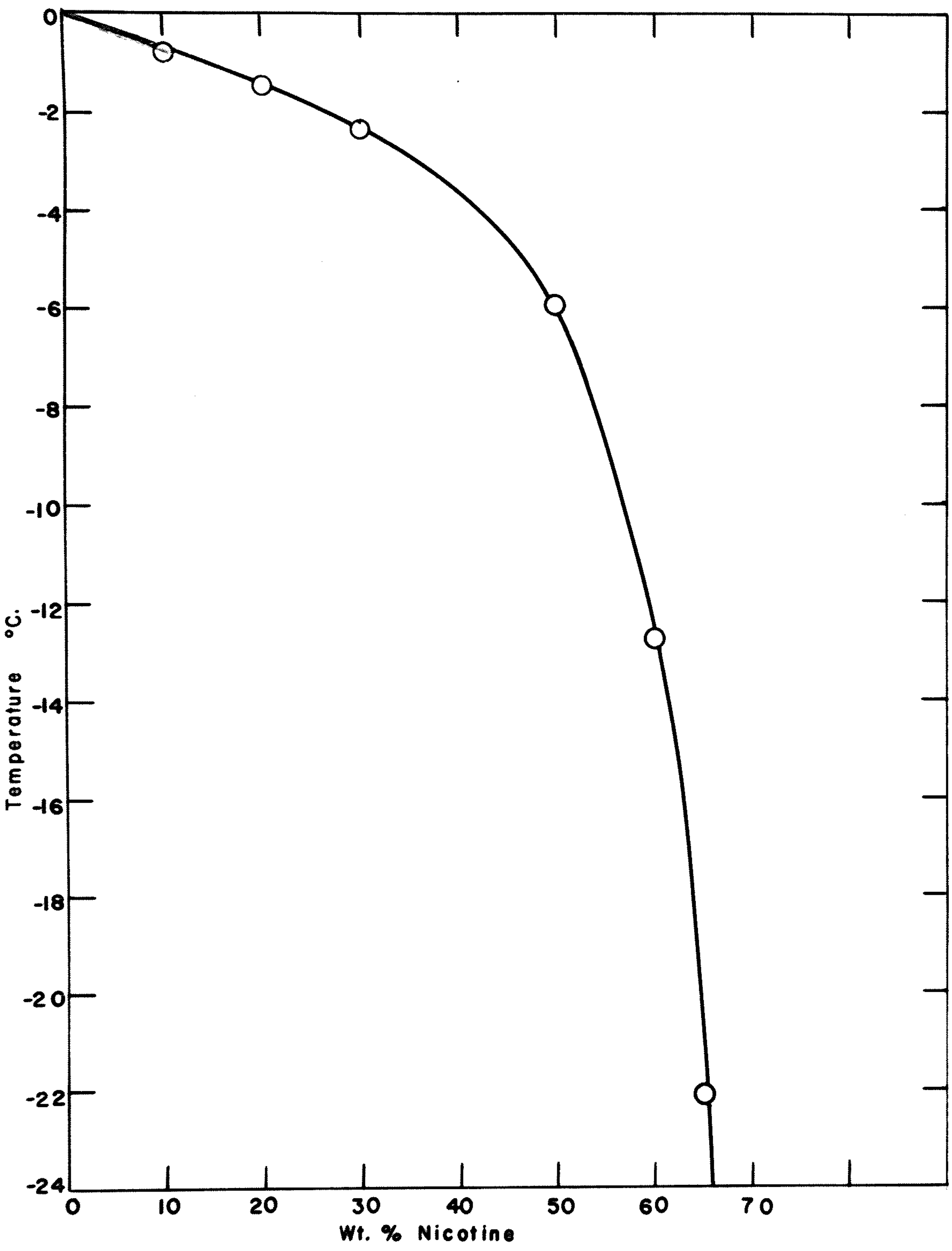
Temperature °C.	Composition of Top Layer		Composition of Bottom Layer	
	Wt. % H_2O	Wt.% MEK	Wt. % H_2O	Wt. % MEK
-11.4	13.2	86.8	56.2	43.8
5.0	13.0	87.0	65.7	34.3
25.0	11.6	88.4	74.5	25.5
50.0	12.9	87.1	79.4	20.6
65.0	14.2	85.8	81.7	18.3
85.0	16.1	83.9	81.4	18.6
115.0	23.1	76.9	78.9	21.1
140.0	40.2	59.8	68.3	31.7
142.6 (CRIT.)	55.0	45.0	55.0	45.0

