ON DETERMINATION OF VAPOR-LIQUID EQUILIBRIUM PHASE DISTRIBUTION RATIOS OF PETROLEUM OILS

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CHAPTER I

INTRODUCTION

Vapor-liquid contacting operations, such as fractionation, absorption, stripping, two-phase conversion, partial condensation, and vaporization are prominent in the chemical, petrochemical, and petroleum industries. A knowledge of the fundamentals of vapor-liquid phase equilibria is therefore important to these industries. A complete understanding of the phase equilibria phenomena of these operations may be obtained by experimental and theoretical methods.

Temperature, pressure, and composition of the equilibrium phases are independent variables determining the state of phases in equilibrium. The thermodynamic treatment of equilibrium vapor and liquid phases of an ideal binary system is rather simple, but the thermodynamic relationships for real systems are complex. In the case of petroleum fractions, the theoretical treatment is impossibly difficult, so experimental measurements and empirical correlation of data are required.

Vapor-liquid equilibrium phase distribution coefficients for each component of a system are commonly expressed in the form of mole fraction of the component in the vapor phase divided by the mole fraction in the equilibrium liquid phase. Therefore,

$$K_{i(P_e,\ T_e,\ x)} = y_i/x_i \qquad (1)$$

The main objective of this investigation was the evaluation of vapor-liquid phase distribution coefficients (k-values) of petroleum oils. Except for a few equipment tests, all the experiments were made at an isobaric condition of one atmosphere.

The direct measurement of a great number of components existing in minute quantities in a petroleum fraction is impractical, therefore the distribution coefficients were found indirectly and as follows:

1 - Equilibrium flash vaporization of the petroleum fraction at some temperature.

2 - Batch fractional distillation (true-boiling-point distillation) of both vapor and liquid phases.

3 - Conversion of the results of step (2) from volume per-cent to mole per-cent, and finally establishment of distillation curves (boiling temperature vs. mole per-cent off) for each phase.

4 - Calculation of K-value (at equilibrium pressure and temperature of step 1) of each component of the mixture represented by its distillation temperature, obtained from the ratio of the slopes of liquid and vapor phase distillation curves at that temperature.

The idea of representing the petroleum continuum by a series of hypothetical differential quantities was first suggested by Katz and Brown (70), and later improved and applied by Edmister (31).

Evidently this investigation is the first attempt for experimental evaluation of K-values of petroleum fractions, and the project will be followed for compilation of extensive information, which would ultimately lead to general empirical relationships giving the K-value as a function of fraction boiling point and the system temperature and pressure.

During the course of this investigation a theromostatic flow and a recirculating type of equilibrium still were modified and used. These stills were evaluated, and reliable techniques for ascertaining equilibrium conditions established. Also a new flow equilibrium apparatus with good possibilities was introduced.

An analytical fractional distillation was carried out in an efficient sieve plate column. The operational characteristics of this column were first evaluated, and then a satisfactory T.B.P. distillation procedure was formulated. The average molecular weight of each narrow boiling cut of petroleum mixture was measured by a cryscopic method. An improved technique for evaluation of this physical property, as well as suggestions by a related method for characterization of petroleum fractions are given. Chromatography was used for determining the equilibrium condition of the petroleum fraction, and it was also applied for direct measurement of K-values of a relatively simple petroleum mixture. Finally, various techniques and simplifying suggestions are presented for calculation of K-values.

The second chapter contains important thermodynamic relationships for vapor-liquid equilibria. The independent nature of the subjects presented in Chapters III, IV, V, and VI necessitates separate treatments. In each of those chapters, the related theory, equipment, procedure, representative results, and discussion are given. Chapter VII deals with calculation of vapor-liquid phase distribution coefficients. Some specific uses of these values are discussed in Chapter VIII.

CHAPTER II

CRITERIA OF EQUILIBRIUM

It has been shown thermodynamically that a system is subjected o spontaneous change if there is any conceivable process for which $S>0$. Consequently, a state of equilibrium is one in which every ossible infinitesimal process is reversible, or one with a constant otal entropy. Therefore the necessary criterion for equilibrium of ny process is $dS = 0$. Since it is not always easy to study the ntropy change of all the systems that may be affected by a certain rocess, many thermodynamic functions, which are less fundamental nd less general than the entropy, but are of more practical convenence have been invented. In order to have a deeper insight into his concept, some of these thermodynamic functions will be briefly iscussed here.

A property of the system called its Helmholtz function, A, is efined by the equation,

$$A = U - TS \tag{2}$$

nother property of the system called its Gibbs function, G, or ts free energy, shown by the equation,

$$G = H - TS = (U + PV) - TS = A + PV \tag{3}$$

here U is the internal energy, H the enthalpy, V the volume, T the temperature, and P the pressure of the system.

Now considering a closed system on which a constant pressure is acting as the only external force, then for an infinitesimal reversible process at constant temperature and pressure (i.e. at equilibrium) the Gibbs function of the system should not change. That is to say

$$dG = 0 \tag{4}$$

The G function of the system can be given by the sum of G', G'', etc. of the constituent phases of the system. So,

$$dG = dG' + dG'' + dG''' + \cdot\cdot\cdot \tag{5}$$

The free energy is a state function and depends on all the variables which determine the state of the system.

$$G = G(T,\ P,\ \cdot\cdot\cdot,\ n_1,\ n_2,\ \cdot\cdot\cdot,\ n_k) \tag{6}$$

For most chemical engineering purposes the above equation can be reduced to the following equation.

$$G = G(T,\ P,\ n_1,\ n_2,\ \cdot\cdot\cdot,\ n_k) \tag{7}$$

or

$$dG = \left(\frac{\delta G}{\delta T}\right)_{P,\ n_1,\ n_2,\ \cdot\cdot\cdot,\ n_k} dT + \left(\frac{\delta G}{\delta P}\right)_{T,\ n_1,\ n_2,\ \cdot\cdot\cdot,\ n_k} dP$$

$$+ \left(\frac{\delta G}{\delta n_1}\right)_{T,\ P,\ n_j \neq 1} dn_1 + \left(\frac{\delta G}{\delta n_2}\right)_{T,\ P,\ n_j \neq 2} dn_2 + \cdot\cdot\cdot +$$

$$+ \left(\frac{\delta G}{\delta n_k}\right)_{T,\ P,\ n_j \neq k} dn_k \tag{8}$$

Although the molal free energy makes a very satisfactory quantitative measure for criteria of equilibrium, there are certain respects in which this function is awkward. It is therefore desirable to introduce another scale of measurement of equilibrium, which is called the fugacity, f (81). The fugacity will be equal to the vapor pressure when the vapor is a perfect gas, and in general it may be considered as an "Ideal" or corrected vapor pressure. The fugacity is partially defined in terms of molal free energy through the equation,

$$G = RT \ln f + \theta(T) \qquad (9)$$

where θ is a function of temperature only.

In a differential form, the fugacity of a component in a solution is thermodynamically defined by the relation,

$$(d\bar{G}_1 = RT \; d \ln f_1)_T \qquad (10)$$

$\bar{G}_1 = \left(\frac{\delta G}{\delta n_1}\right)_{P, T, n_2, \ldots, n_k}$, the partial molal free energy of component one.

f_1 = fugacity of component one at temperature T.

It follows by equations (4, 5, 10) that at equilibrium, he fugacity of a component in the liquid phase is equal to the ugacity of that component in the vapor phase.

The fugacity of a pure gaseous component is related to its ressure by the equation,

$$\ln \frac{f}{P} = \int^{P} (Z - 1) \frac{dP}{P} \qquad (11)$$

hus, if data are available which relate the compressibility factor Z f a gas, to P and T for the pure gas, the fugacity of the pure gas t any chosen temperature and pressure is obtainable from equation 11). However, in the usual case, these data are not available.

Hougen and Watson (64), employing the concept of correspondng states, have constructed plots of Z as a function of the reduced ressure and reduced temperature, using available data for seven ases. The same authors have constructed plots of f/P solely as function of the reduced pressure and reduced temperature. The atio of f/P is termed the"fugacity coefficient" ν, and for ideal as behavior is equal to one.

Benedict *et al* (12) also derive a generalized method for redicting fugacity of pure gases. They utilize the virial equation state and consider the first coefficient, B_1, as sufficient to xpress the non-ideal behavior of the pure gas,

$$PV = RT + B_1P \qquad (12)$$

he preceding two equations will yield the result,

$$f/P = \nu_P = e^{\left(\frac{B_1P}{RT}\right)} \qquad (13)$$

he virial coefficients B are explained by the kinetic theory of ses (113).

The fugacity of a pure liquid at a pressure other than its n vapor pressure is evaluated by means of equation (13) rived by Hougen and Watson (63),

$$\ln \frac{f_P}{f_p} = \frac{Vm(P - p)}{RT} \qquad (14)$$

f_P = fugacity of the pure liquid at P and T.

f_p = fugacity of the pure liquid at a pressure equal to the vapor pressure of the pure liquid at T.

Vm = arthmetic mean molal volume of liquid from P to p.

r problems involving solutions, it is convenient to define a ermodynamic property called "activity", a.

$$a = \left(\frac{f}{f^o}\right)_T \qquad (15)$$

f = fugacity in solution.

f^o = fugacity in standard state at the same temperature.

r vapor-liquid equilibria consideration, it is convenient to oose the standard state for each component in the liquid phase, the pure liquid component at the pressure and temperature of lution. Similarly, the standard state for each component in the por phase is chosen as the pure vapor at the pressure and temperare of solution. Thus,

$$(f^o)_v = \nu_P \, P \qquad (16)$$

$$(f^o)_L = \nu_p \, p \, e^{\frac{Vm(P - p)}{RT}} \qquad (17)$$

$(f^o)_v$ = fugacity of pure vapor at P and T ~ fugacity of the component in its standard state.

$(f^o)_L$ = fugacity of pure liquid at P and T ~ fugacity of the component in its standard state.

The "activity coefficient in terms of mole fractions" γ, is efined as the ratio of activity of the component in solution to mole raction of the component in solution.

$$\gamma = \frac{a}{N} \tag{18}$$

us for component one in the liquid and vapor solutions, the tivities are expressed in terms of mole fractions.

$$(a_1)_L = \frac{(f_1)_v}{(f_1^\circ)_L} = x_1 \, (\gamma_1)_L \tag{19}$$

$$(a_1)_v = \frac{(f_1)_v}{(f_1^\circ)_v} = y_1 \, (\gamma_1)_v \tag{20}$$

The thermodynamical relation of vapor and liquid at equilibrium established as follows,

At equilibrium $$(f_1)_v = (f_1)_L \tag{21}$$

Therefore $$K_1 = y_1/x_1 = \frac{(\gamma_1)_L}{(\gamma_1)_v} \; \frac{(f_1^\circ)_L}{(f_1^\circ)_v} \tag{22}$$

K_1 = vapor-liquid equilibrium constant of component one at P and T.

uation (22) may also be shown in the following forms,

$$K_1 = y_1/x_1 = \frac{(\gamma_1)_L}{(\gamma_1)_v} \left[\frac{(f_1^\circ)_L/p_1}{(f_1^\circ)_v/P}\right] \left(\frac{p_1}{P}\right) \tag{23}$$

$$K_1 = \left[\frac{(\gamma_1)_L}{(\gamma_1)_v}\right] (K_1)_{ideal} = \left[\frac{(\gamma_1)_L}{(\gamma_1)_v} \; \frac{(f_1^\circ)_L/p_1}{(f_1^\circ)_v/P}\right] (K_1)_{Raoult} \tag{23a}$$

though equation (22) could be written in terms of other thermonamic quantities instead of activity coefficients. However, activity efficients are much preferable, since they vary less with tempera-re and composition than some other thermodynamic quantities which uld be utilized. For all conditions except those close to the itical point for the solution, $(\gamma_i)_V$ could be taken as unity. uation (22) for any two components can be written as follows,

$$\frac{K_1}{K_i} = \left(\frac{\gamma_1}{\gamma_i}\right)_L \left(\frac{f_1^{\circ}}{f_i^{\circ}}\right)_L \left(\frac{f_1^{\circ}}{f_i^{\circ}}\right)_V \qquad (24)$$

perimental K-values: Engineers generally utilize vapor-liquid phase stribution coefficients for design purposes, and this subject for e case of complex hydrocarbon systems has been fully reviewed and scussed by Edmister (32). The summaries of some of the more ominent experimental works are presented here.

Matheson and Cummings (87) studied the vapor pressure of five w-boiling paraffin hydrocarbons in an absorber oil over a wide range concentration. The results indicate positive deviation from oults' Law. Katz and Hachmuth (71) determined vapor-liquid uilibrium phase distribution coefficients of methane, ethane, opane, butanes, pentanes, and hexanes in a system of natural gas d a mid-continent crude oil at 40°, 120°, and 200°F, over a large essure range. This work showed that the effect of temperature on e equilibrium constant is greater at lower pressures, and for gher molecular weight hydrocarbons. Sage and Lacey (131) showed at the equilibrium constant for methane in various binary systems not only a function of equilibrium pressure and temperature, but so of the composition of the system.

The experimental work of Webber (150) includes the determination vapor-liquid equilibrium constants of methane through hexane in a pical absorption oil, at temperatures from 33° to 180°F, and essures from 100 to 5000 psia. The experiment showed that at essures above 3000 psia, the composition of the mixtures has a onounced effect on the equilibrium constant values. Vink, Ames, vid and Katz (149) gave the vapor-liquid equilibrium phase dis- ibution coefficients of methane, ethane, and propane in a crude l.