TABLE VII

DATA FOR THE MUTUAL SOLUBILITIES OF THE NICOTINE-WATER SYSTEM

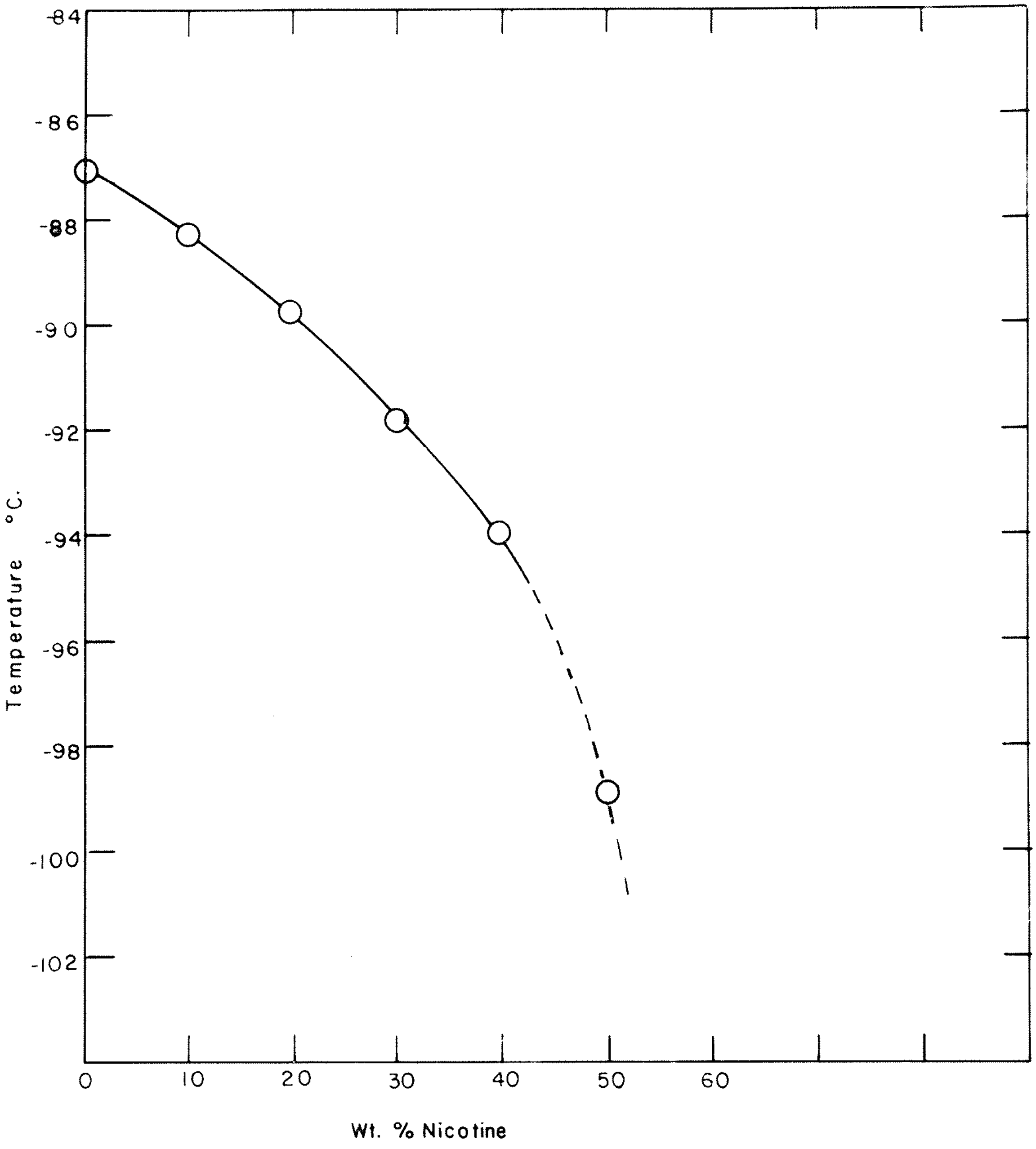
Temperature °C.	Composition of Top Layer		Composition of Bottom Layer	
	Wt.% H_2O	Wt.% Nic.	Wt. % H_2O	Wt. % Nic.
61.5 (CRIT.)	64.0	36.0	64.0	36.0
62.0	70.0	30.0	57.1	42.9
65.0	82.4	17.6	43.4	56.6
70.0	87.2	12.8	35.7	64.3
85.0	90.5	9.5	25.0	75.0
115.0	19.3	80.7	96.8	3.2
140.0	17.0	83.0	93.7	6.3
150.0	16.8	83.2	94.0	6.0