Roland et al (121) presented some equilibrium data for the lf Coast distillate - natural gas mixtures at 40°, 120°, and 0°F, and high pressures with a reasonable degree of accuracy. e data indicate that the composite composition of the mixtures gas and distillate has small effect on the value of the equili- ium constants, although this may not be considered conclusive so r as heptane plus is concerned.

Eilerts and Smith (35) published equilibrium data at 228°F and 92 psia, with some considerable variation in the constant for rious mixtures. White and Brown (152) reported experimental por-liquid phase equilibrium data for petroleum fractions boil- g from 85° to 750°F at temperatures from 300° to 820°F and pressures from 50 to 700 psia. The equilibrium phases were alyzed by fractional distillation in a Podbielniak column. The rresponding cuts from both vapor and liquid phases were analyzed r molecular weight and density. K-values are reported for pentanes, xanes, heptanes, and higher boiling cuts, having boiling ranges om 25° to 100°F. The data show a consistent trend for the light phtha, while it indicates some discrepancy for the furnace oil.

Kirkbride and Bertetti (72) published equilibrium constant ta for methane, ethane, propane, n-butane, and n-pentane in raffinic, naphthenic, and aromatic types of absorbing oils, at °F, and pressures from 125 to 3100 psia. The K-values of these ses at any condition of equilibrium are dependent on the type of l1 used.

Standing and Katz (141) presented equilibrium constant data r four mixtures of natural gas - crude oil, at 35°, 250°F, and gh pressures. Roland (122) used Katz and Hachmuths' equipment d method for study of vapor liquid equilibrium properties of tural gas in contact with crude oil at 120°, 200°F, and pressures om 1000 to 10,000 psia. The equilibrium constants are reported r methane, ethane, propane, butanes, pentanes, hexanes, and ptanes plus. The plots indicate a rather large scattering of sults, which may partially be attributed to the grouping of e hydrobarbons.

Rzasa and Katz (129) have studied the vapor-liquid phase havior of methane - Kensol 16 system to pressures of 25,000 psia, d to temperatures of 260°F. Kensol 16 is a commercial high-narrow-lling oil. The equilibrium vaporization constants have been lculated from the experimental data and extrapolated to 700°F.

CHAPTER III

VAPOR-LIQUID EQUILIBRIUM EQUIPMENT

The need for vapor-liquid equilibrium information has been tioned. For many systems of industrial importance, the vapor-uid equilibrium relationships must be determined experimentally.

Although the experimental measurement of vapor-liquid equili-um may at first appear to be a rather simple task, it frequently ves to be one of the most difficult physico-chemical measurements execute precisely. The complete equilibrium study of a system either be done at isothermal or isobaric conditions.

Thermodynamic consistency tests can only be applied to a ple system, and the result is frequently inconclusive. Gilliland 0) states that it is not uncommon to find experimental deviations order of ± 10 percent between different investigators using es-tially the same technique. The experimental study refers to position measurements of both vapor and liquid while in equili-um with each other at some known temperature and pressure. Be-es the operational errors, the inconsistency in equilibrium study be due to; purity of sample, the experimental measurements, the ure of the system, and/or the design and construction of the ilibrium equipment.

It is almost impractical to make a complete and exhaustive vey of the literature on this subject, and evaluate all the ferent designs of vapor-liquid phase equilibria apparatus. There- e, a brief review of some of the more common, and reliable types presented here.

Three different equilibrium apparatus were constructed and d in this investigation. Complete design and operational details, well as their evaluation and comparison are presented in this pter. Two of the equilibrium stills are modifications of a well wn recirculating (Othmers'), and a thermostatic flow apparatus.(85). third one which was developed as a result of this work, is based a radically different and highly satisfactory design.

Theory of Equipment Design and Survey of Literature

The discussion in this chapter will only include the vapor- uid contacting devices, and no reference will be made to the perature and pressure measuring apparatus. Vapor-liquid ilibrium devices are normally classified according to their method operation, and as follow:

1) Simple distillation
2) Dynamic flow
3) Static or Autoclave
4) Dew and bubble-point
5) Vapor-recirculating
6) Vapor and liquid - recirculating
7) Flow

1. Simple Distillation: This method is the oldest technique vapor-liquid equilibrium investigation, and it has practically

n abandoned ever since the invention of the other techniques. e thermodynamically consistent results are attributed to this hod, and with proper equipment modification it may come into stence again. As the name implies, it is basically a simple tillation, where the vapor composition is measured at various peratures. The corresponding composition of liquid left in the is then calculated by material balance. There are many inherent ficulties associated with this method, when simple distillation ipment is used. The large quantity of boiling liquid in the ll may not be homogeneous, unless a proper heater such as internal -wire is used.

Hanson (58) and co-workers, believe that vapor formed from a ling liquid may be slightly super-heated in some instances, and s subsequently can cause an erroneous temperature measurement. not properly designed, the vapor before entering the condenser cool and partially condense (52,156); therefore, the vapor position would be richer in the more volatile components. The or coming from the still can entrain and transport liquid, when velocity is sufficiently high, or when the boiling is quite orous. This phenomenon, of course, enriches the vapor with less atile components.

There are many different designs and sizes of one theoretical ge simple distillation stills (16,19,80,107,145,158). A design h the vapor arm extending into the still, which also holds the rmometer, has proven to be satisfactory for many systems. The or in the pot is vaporized slowly by both internal and external eaters. Cornell *et al* (23), used the technique of Rosanoff (123,124, 25) and obtained reliable equilibrium relations for binary mixtures f ethanol-water, methanol-water, and acetic acid-water. The equipent basically consists of two concentric tubes, where the central one s provided with an internal electric heater, and acts in the capacity f a small distillation flask. The vapor flows down the annulus and nto a condenser. With the exception of the vapor condenser, the ntire equipment is placed in an oil bath.

2. *Dynamic Flow*: In this method the vapor is passed through liquid until the composition of the effluent is the same as that f the entering vapor. At this point the composition of liquid is ufficiently changed as to be in equilibrium with the vapor. nother method is one in which the vapor is passed through a series f liquid containers with liquids of approximately the same composiion. The number of these liquid containers must be such that the apor entering the last one remains unchanged as it bubbles through t. Entrainment and pressure drop are two of the major difficulties f the dynamic flow method. In some cases an inert carrier gas is ntroduced in the first vessel. This inert gas transports the quilibrium vapor from the last one. In such a case, and when the ressure is high, the effect of total pressure on vapor pressure of he components can not be neglected.

A well known laboratory size dynamic flow equipment is the athala (20) still. In this equipment, the preheated liquid is fed ontinuously into the mixing section between two layers of fritted lass. Vapor in a super heated state is also fed continuously to he equipment, but below the lower fritted disc. Vapor and liquid ix well together as they pass through the discs, and finally enter short Cottrell pump. Both phases separate at the top, where the quilibrium temperature is measured. More successful design variaions depend on accurate flow of phases, and some are vacuum jacketed.

Colburn (21) used two insulated concentric chambers, where the nner one contained the liquid. Vapor passes between the two ompartments, and contacts the liquid in the inner chamber. This quipment and its modification (92) have produced some excellent esults. Aroyan and Katz (6) modified the apparatus of Dodge (29) or low temperature and high pressure equilibrium studies. The quilibrium gas is recirculated by a magnetic pump through the iquid, until the steady state is attained. Similar designs 57,90) have produced some satisfactory results.

3. Static: The liquid sample is placed in an evacuated bomb hich is maintained in a constant temperature enclosure, and agitated y rocking or internal mixing. The liquid vaporizes in the bomb, nd when it is in equilibrium with its vapor, the pressure and ompositions of both phases are measured. Theoretically this echnique should produce highly reliable results, although in ractice such factors as sampling and stirring upset equilibrium. ng periods of rocking should eliminate the inherent problems of tirring, and the use of an especially designed sampling valve in nnection with chromatographic analysis should reduce the sampling ifficulties. This equipment is very adaptable for high pressure nvestigation.

Sage and Lacey (98,130,132) have used a high pressure bomb very uccessfully for vapor-liquid equilibrium studies of light gases. enedict (13) used a 4000 cc. steel bomb which was kept in an sothermal oil bath. The bomb pressure was regulated by mercury njection. The equipment showed consistent results for systems such s methane-ethane-isobutane. Katz (71) obtained reliable phase istribution coefficients for hydrocarbon gases dissolved in a heavy il. The equipment is a variable volume bomb with an internal lectric stirrer. There are other apparatus of similar designs 14,15,26,61,148) which have produced some consistent results.

4. Dew and Bubble-Point: This method employs the same equipent as the static method, but with some provisions for changing the olume. The volume can either be changed by mercury or by piston isplacement. Phase diagrams can be prepared by obtaining a number f isotherms, or by visual determination of dew and bubble points n glass equipment. This technique is often used for the equilirium study of binary mixtures, and it requires no analysis of hases. In some cases nucleation may be required, otherwise a ressure higher than that of dew-point, or lower than bubble-point n result.

Young (157) developed the original capillary equipment for udy of equilibrium at dew and bubble-point conditions. Kay (7,8) odified the original equipment for investigation of equilibrium roperties of petroleum hydrocarbons. The liquid under investigaon was confined over mercury in a thermally jacketed Pyrex tube. tube with 1.5 mm. inside diameter, and an intermediate section f 4 mm. bore was used. To bring about equilibrium between the phases uickly, an electromagnetically operated iron rod (1.9 cm.) was laced in the liquid space. Pressure was conveyed to the system hrough mercury, and it was measured by means of two gas manometers.

Cummings (24) very successfully measured dew and boiling point urves for mixtures of nC_5 - nC_7, at high pressures. The equipment as a small "U" shaped quartz tube (0.5 cm. O.D. x 55.0 cm. long), ith its closed end in a reflux jacket. Stirring was accomplished ith a small magnet, and the equilibrium pressure was measured by a ead weight tester, having mercury and an oil as the intermediate luids. There are many modifications of these devices (47,71,95,135) ;ed for equilibrium study of various systems under highly diversi- led conditions.

5. <u>Vapor-Recirculation</u>: This is another satisfactory techni- ıe for vapor-liquid equilibrium study, and there are many complicated ·signs which operate on the same principle. Vapor-recirculation is ısically a continuous simple distillation, where the vapor product totally condensed and recycled back to the still. The recircula- on rate, and the total amount of charge can be selected so as to ve any desired vapor-to-liquid ratio.

A vapor-recirculation equilibrium still was used in this investi- tion, and therefore it will be discussed in more detail later.

Yamaguchi (155) designed the first recirculating equipment for udy of ethyl ether-chloroform system. Sameshima (143) used an proved version of Yamaguchi's equipment for successful study of e acetone-ether system. The apparatus consists of a 200 cc.

ternally heated vessel, submerged in a cryostat. The electrically
ated vapor arm is connected to a condenser and a 10 cc. receiver,
ich are placed directly above the still. The overflow from the
ceiver returns to the pot, and any vapor generated in the return
ne is also condensed and returned.

Othmer (100) improved the design further by extending the vapor
m into the cylindrical still, and placing the condenser-reservoir
the side of the pot. The return connection in this case is an
verted 'U' line with a siphon breaker. The advantages of this
sign over the previous ones are rather small, nevertheless it
rved to popularize the recirculating technique. There are a
eat number of modifications of this still for serving various
rposes (10,17,18,25,30,42,47,48,50,51,52,56,62,78,101,102,103,
5,109,140,143,154).

The recirculating equilibrium still used in this study is a
dification of one of the latest design by Othmer (104). It is
one piece glass equipment, specifically recommended for equili-
ium study of petroleum fractions. The still pot is in the form
two joined hemispheres with a total capacity of 500 cc. The
all lower section of the pot serves for vaporization of small
antities of liquid left in it. The vapor-arm carries saturated
por to the top of the condenser-receiver. The condensed vapor
turns to the bottom of the pot through a small tubing, and its
ow is regulated by a 3-way cock. The entire still is thermally
sulated. Both vapor and liquid temperatures are measured in the
t, and the samples are withdrawn through the 3-way cock.

Kortum (74) jacketed the flask and the vapor-arm with a fluid apor or liquid) about 0.5 ^{o}C warmer than the equilibrium temperare. An internal heater, and a magnetic stirrer were used to improve e uniformity of the pot liquid. The vapor receiver was fitted with swinging funnel to eliminate the interruption in recirculation while mpling. Apparatus based on the same principle has been designed th two or more ideal stages (42,60), and they are highly recommended r systems having low relative volatility.

Jones (69), in order to eliminate the mixing difficulties in the t, superheated the recycling condensate in the tubular vaporizer, l then mixed it with pot liquid. The equipment is very satisfactory, l there are many modifications of it in use (3,4,9,76,117,136). mer (101) has designed a similar still for high pressure equilibrium ıdies, and there are a number of modifications of it also (48).

6. Vapor and Liquid Recirculation: This differs from the vious technique by the fact that both vapor and liquid are reculated. In the vapor recirculation, the liquid and the vapor peratures are measured independently, and are matched. In the es where both temperatures are not the same, neither one can be ısidered as the equilibrium temperature.

In vapor-liquid recirculation equipment, a Cottrell pump por-pump) mixes the phases and then pumps slugs of these onto thermometer. The equilibrium vapor and liquid phases are separed in a disengaging section, and then recirculated back to the ll. In this type of apparatus problems associated with the mperature measurement, entrainment, and partial condensation of por are essentially eliminated.

The Gillespie still (49) and its modifications (46,106,119,126, 7) have produced many reliable vapor-liquid equilibrium relations. the Gillespie still, a Cottrell pump operates from a boiling flask 00 cc.), heated both internally and externally. The pump throws ugs of both phases on the thermometer well, and the phases are en separated for obtaining representative samples. The condensed por is finally mixed with the liquid, and they are recycled back the pot. The design is very sensitive to the nature of the system, d details of the still construction (65). The equipment, although all, may require many hours to approach the equilibrium state, and some instances it may cycle.

Ellis (36,37) used a spiral Cottrell pump, which caused a much orter time for attainment of steady state condition. In the Thornton ill (147) and its modification (41), both vapor and liquid receiv- s are placed below the disengaging section in the vapor space. is method eliminates the difficulties associated with the liquid oler, and phase mixing.

The Altsheler still (2) is reliable and fast coming to equilib- um. A mixture of both phases spurts from one leg of the tubular iler into a cyclone separator, located just above the Cottrell np. Condensed vapor returning from the condenser mixes with the quid phase surrounding the Cottrell pump.

7. *Flow Equipment*: In this apparatus, feed is continuously ted, and partially vaporized in some sort of vaporizer. The

ixture of the two phases is then separated in a disengaging chamber, here the equilibrium temperature and pressure are measured. Such a nit compares with industrial flash vaporizers, and is commonly used n pilot plant studies of petroleum oils.

The Hala *et al* equilibrium still (55), is a small flow apparatus here the material is heated for a few seconds. Feed flows from a upply vessel to a short vaporizer, and then it spurts on the thermoeter well. Both phases pass through the disengaging section, before ach is cooled and collected. This all glass equipment requires at east 50 cc. of material, and is specifically useful for heat sensiive substances.

A constant temperature, high pressure instrument was designed y Zinn and Stechel (142) for the equilibrium study of the H_2-N_2-CH_4 ystem. This equipment was later modified (54,128) for equilibrium nvestigation of low boiling hydrocarbons. Feed, in this instrument, lows through many parallel branches of copper capillary tubes, and s then sprayed on the walls of the equilibrium chamber to obtain a etter contact between the phases. The entire apparatus is kept n a constant temperature jacket.

Smith *et al* (139) used a similar design for study of flash aporization of petroleum fractions. The metallic vaporizer is acketed with mercury vapor as the thermostatic fluid. The isengaging section is over-sized in order to eliminate any possible ntrainment. A low pressure, all glass version of this equipment was esigned by Lockwood *et al* (85). One of the equilibrium stills used n this investigation is a modification of the above equipment.

A flow equilibrium flash vaporizer was designed by Edmister *et* *l* (33) for investigation of equilibrium properties of petroleum fracions. In this metallic equipment, feed is continuously pumped hrough a lead-pot partial vaporizer. The pressure of the feed is hen reduced, and it is finally flashed in a large insulated disengagng chamber. Both vapor and liquid phases are withdrawn in such a rate s to have a constant interphase in the flash chamber.

Okamoto (96) introduced a metallic equilibrium apparatus for tudy of petroleum oils. The partially vaporized feed from the ipe still is atomized in a large chamber by a rotary nozzle. Vapor s then dried in a cyclone, and the phases are cooled for sampling.

Equipment

odified Othmer Recirculating Equilibrium Still (99,104): Figure (1) hows the modified unit adopted for this work, and it is made up of our separate parts. The boiler section has a total capacity of 000 cc., and is made of two joined hemispheres, with the larger one n the top and the smaller one on the bottom. The geometry of the ntire pot is as follows:

Distance from bottom (cm.)		Approximate volume (cc.)
1.5		50
2.5		100
3		150
4		200
5	Converging from the small to the large hemisphere	250
5.5		300

Distance from bottom (cm.)		Approximate volume (cc.)
5.5	11 cm. wide	500
7		500
10		950
12.5	Recommended maximum operating capacity	1500
16		2000
	maximum possible hold-up	2350

The 100 cc. mark on the condenser is equilevel with the 2000 cc. mark on the pot.

A ball joint (§ 12/5) is provided at the bottom of the pot to ke a convenient connection for the condensed vapor return line. large evacuated ball joint (§ 65/40) is at the top center of the t, and on one side of it a thermometer well (₮ 19/38) is provided, ile on the other side the long vapor-line (1 inch I.D.) is con- cted. A short thermometer well for measuring the vapor temperature fixed to the central joint. The side thermometer well extends to e center of the extended section of the pot for measuring the quid temperature. The vapor-arm at the top is connected to a rved return line by means of a large ball joint (§ 65/40). One de of the curved vapor-line-extension has a small thermometer ll, and the other side is connected to the top of the vapor con- nser.

The condenser consists of five balls, and the last one is ovided with a side opening to an auxiliary condenser, and a ort tapered inlet to the receiver. This tapered nozzle allows

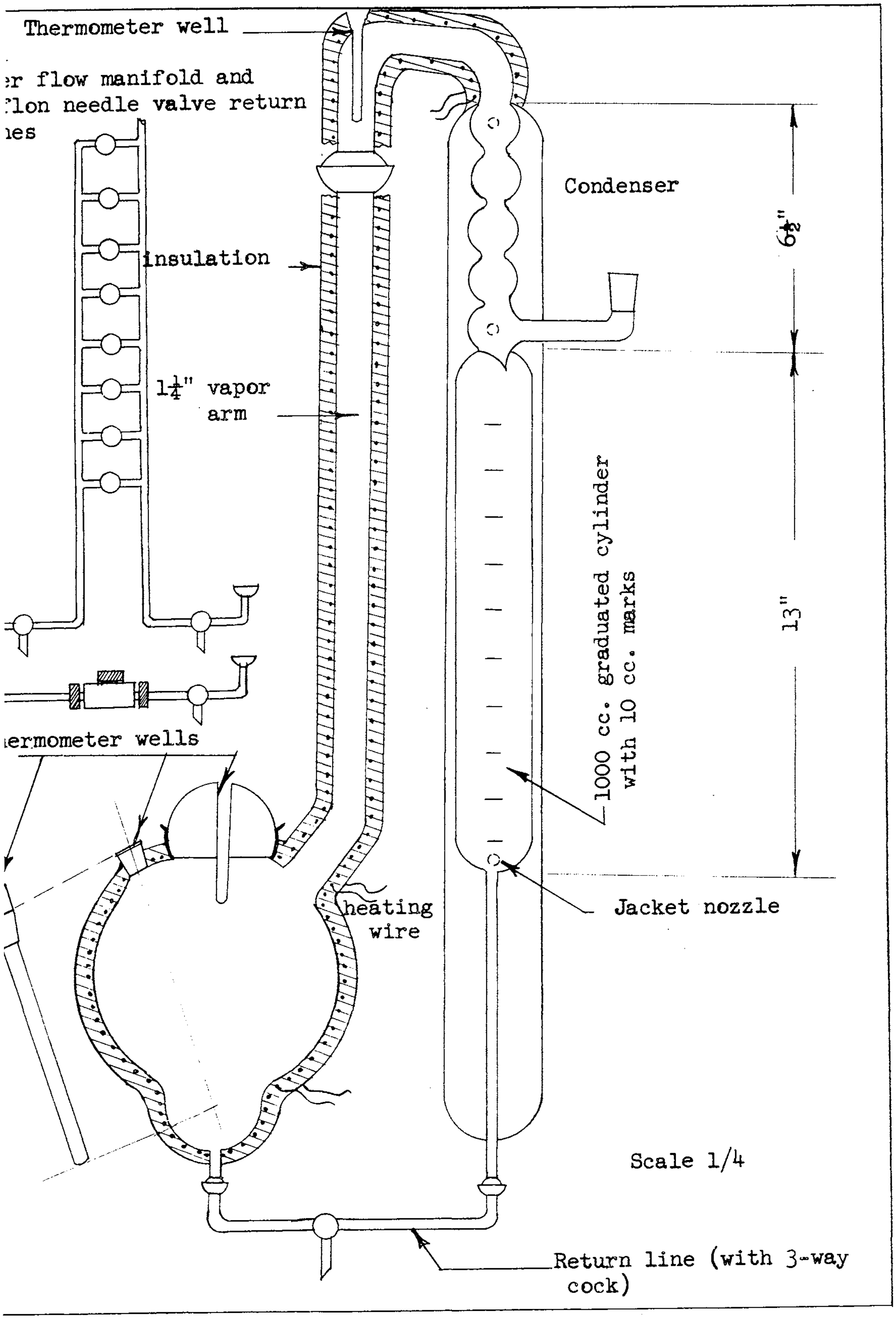


Figure 1 - Othmer Equilibrium Still

counting of drops of condensate to the reservoir, which serves to ure the boil-up rate. The condenser and the condensate-reservoir placed in a single water cooled jacket, which extends down to the joint of the return line. Three water nozzles are provided for cooling jacket, one being at the top, and one at the end of the denser, while the third is located at the end of the receiver.

A water connection from a constant head and constant tempera- tank is made to the central nozzle. The condensate reservoir graduated from 20 cc. to 1000 cc. in 10 cc. divisions. Either uxiliary condenser or a cold trap, depending on the nature of roleum fraction under study, can be attached to the side-arm by ns of a tapered ground glass joint (₸24/40).

Three different types of condensate return lines were made, each one was examined independently. A three-way regulating k similar to the original one used by Othmer, but with ball con- tions to the pot and the reservoir, comprised one of the condensate urn lines. The second one is similar to the first one, only it a highly sensitive Teflon needle valve in the line for control the recirculation rate. The third one is of entirely different nciple, and simply consists of a manifold of overflow connections. manifold has eight equally spaced connecting cross flow lines, re each one is controlled with a cock. The drainage of both pot the reservoir are through the three way cocks.

The pressure regulating line is connected to the top of the iliary condenser or the cold trap, and the siphon breaking xtension of the manifold.

A thin layer of asbestos paper is molded over the entire pot nd the vapor-arm. The asbestos paper is coated with graphite imregnated asbestos cement. The small extension of the pot, the main ody of the pot, and also the entire vapor-arm, are wrapped with hree 1000 W. heaters. Each of these heaters consists of 30 Ft. 1omh/Ft.) of asbestos insulated Nichrome wire. The wires are wound niformly over and around the pot and the vapor-arm. The heating ires are covered with a layer of asbestos cement, and then many ayers of asbestos paper. The entire heating section is covered ith asbestos cloth tape, and finally with aluminum foil to make a atisfactory heat insulator. The Nichrome wire is more closely ound at the lower section of the pot. The power input to each of he three heaters is controlled by three independent variable powertats.

Modified Thermostatic Flow Equipment (85,68): The equipment onsists of a 100 cm. integral, vacuum jacketed still with a constant emperature heater. The silvered vacuum jacket is made of 10 cm. lass tubing, and 14 expansion bellows are made into it. It is also rovided with two 1 cm. wide vertical windows for visual observation nd inspection. Heat is supplied by condensation of a saturated apor to a heater-vaporizer, which consists of about 16 Ft. of ouble-coiled 8 mm. glass tubing. A small distillation flask (300 cc. r 500 cc.) provides the saturated vapor, and a condenser at the top f the reflux jacket, condenses the excess vapor.

Feed at a constant rate passes through an auxiliary pre-heater, nd enters the heater-vaporizer coil at the top of the reflux jacket. he auxiliary heater is an electrically heated glass U tube, which is onnected to the column by a ground tapered joint. As feed flows into he column, it distributes itself between the two helical coils, and hen flows down to the flash chamber. The flash chamber is located lmost at the bottom of the heating jacket, and is about 5 cc. in iameter and 7 cm. high. Feed enters the flash chamber from both ides through two small (12 mm., E.C.) fritted glass plugs. The iquid outlet from this chamber is a small siphon tube, which asses through both walls of the jacket, and has a ball joint at ts end. The 22 mm. glass vapor line extends from the flash chamber alfway through the column, inside the heater coils, and then bends ut at about 80 degree angle. The vapor line is connected to an specially designed vapor condenser by means of a ground joint.