Composition		Upper Temperature Limit of Heterogeneous Area °C.
Wt. % H_2O	Wt. % Nic.	
20.0	80.0	183.0 ± 0.5
25.0	75.0	203.5
32.0	68.0	219.5
43.0	57.0	231.0
54.0	46.0	232.5
60.0 (CRIT.)	40.0	233.0
62.0	38.0	233.0
68.0	32.0	232.5
73.0	27.0	231.5
85.0	15.0	218.0
90.0	10.0	200.0



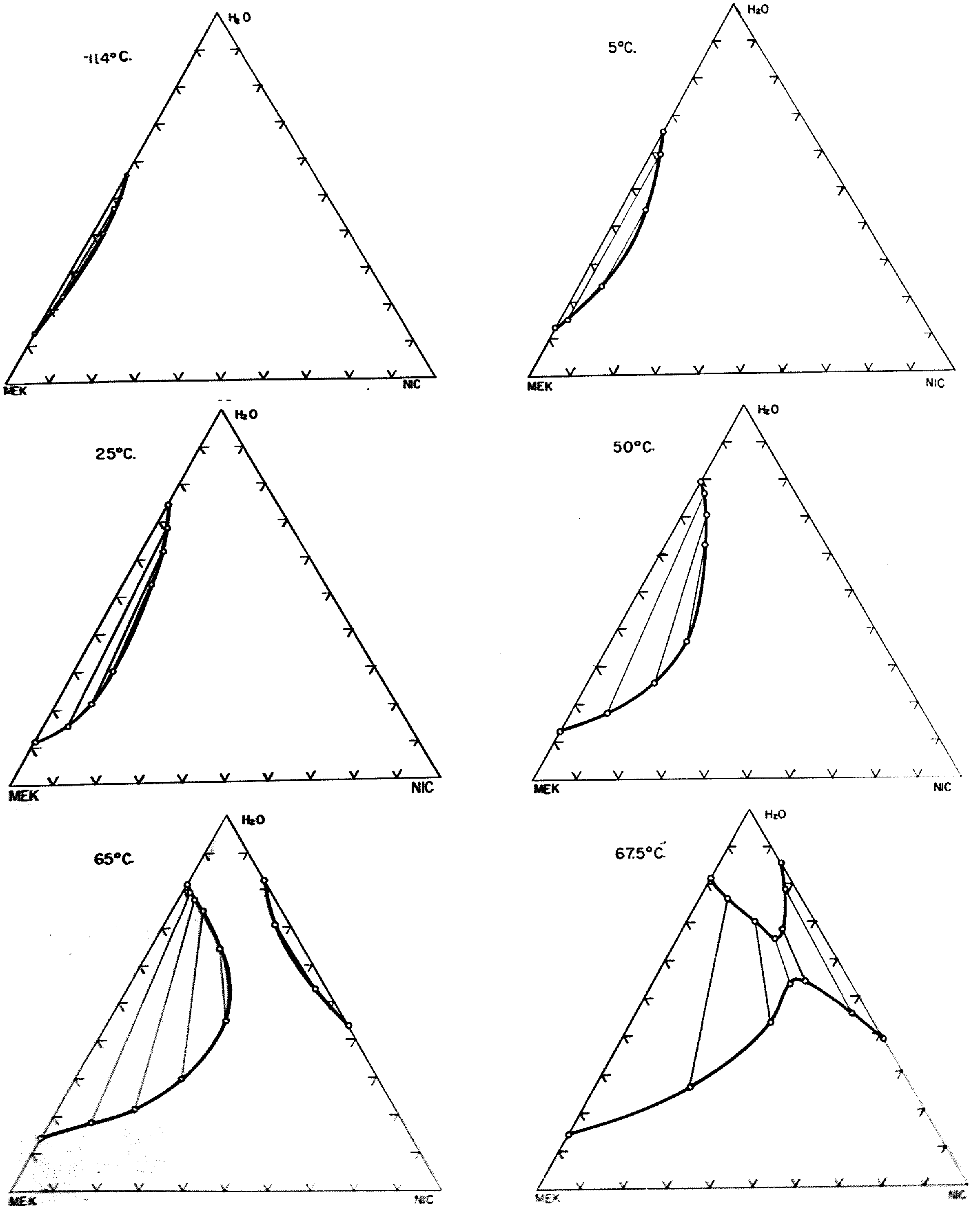