The vapor condenser is made of many small bulbs, alternately ocated on both sides, which procures an effective method for conensation of vapor in a short condenser, with minimum of liquid hold-up. he liquid outlet is connected to a 10 inch liquid cooler through a mall crank by means of ground ball joints. The crank can be revolved bout the axis of liquid outlet, and therefore change the relative osition of the cooler. When the crank is at its highest position, he liquid hold-up in the flash chamber is at its maximum, and it overs the fritted plugs. As the crank is turned from its highest osition, the amount of liquid hold-up in the flash chamber dereases. The sintered plugs (extra coarse, pore size 170-220 icrons), break-up the vapor into a great number of infinitely small

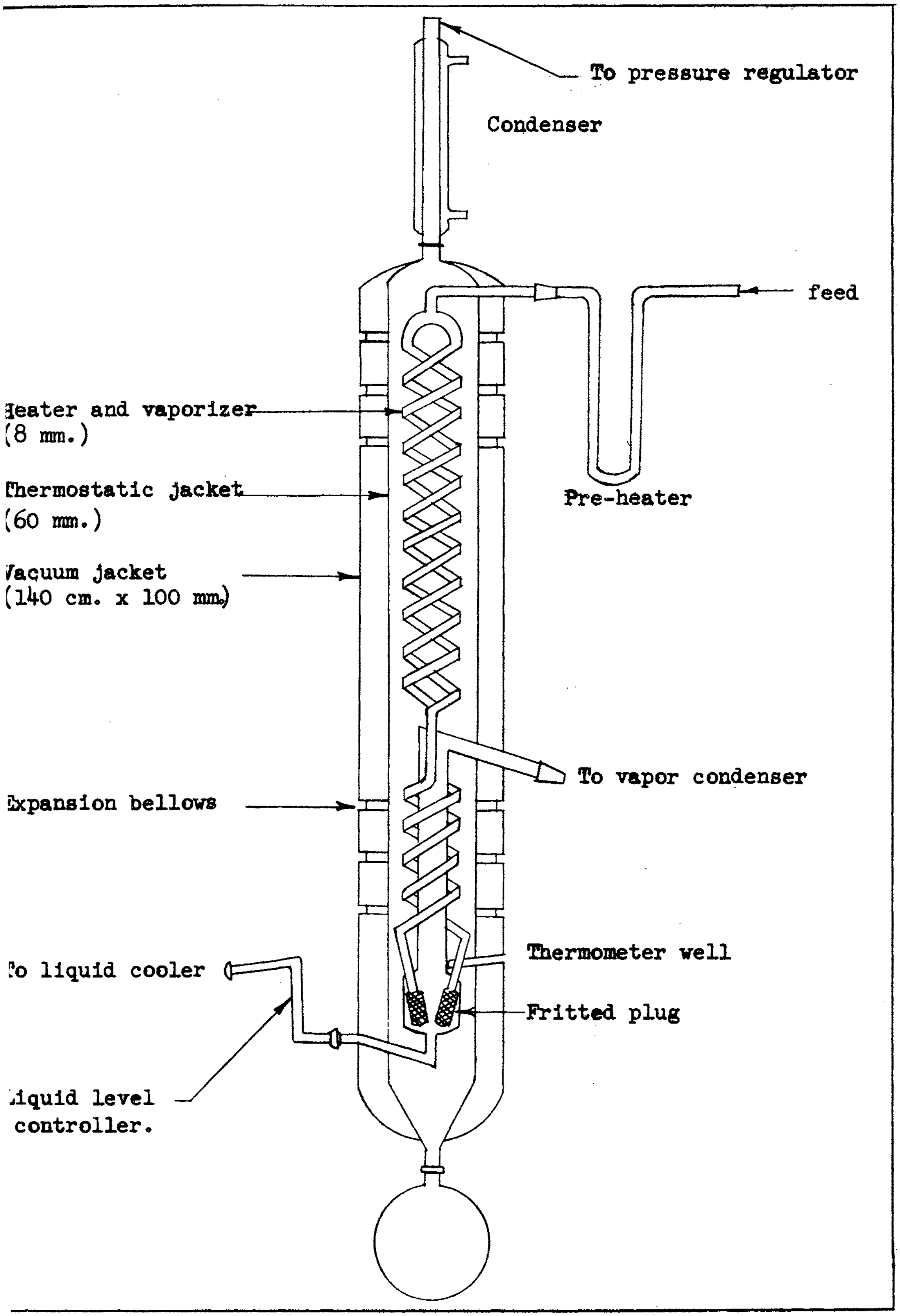


Figure 2 - Thermostatic Equilibrium Equipment

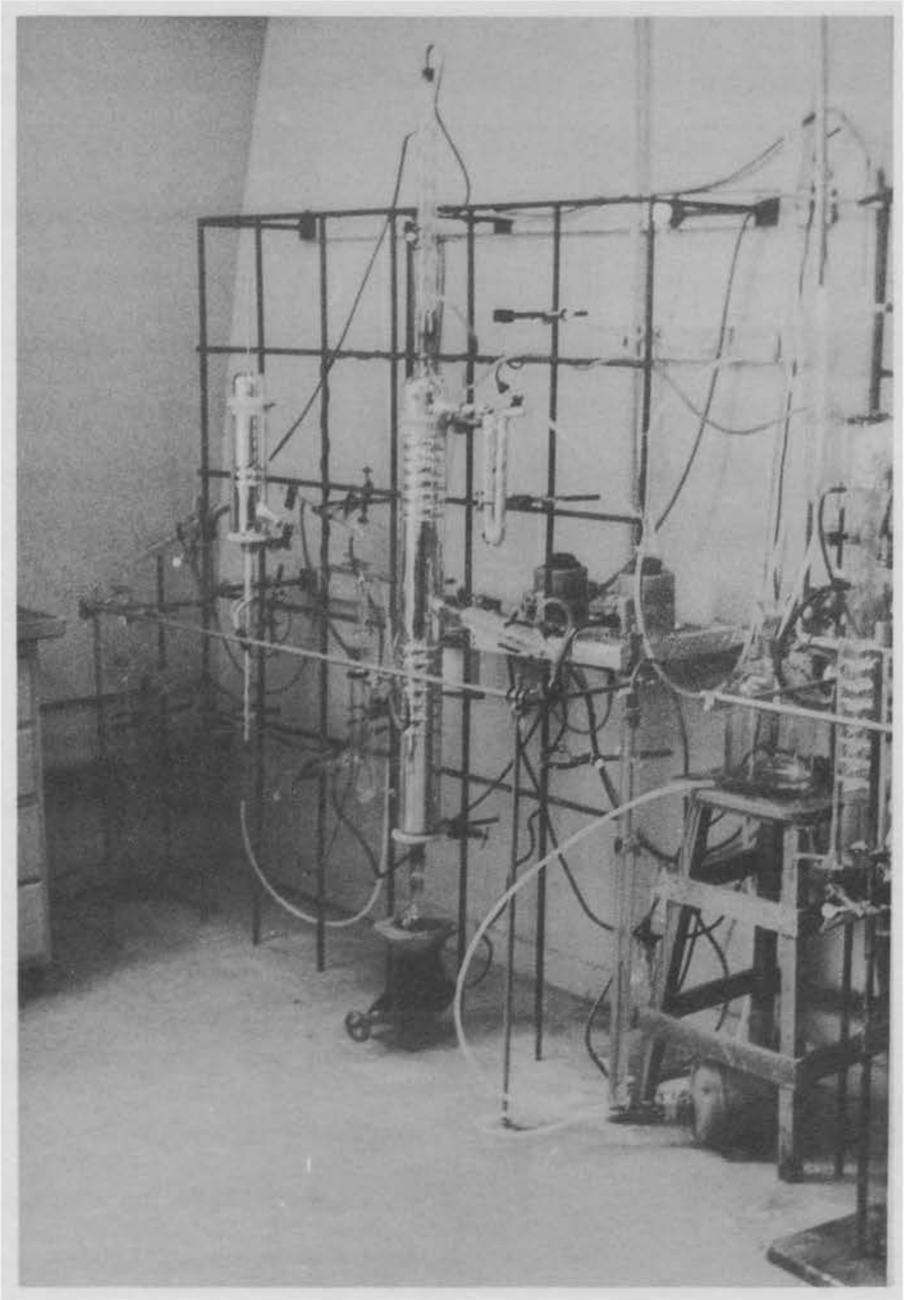


Figure 3. Picture of Flow Equilibrium Apparatus

ubbles. This, therefore, creates maximum contact between vapor nd liquid phases before they are separated from each other.

The important changes in the equipment are: a new design for ondensers, a separate boiling flask, the crank arrangement for the ontrol of liquid hold-up, and the addition of the sintered plugs. his equipment is shown in Figures (2) and (3).

New Flow Equilibrium Flash Vaporizer: Figures (4) and (5) show he design and the set up of this all glass equipment. The apparatus onsists of a heater-vaporizer, a flash chamber, a vapor condenser, nd a liquid cooler with a small crank attachment.

The heater-vaporizer is made of 50 cm. of 7 mm. glass tubing ith a ball joint at the inlet end, and a fritted glass plug (12 mm. n diameter, extra coarse) at the other end. This heater is atached to the flash chamber by a tapered ground glass joint ($\overset{T}{s}$ 24/40), hich holds the fritted plug inside the chamber. A thin layer of abestos paper is molded over the glass heater, and is coated with raphite impregnated cement for improving heat conduction and disribution. An asbestos covered Nichrome heating wire is wound niformly around this heater. The heating wire is covered with sbestos cement, and then completely covered with three layers of sbestos paper. The heater has outer layers of glass tape, and luminium foil. A removable 2 mm. glass rod is placed inside the eater.

The flash chamber is isothermally insulated by the vapor, nd the entire internal section is adiabatically insulated by a acuum jacket. The jacket is 40 cm. long, and 10 cm. in diameter

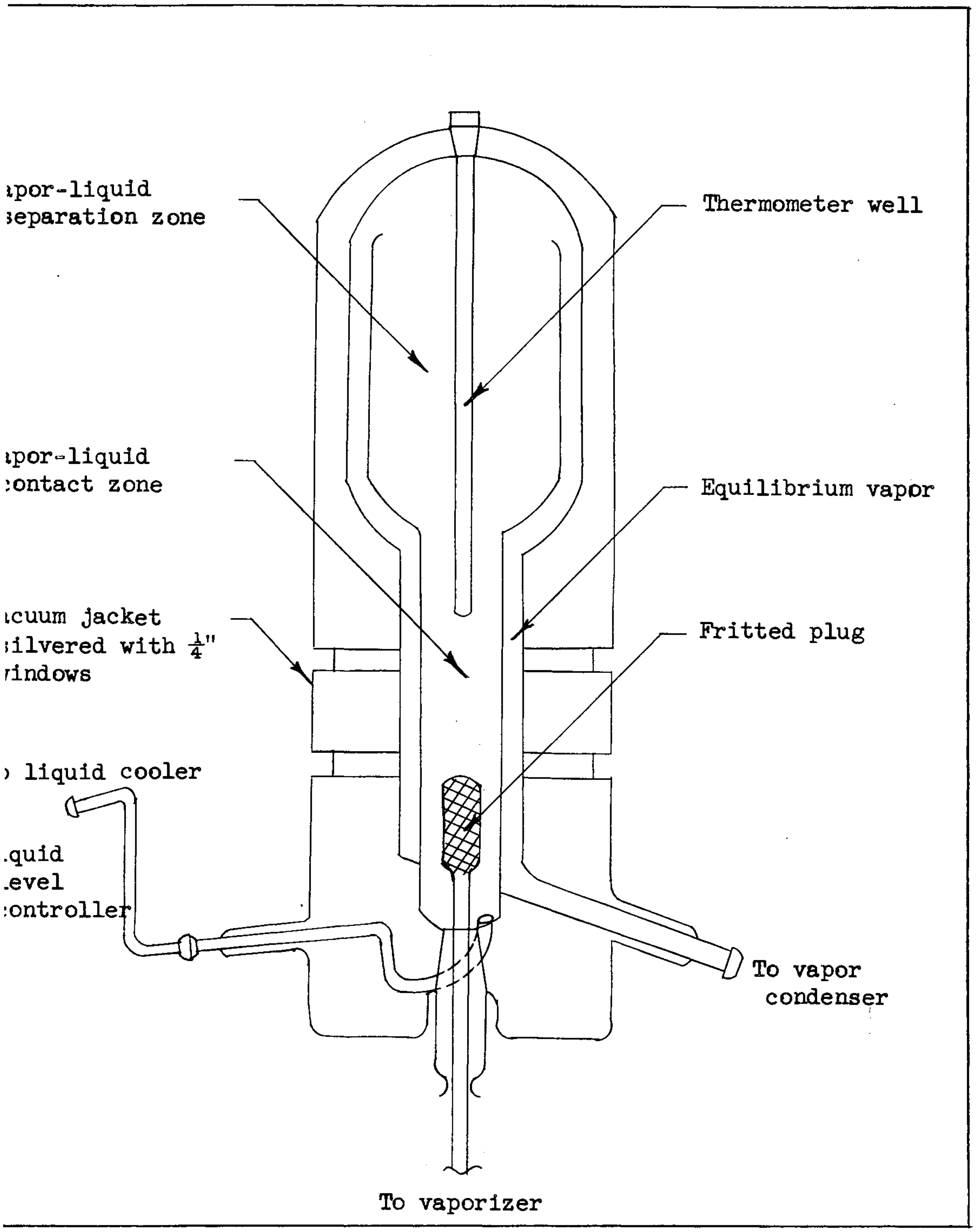


Figure 4 - The New Equilibrium Equipment

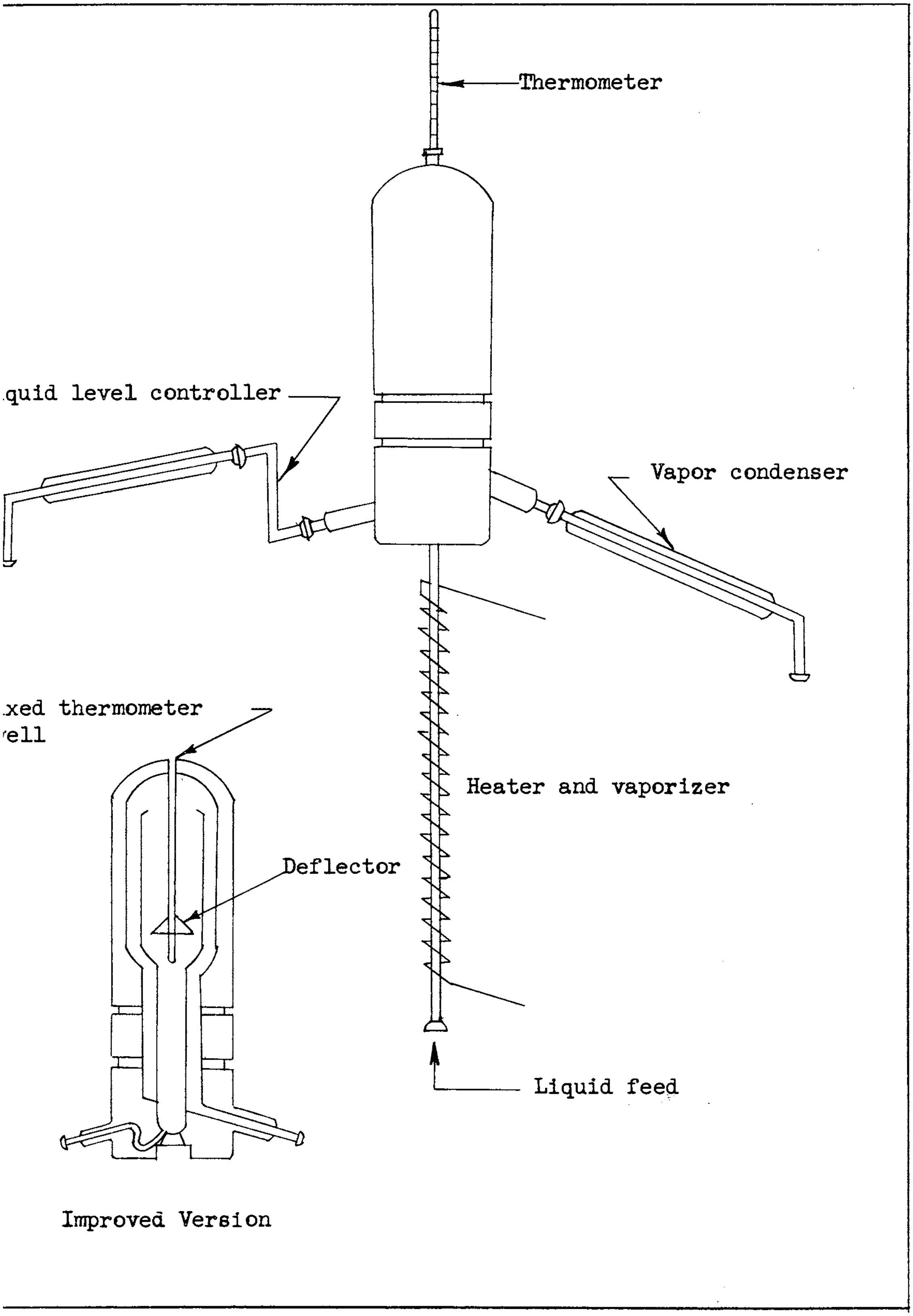


Figure 5 - The New Equilibrium Equipment

h two expansion bellows at the upper section. The vacuum jacket completely silvered with the exception of two narrow observation ndows. A thermometer well extends from the top of the jacket down the flash chamber. A condenser similar to the one used for the ner flow equipment is connected to the vapor out-let by means of ball joint. As the feed flows from the heater-vaporizer to the ash chamber, the vapor portion of it is divided into a large number very small bubbles in the narrow (25 mm.) section of the flash amber. Vapor then passes through the disengaging section (55 mm.). x 80 mm. high) with a much reduced velocity, where it loses s liquid droplets. The vapor finally flows downward around the ash chamber, and in between the composite walls to the condenser.

The liquid line with a small U-shaped trap is attached to e bottom of the flash chamber in such a way as to eliminate any ssible dead space. The liquid outlet is connected to the crank d the liquid cooler by ball joints. The position of the crank ntrols the amount of liquid hold-up in the contacting section of e flash chamber. This governs the extent of contact between the ases.

Liquid Flow: A well controlled flow of feed is essential r flow equilibrium apparatus, and Figures (3), (6) show the ccessful flow system used in this work. The flow rate was easily d accurately controlled over a wide range (from 1 cc./min. to cc./min.) with a negligible variation during a long period of eration. Liquid feed is transported by a small gear pump (Eastern) om the bottom of a large glass surge tank to a one liter constant

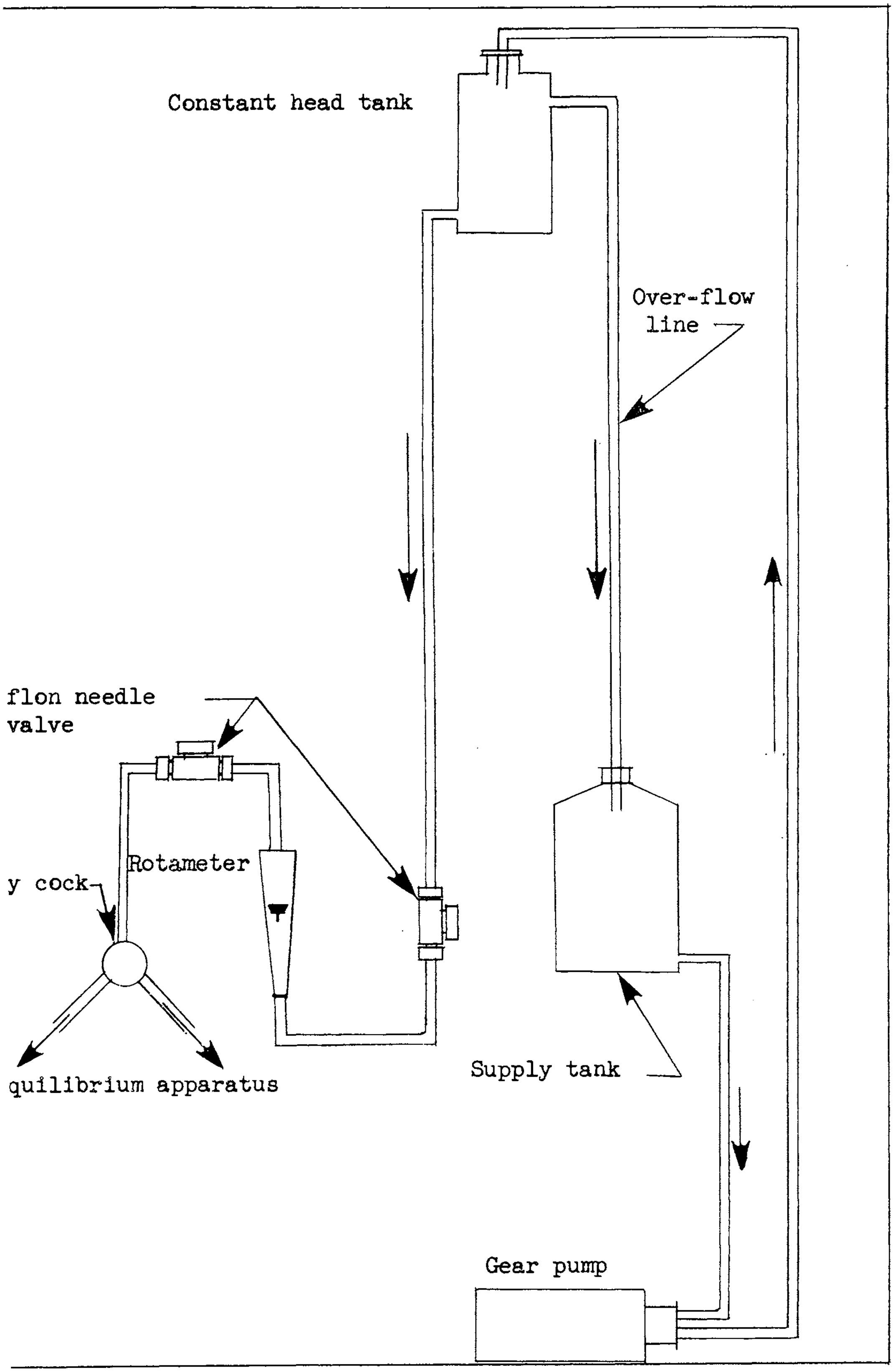


Figure 6 - Feed Flow System

ad tank, located at about 10 ft. above the pump. The constant ad tank has an over-flow connection at the top, which returns the cess liquid to the surge tank.

From the bottom of the constant head tank, the feed may flow either one of the two flow equilibrium apparatus, depending on e selected position of a three-way cock.

Control of flow is accomplished by two sensitive Teflon edle valves, placed on both sides of a rotameter in the transfer ne. All the connecting lines are of 1/4 inch heavy wall polyhylene tubing. Two fine screens are placed on each end of the tameter for keeping the fritted plugs free from any solid particles. ed was always filtered through glass wool, and its contact with air s kept to a minimum.

Atmospheric Pressure Correction: The atmospheric pressure the laboratory is variable and usually less than 760 mm. Hg. dependable and accurate pressure compensator was designed to eliminе this discrepancy (Figures 3, 7). Air from a high pressure line reduced by means of a pressure regulator, and is dried and cleaned it passes through a bed of silica-jel. The air pressure is then rther reduced by a needle valve, before it enters into a surge tank. essure in the surge tank is controlled and regulated by a sensitive s-bubbler.

The bubbler consists of an approximately 30 inches of 2 mm., D. glass tubing, partially immersed in a 1 1/2 inch glass pipe ntaining water. The other end of the small glass tubing which is t in the water, is connected to the surge tank. Air pressure is so

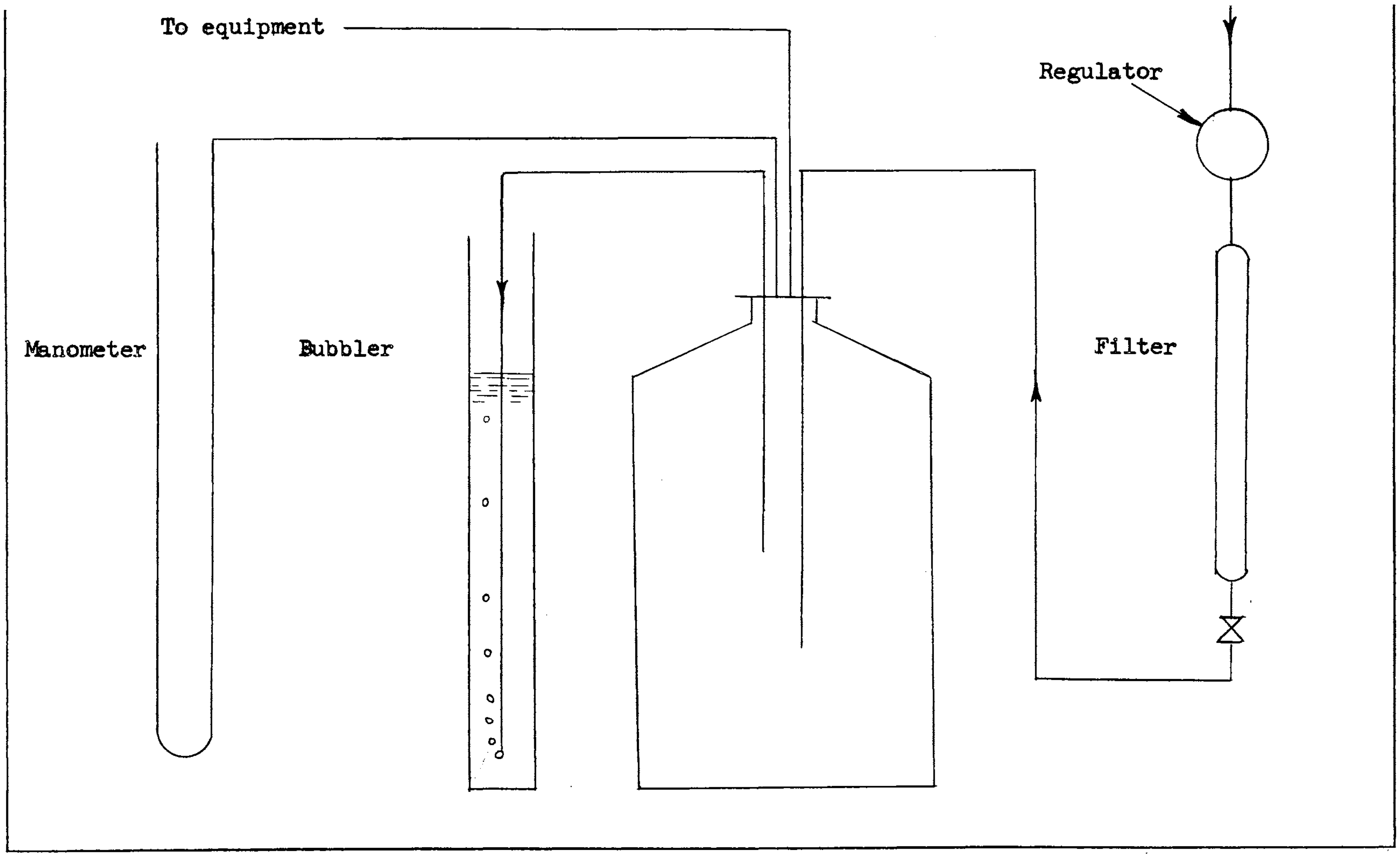


Figure 7 - Pressure Compensator

;ulated as to cause a very small flow (one or two bubbles/sec) :ough the glass tubing. Air bubbles which are released from the › of the tubing pass through water, and into the atmosphere. The ıss tubing can be moved up or down to change the static head of :er at the point where air is released. The immersion dept of the ıss tubing in water is equivalent to the air pressure in the surge ık, because the pressure drop due to a small flow of air through : bubbler is negligibly small.