NICOTINE-WATER FREEZING POINT DIAGRAM

FIGURE 12



NICOTINE-METHYLETHYLKETONE FREEZING POINT DIAGRAM

FIGURE 13



ISOTHERMAL SOLUBILITY DIAGRAMS

FIGURE 14

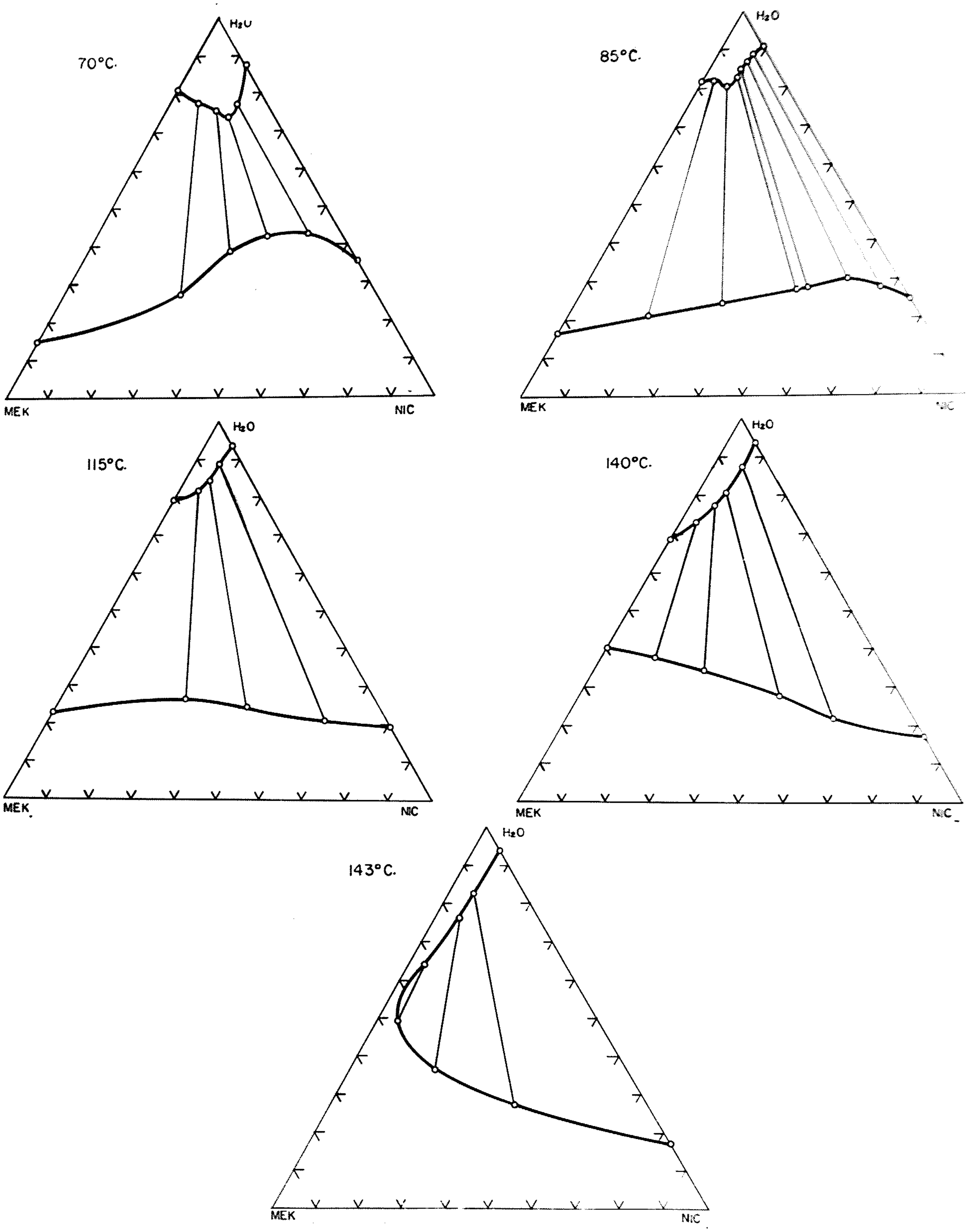
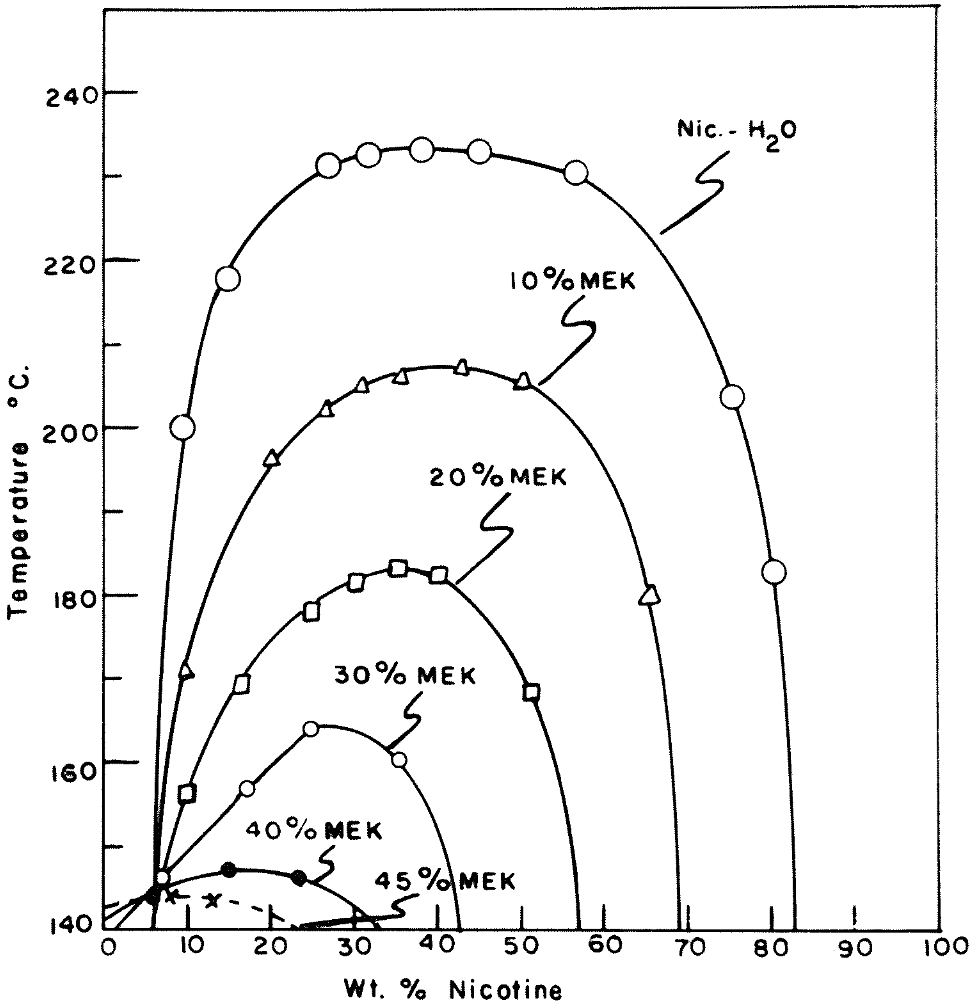
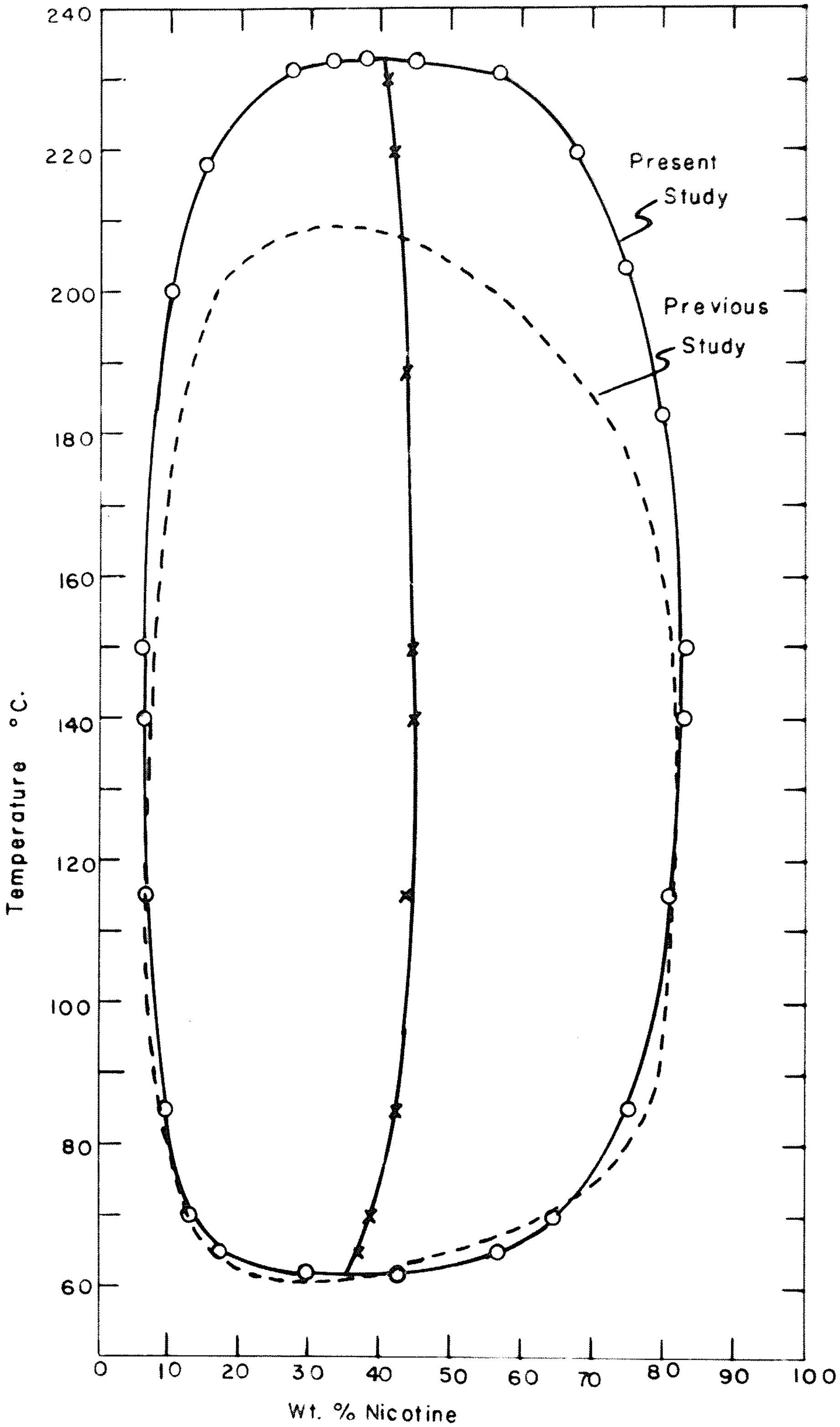