Lines which convey the pressure to the equipment, and to a ısitive manometer, are also connected to the surge tank. The :ferential pressure measured by this manometer, plus the baro- :ric pressure constitute the absolute pressure of the equipment.

Vacuum System: A simple but adequate vacuum system which was :d in this investigation, is shown in Figures (3, 8). The vacuum ıp is directly connected to a large metal surge tank, provided :h a vacuum release and drain valve at the bottom. The surge tank connected to a Cartesian manostat, which controls the vacuum. A :rogen bubbler, located between the manostat and the cold traps, leases enough nitrogen into the system to eliminate any possible :tion of hydrocarbons, therefore loss of products. Nitrogen ›m a high pressure cylinder is reduced, and bubbled at the rate of : or two bubbles per second through a liquid of very low volatility. : percolation of nitrogen facilitates its rate control by visual ›ervation. Atmospheric air can also be used successfully, when :re is no possibility of material oxidation. The vacuum line can :her be connected to the cold trap of the recirculation still, or

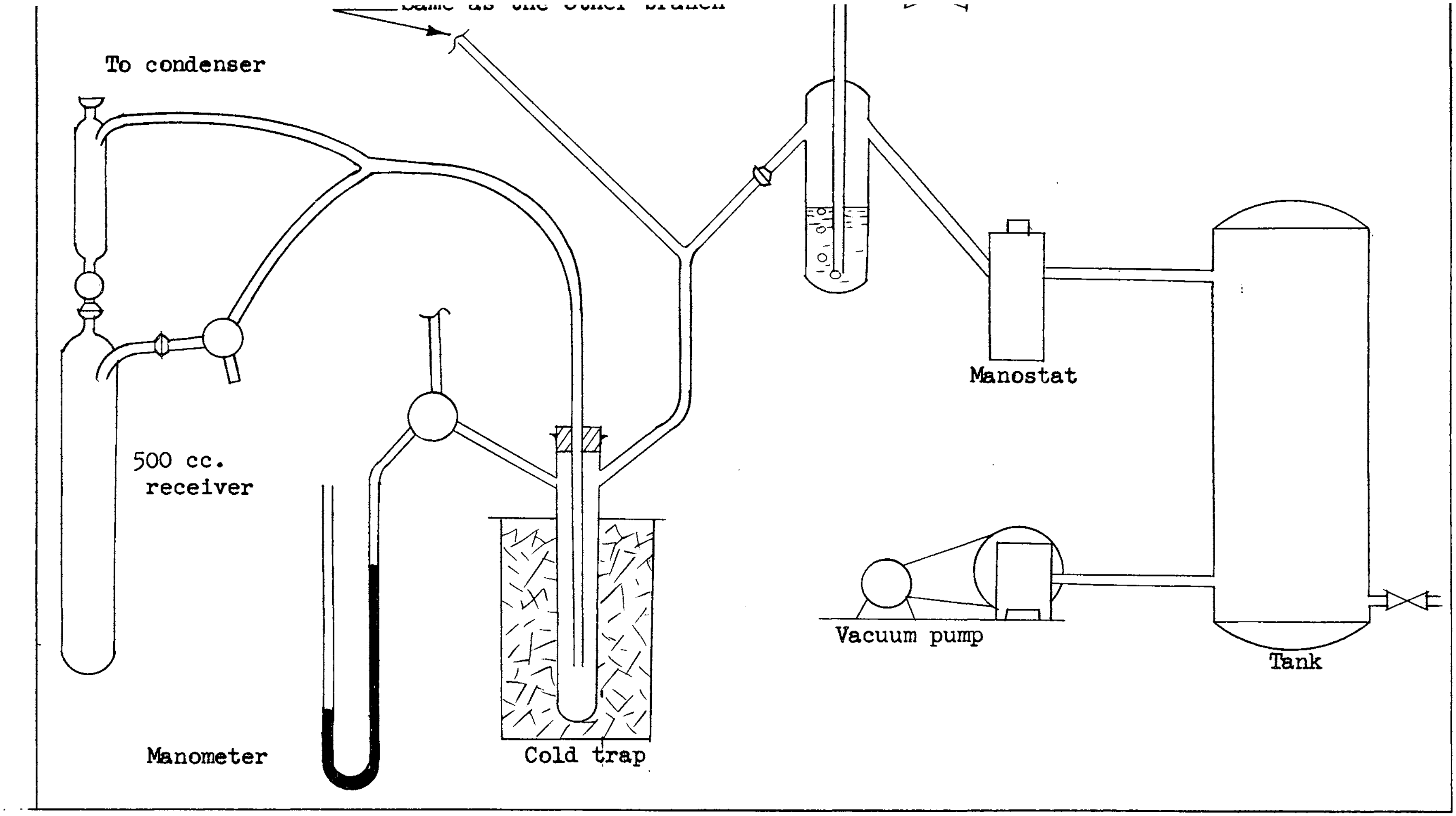


Figure 8 - Vacuum System

the traps of the flow apparatus. One system of traps and re-
.vers is designed for the flow apparatus, and it can be attached
either of the two flow apparatus.

In the vacuum connection for the flow systems, there are
inches for vapor and for liquid sides. There is a cold finger trap
each vacuum line , which insures against loss of volatile compon-
;s. The cold traps can either be kept in ice or solid CO_2, as
juired. A three-way cock can connect any one or both of the cold
ips to a mercury manometer. Heavy rubber lines connect the cold
ips to product receivers and collectors.

Each product receiver is a small 50 cc. glass container,
.ch at one end can be connected to the product condenser, and at
other end to a 500 cc. collector, by means of ball joints. A
ee-way cock connects each product collector to the vacuum system.
h product collector can be removed from the system by first
sing the glass stop cock between the receiver and the collector,
then releasing the vacuum.

All the vacuum lines are made of a sufficiently large tubing,
the connections are sealed with special rubber cement.

Temperature Measurements: Temperature measurements were made
h both calibrated thermocouples and thermometers. Figure 9 shows
thermocouple circuit as it was used in the experiment. The
rmocouples are made from Chromel-Copnic wires, and are flash
.ded together. The cold junctions, as well as copper lead junc-
ns were placed inside of individual oil filled glass tubing,
.ch were kept in an ice bath. The lead lines were then connected

a two-gang-multipole selecting switch, and finally to a very sensie Leeds and Northrup type K potentiameter. Standard accessories, n as a sensitive Leeds and Northrup galvanometer, batteries, and a ndard cell, were used.

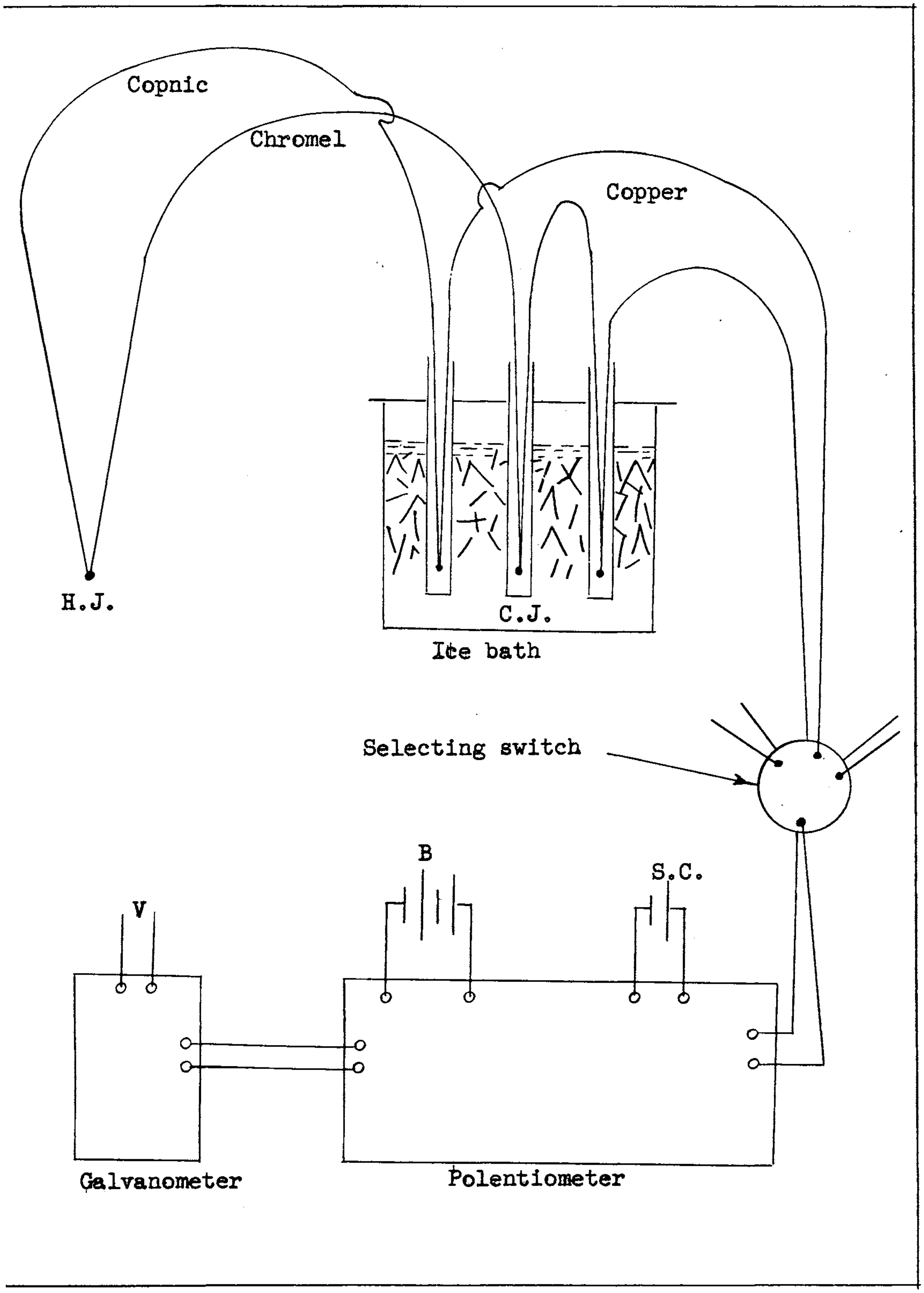


Figure 9 - Thermocouple Circuit

Procedure and Tests

Othmer Still: This still was tested for pressure drop by aecting one leg of an inclined manometer to the thermometer well ning of the pot, and the other leg to the auxiliary condenser. manometer liquid was selected to be the same as the pot liquid, the vapor condensing in the leg of manometer connected to the pot ld be of the same composition as the manometer liquid. Two liquids, uene and water, were used for this purpose, and it was noticed that n at the highest flow rate (2.4 liter/hr) the pressure drop ctuated between 0.8 and 1.0 mm. of liquid. The pressure drop at operating rate is even smaller, therefore, quite negligible.

Entrainment, which often causes trouble in many stills was mined by a colorimetric method. A known quantity of dye was solved in the pot liquid, and after distillation at various es and with various levels in the pot, the reservoir liquid was mined for dye. Toluene and water which have different inter- ial properties, were arbitrarily chosen for this test. Tests e conducted at 200, 1000, and 2000 cc. pot hold-ups, and boil- rates ranging from the normal operating condition (1-2 drops/sec) the maximum rate of about 2.5 liter/hr. The complete absence of in the reservoir liquid, even at the most severe condition was erved. This test clearly indicates that entrainment is not a tor for the equipment.

The material loss (as vapor or decomposition) was investigated h the following typical results:

Charge	2000 cc.
Rate	1 drop/sec.
Water temperature	23 - 25 °C

	duration of operation	loss
benzene (B.P. 80.1 °C)	5 Hr.	8 cc.
toluene (B.P. 110.8 °C)	5 Hr.	3 cc.
o-xylene (B.P. 144 °C)	5 Hr.	3 cc.
o-xylene	10 Hr.	8 cc.
n-decane (B.P. 174 °C)	2 Hr.	2 cc.
With 2" Hg positive pressure		
toluene	1 Hr.	5 cc.
toluene	3 Hr.	9 cc.
toluene	5 Hr.	12 cc.

Test for thermal decomposition, using a heavy petroleum cut ith A.S.T.M., I.B.P. 132 °C, E.P. 311 °C, flashed at 218 °C

time - Hr.:	1	3	7
condition :	no discoloring or loss	yellow color	light brown

A very important factor in all the recirculating stills is the ime which the system requires to come to equilibrium, and the following test was devised for this purpose. In the case of binary mixures, the returning vapor condensate to the pot was analyzed at arious time intervals and was plotted versus time to ascertain the rue equilibrium condition. The same technique was applied to the ase of multicomponent mixtures, but here only the relative amounts f some of the components were plotted. The experiments showed that he determination of the relative quantities of only two predominantly

ccurring components (preferably one near each end) are adequate for
his test. These relative quantities were determined by the method
f Chapter V. The identification of these components evidently is
ot necessary. The representative curves are shown in Figure (10).