FIGURE 14 (CONTINUED)



TEMPERATURE VERSUS COMPOSITION PLOTS WITH FIXED PERCENTAGES OF METHYLETHYLKETONE

FIGURE 15



NICOTINE-WATER MUTUAL SOLUBILITY DIAGRAM

FIGURE 16

DISCUSSION OF RESULTS

1. THE BINARY SYSTEM METHYLETHYLKETONE-WATER

At 25°C. methylethylketone and water are not completely miscible. The physical properties investigated: density, viscosity, dispersion, and refractive index, were determined only for the completely intersoluble regions.

No freezing curves were investigated for this binary system.

The mutual solubility of these two liquids above 0°C. was in very close agreement with the results obtained by Marshall (13) and the Shell Laboratories (6). It disagreed with the earlier work of Rothmund (2). The upper critical solution temperature was found to be 142.6°C., and the critical composition was forty-five percent methylethylketone, fifty-five percent water by weight.

The lower critical temperature of this system could not be attained in this study. At temperatures below -12°C. crystallization began, and mutual solubilities could not be determined. The points previously determined at -20°C. could not be reproduced because of this crystallization. The solubility of water in methylethylketone is in exact agreement with that found by Randall and McKenna (3), but the solubility of methylethylketone in water appears to be slightly greater in this study.

It is estimated that the lower critical temperature of this system would be about -35°C., and the critical composition would be about seventy-five percent by weight methylethylketone if the solubility curves could be extended below the ice line.

The data for the mutual solubilities of the methylethylketone-water binary system are tabulated in Table VI, page 62.

2. THE BINARY SYSTEM NICOTINE-WATER

Nicotine and water are miscible in all proportions at 25°C., and the physical properties density, viscosity, dispersion, and refractive indices were investigated at ten percent intervals from zero to one hundred percent nicotine in water. A maximum in density was observed at seventy weight percent nicotine; while a maximum in viscosity occurred at seventy-seven percent by weight nicotine. The viscosity maximum was a sharp peak, whereas the density maximum appeared on a more gradual curve. The hydrogen C (λ= 6563Å) and hydrogen F (λ= 4861Å) refractive indices were straight line plots. The plot of the relative dispersion exhibited a slight concavity, but neither a maximum nor a minimum appeared. The density inversion at 90°C. observed by Hudson (1) was reconfirmed; the water rich layer became heavier than the nicotine rich layer about this temperature.

The freezing curve of the nicotine-water system was determined from zero to sixty-five weight percent nicotine. Solutions having a higher nicotine concentration could not be crystallized, due to the extreme viscosity and supercooling of the solutions. Repeated attempts to crystallize pure nicotine were unsuccessful. From the rapid temperature fall with increasing nicotine content, it is estimated that the eutectic composition would be seventy-five to eighty percent nicotine by weight.

The freezing curve is shown in Figure 12, page 64, and the data are tabulated in Table II, page 57.

The mutual solubility of this pair of liquids was studied by the method of isothermal analysis from the lower critical temperature to 150°C. Above this temperature the method of Alexejew was used. The results of the isothermal analysis varied slightly from previously determined measurements, and tended to flatten the lower part of the solubility curve somewhat. The rectalinear diameter was plotted (Figure 16, page 69) to find the critical compositional. It curved slightly towards the temperature axis. The lower critical temperature was found to be 61.5 ± 0.2°C., and the lower critical composition was thirty-six percent nicotine, sixty-four percent water by weight.

The upper half of the solubility curve was outlined using the method of Alexejew. Identical solution temperatures were obtained using nicotine directly from a newly opened bottle, and redistilled nicotine to make up the critical solution; as well as with a nicotine-water critical solution that had been allowed to stand in the equilibrium cell for two weeks. One sample was agitated in a thermostat at 230°C. for twenty hours to ensure the attainment of equilibrium. The upper critical temperature was found to be 233.0 ± 0.5°C., twenty degrees higher than had previously been reported (1), (14), (15). The upper critical composition was found to be forty percent nicotine, sixty percent water by weight.

The data for the mutual solubilities of the nicotine-water system are tabulated in Table VII, page 63; the solubility curve is shown in Figure 16, page 69.

3. THE BINARY SYSTEM METHYLETHYLKETONE-NICOTINE

Methylethylketone and nicotine are intersoluble in all proportions at all temperatures. The densities, viscosities, refractive indices, and dispersions were determined at intervals of ten percent by weight composition change. The graphs of these properties against composition at 25°C. were all very nearly linear, with the exception of the viscosity curve, whose slope began to increase at a concentration of fifty percent nicotine, and continued to increase to a maximum at pure nicotine.