Equilibrium tests were conducted under various conditions
Appendix B), and the results can be judged from Figures (11, 12),
hich compare very favorably with those of literature. Two binary
ystems of acetic acid-toluene, and benzene-toluene were selected.
he acetic acid-toluene system was analyzed with 0.0965N - NaOH.
or the titration, sufficient quantity of water was added to the
ample to reduce the concentration of the acid and also to aid in
ts extraction from the organic phase. The time required for the
xtraction of the acid from the organic phase was noted. The possi-
ility of interference of atmospheric CO_2 in the titration due to
he existance of organic layer on the top was nil.

The benzene-toluene system was analyzed by chromatography.
wo sets of experiments were performed, one with the overflow mani-
old, and the other with the Teflon neddle valve connection. As
xpected, the results were in agreement. The procedure for studying
quilibrium vaporization of petroleum fractions was conducted
xactly as the test runs, and by use of the overflow manifold. The
ame method for knowing the true equilibrium condition (plot of
oncentration vs time) was applied. Under all operating conditions,
he maximum quantity of liquid in the pot was never more than 2000 cc.
he analytical requirement was such that at least 1000 cc. of each
hase was needed. For instance, for a 10 percent vaporization, the

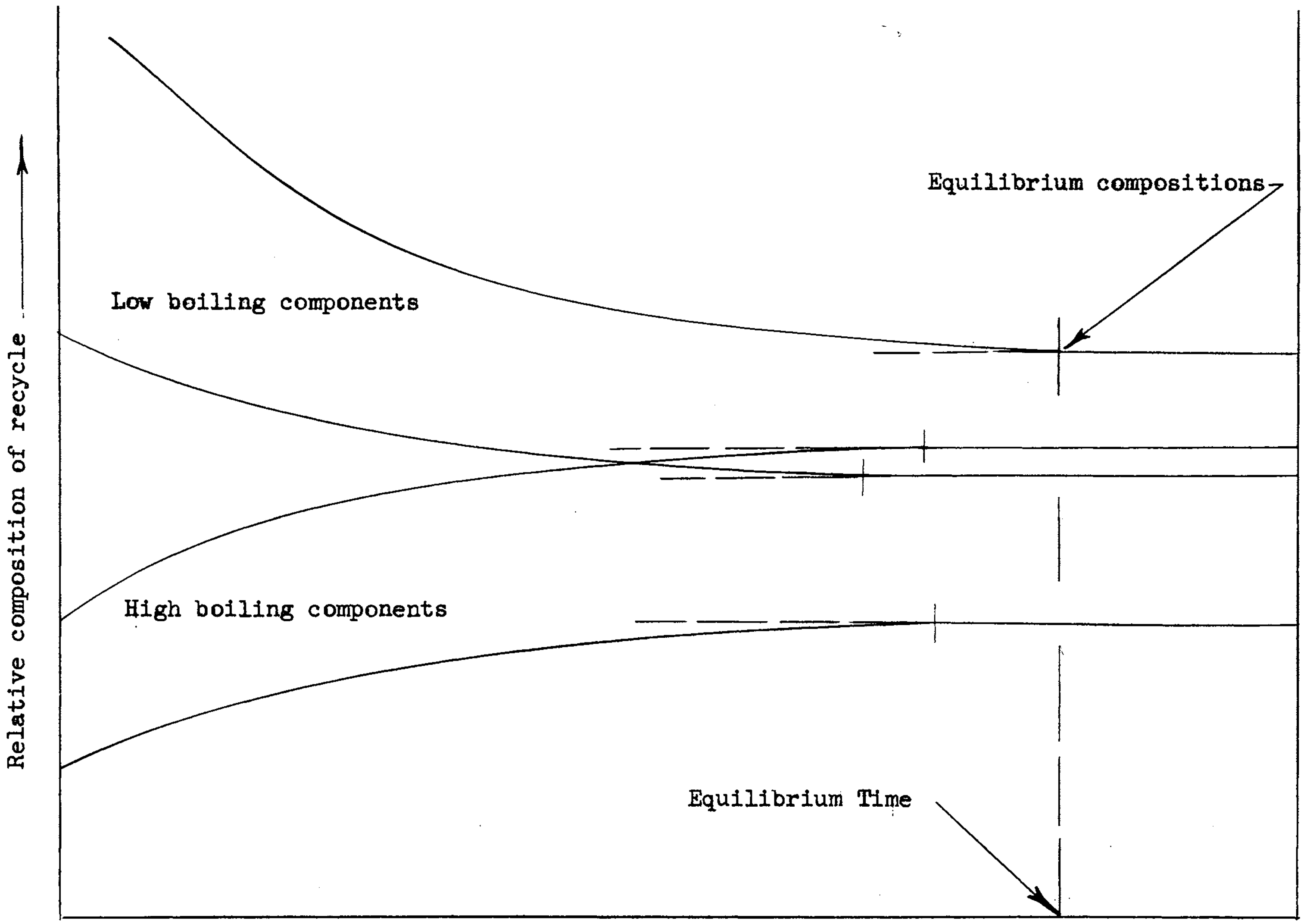


Figure 10 - Rate of Approach of Othmer Still to Equilibrium

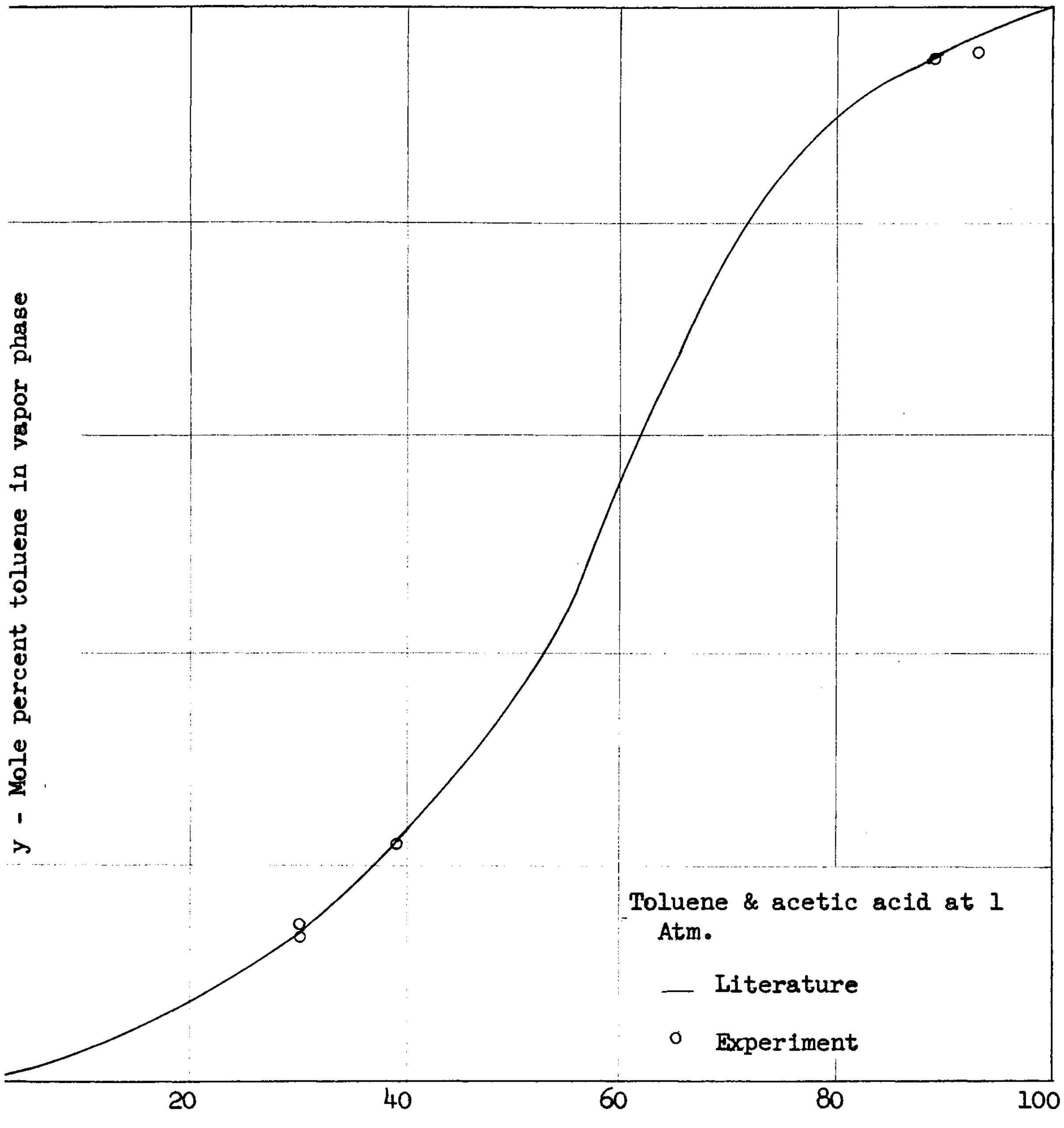
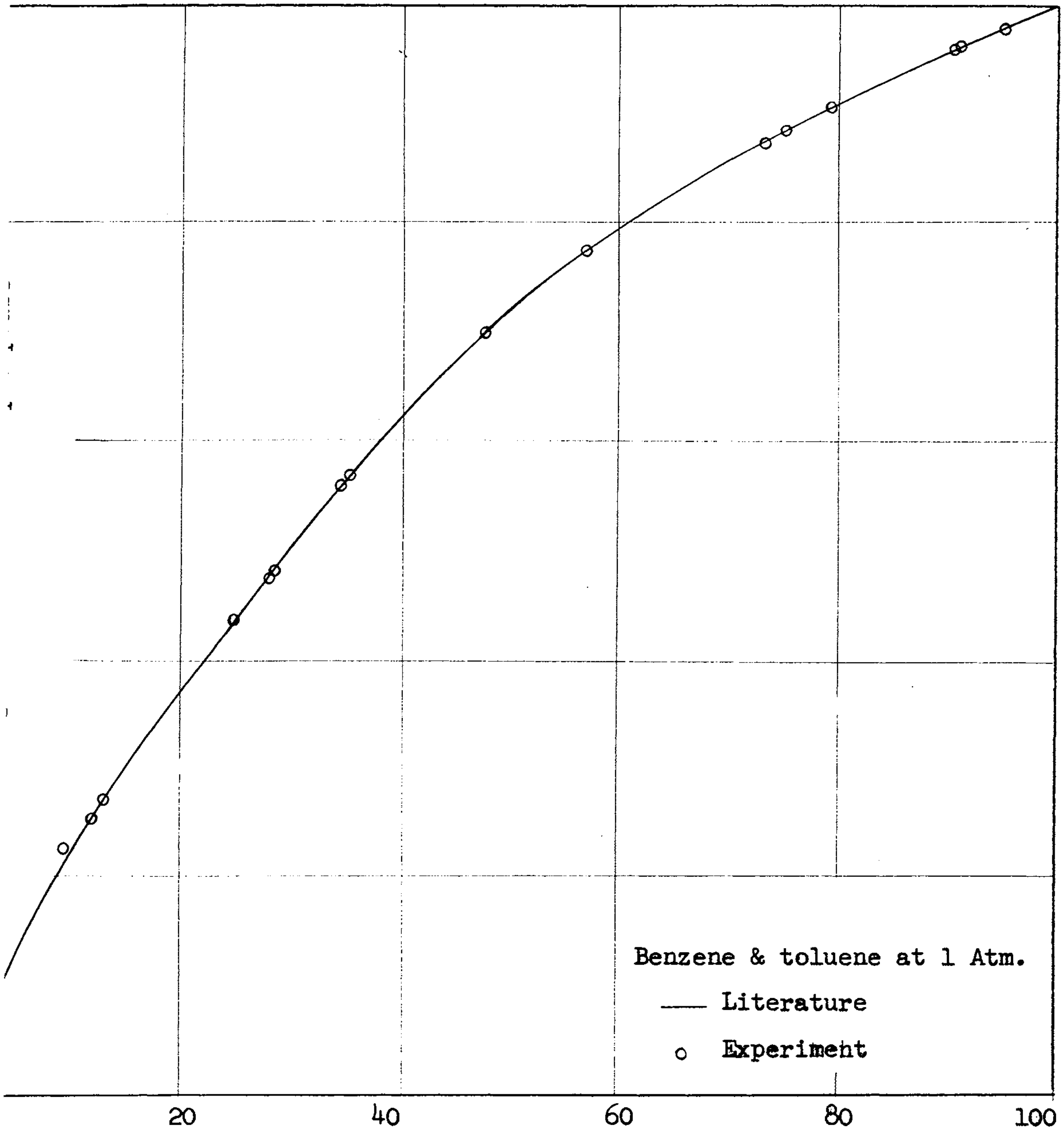


Figure 11 - Equilibrium Test - Othmer Still



x - Mole percent benzene in liquid phase

Figure 12 - Equilibrium Test - Othmer Still

experiment was repeated six times to collect enough samples. It is important to establish exact heat inputs by trial runs. In the case of even the smallest amount of leak, the experiment was repeated again.

A small amount of carbon was deposited each time inside the flask whenever a long period and high temperature were used. This layer of carbon was removed by heating the empty pot, and raising its temperature very slowly, and at the same time blowing air into it. In some instances it became necessary to treat the pot with a cleaning solution.

<u>Thermostatic Flow Equilibrium Equipment</u>: The two important tests for this equipment are entrainment and equilibrium. The same colorimetric technique was used to study entrainment characteristics. A series of tests was conducted at various vapor rates and at various liquid hold-ups in the flash chamber, using water, toluene, benzene, and a light naphtha as the test liquids. The experiments show that vapor rates up to about 1.3 liter/min. (at the standard condition) would not cause any entrainment.