The freezing curve of the methylethylketone-nicotine system was determined from zero to fifty weight percent nicotine, but was rather uninformative. Solutions containing more than fifty percent nicotine could not be crystalled, and a sharp freezing point could not be obtained for the fifty percent solution. No rapid change of slope was observed, so it was impossible to estimate the eutectic temperature.

The freezing curve is shown in Figure 13, page 65, and the data are tabulated in Table III, page 57.

4. THE TERNARY SYSTEM NICOTINE-METHYLETHYLKETONE-WATER

At 25°C. these three substances are completely miscible except for a small region with a composition of less than nine percent nicotine, and between twenty-five and eighty-eight percent methylethylketone. The physical properties: density, viscosity, dispersion, and refractive indices were determined for random compositions in the completely soluble region. Curves joining compositions of identical physical properties in general were found not to be straight lines. The viscosity plots in particular were very sharply curved. The density and refractive index curves exhibited only a little change of slope, and intersected most nearly orthogonally. They were therefore chosen as the properties to be used in the analytical scheme.

Since the binary eutectics could not be found, little hope was held for locating the ternary eutectic, and no freezing curve determinations were made in the three component system.

A picture of the solid composition-temperature model can be had by imagining the isotherms shown in Figure 14, page 66, to be placed in a vertical column at appropriate distances, and the plots shown in Figure 15, page 68 to be located appropriately above the uppermost isotherm.

If this is done it will be seen that of the possibilities for a three dimensional curve, one of the "tunnel type" shown in Figure 1, page 3 results. The upper part of this tunnel forms a smooth surface running from the upper critical solution of the methylethylketone-water system to the upper critical solution of the nicotine-water system. However, on the lower surface a maximum in the soluble region is to be found. The solubility surface rises from the ice line of the methylethylketone-water system and meets a surface rising continuously from the lower critical solution of the nicotine-water binary system. The maximum of this "dent" in the surface lies at a temperature of $67.3 \pm 0.2^{\circ}C$. and at a composition of twenty-seven percent by weight nicotine, fourteen percent by weight methylethylketone, and fifty-nine percent by weight water. This point represents a ternary critical solution in the three component system. If a corresponding critical point exists on the upper surface of the solubility model, the solution must contain so little nicotine, less than say one percent, as to be non-detectable with the temperature control available, that is, within ± 0.2°C.

The isothermal rectalinear diameters are obtained by joining the midpoints of all tie lines. Although in general these were found to be far from straight lines, they could be extrapolated to give the isothermal critical compositions, or plait points, listed in Table IV, page 58.

All data for the three component isotherms are tabulated in Table IV. The data for the solution temperatures shown in Figure 15, page 68 are listed in Table V, page 61.

SUMMARY AND CONCLUSIONS

The freezing curves of the two binary systems methylethylketone-nicotine, and nicotine-water were determined as far as was possible (fifty percent and sixty-five percent nicotine respectively). Whether or not compound formation occurred beyond this composition was impossible to determine.

The solubility curve of the methylethylketone-water system was repeated, and the results confirmed the presently accepted data (6). The mutual solubilities of the nicotine-water system were repeated, and were found to be less than those of previous workers, particularly at higher temperatures (Figure 16, page 69). The upper and lower critical solution temperatures were found to be 233°C. and 61.5°C.; and the critical compositions were respectively forty and thirty-six percent nicotine by weight.

The mutual solubilities of nicotine-methylethylketone-water were determined over the entire temperature range of immiscibility, which extended from the ice point of the methylethylketone-water system to the upper critical solution temperature of the nicotine-water system. The heterogeneous volume was found to be a "tunnel," passing through the equilateral prism; joining the two component areas of heterogeneity. A ternary critical point was found on the lower surface of this volume, at a temperature of 67.3°C., and at a composition of twenty-seven percent nicotine, fourteen percent methylethylketone, and fifty-nine percent water by weight. No corresponding upper critical point could be found; a smooth surface joined the upper critical solutions of the nicotine-water and the methylethylketone systems.

A positive deviation from Raoult's law existed for these three liquids, at least over a certain temperature range.

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