Figures (13,14) show the comparison between the equilibrium data obtained with this equipment, and those which were taken from the literature. The benzene-toluene system was analyzed as before, while refractometry was used in the case of toluene - n-octane system. Refractive indices were measured by an Abbe refractometer (Spencer 1591) at 25.0 °C, and using a yellow light. Thirty six standard solutions were prepared by volumetric method at a constant room temperature, and with a maximum possible error of less than 0.5%. The calibration curve was prepared on a large graph paper for improving its

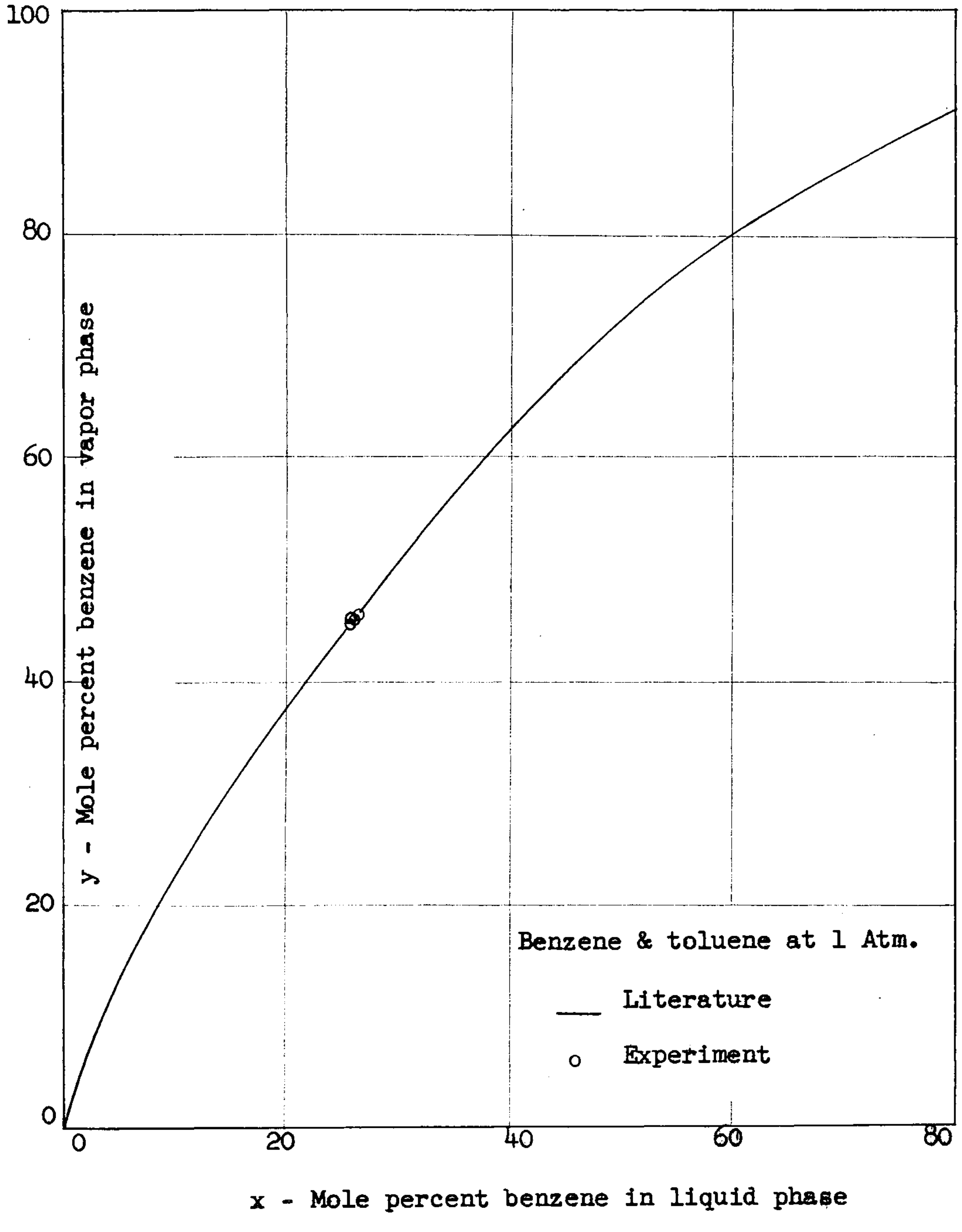


Figure 13 - Equilibrium Test - Thermostatic Flow

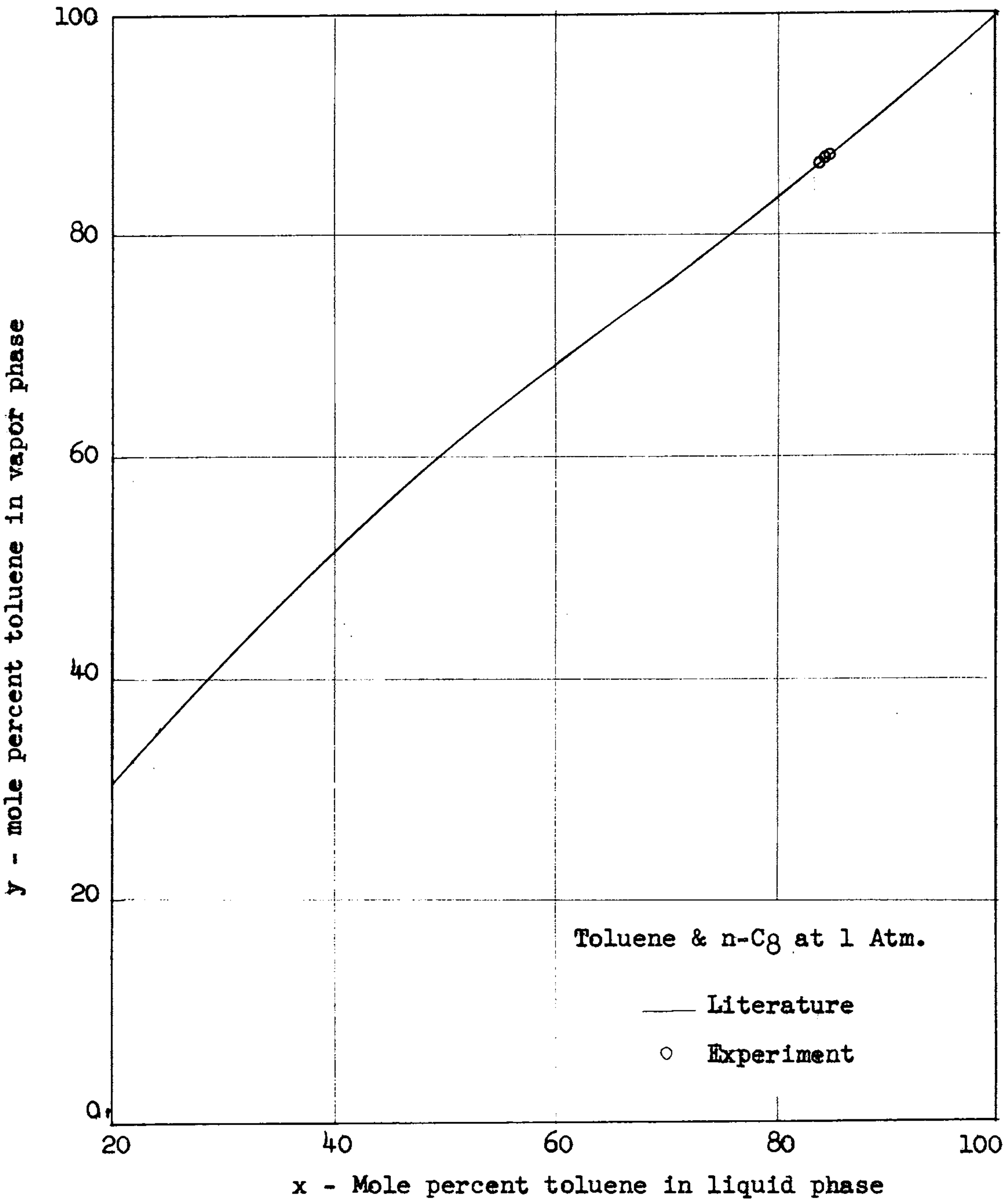


Figure 14 - Equilibrium Test - Thermostatic Flow

accuracy. All the samples were kept in a refrigerator, and they were analyzed as soon as possible. The small glass sampling containers were cleaned with a cleaning solution, and were dried in an oven.

Two techniques were used to establish the desired operating conditions whenever petroleum fractions were flash vaporized. A plot of $(\frac{L}{V})$ versus feed rate was prepared to investigate the operating range at which $(\frac{V}{L})$ ratio is independent of the feed rate. The second test consisted of plotting the relative quantities of some of the components versus feed rate. These relative quantities of components were measured by chromatography as before. The trial test was conducted for each case, before collecting 1000 cc. samples. Figures (15, 16) show some representative plots.

The jacket temperature was maintained by refluxing one of the following organic materials, at 760 mm. Hg. Atmospheric pressure compensation was accomplished as already described.

2, 2, 4 - trimethyl pentane
2, 3, 4 - trimethyl pentane
n - octane
ortho xylene
ortho toluene
n - decane
n - dodecane
1, 2, 4, 5 - tetramethyl benzene
Naphthalene
n - tridecane
2 - methylnaphthalene

α - chloronaphthalene

1 - bromonaphthalene

Some of the high boiling thermostatic materials were not stable with heat, therefore two thermometers were placed inside the jacket to detect any possible change of temperature. Although, the discoloring of thermostatic materials with heat is not an indication of a large conversion, nevertheless, these materials were often distilled or replaced. The thermostatic system was always cleaned after each use, by refluxing benzene or toluene for some time and drying with air.

The time required to bring the column to the operating temperature depends only on the boiling point of the refluxing liquid, and is often short.

New Flow Equilibrium Equipment: In the operation of this equipment, both feed and heat flows to the vaporizer must be kept absolutely constant during each run. The flow of feed to the vaporizer, as explained before, was highly dependable. The input of electrical power through a variable powerstat, as it was tested by sensitive meters, changed but insignificantly at all times.

Entrainment, and equilibrium tests were conducted as for the other flow equipment. Figures (17, 18) show the equilibrium data obtained by this equipment, using benzene-toluene, and toluene-n octane systems. Figure (19) compares the results of equilibrium vaporization of a petroleum fraction, obtained by the mentioned devices.

The procedure for vacuum operation is basically the same for

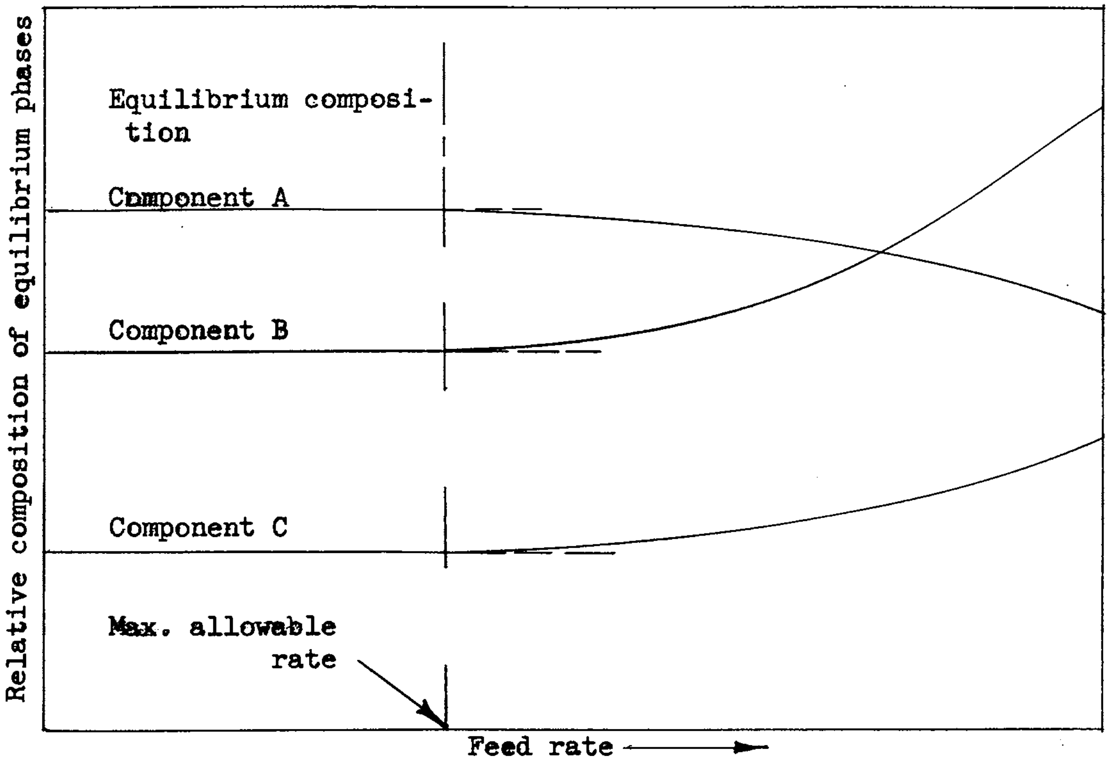


Figure 15 - Condition of Equilibrium for the Thermostatic Equipment

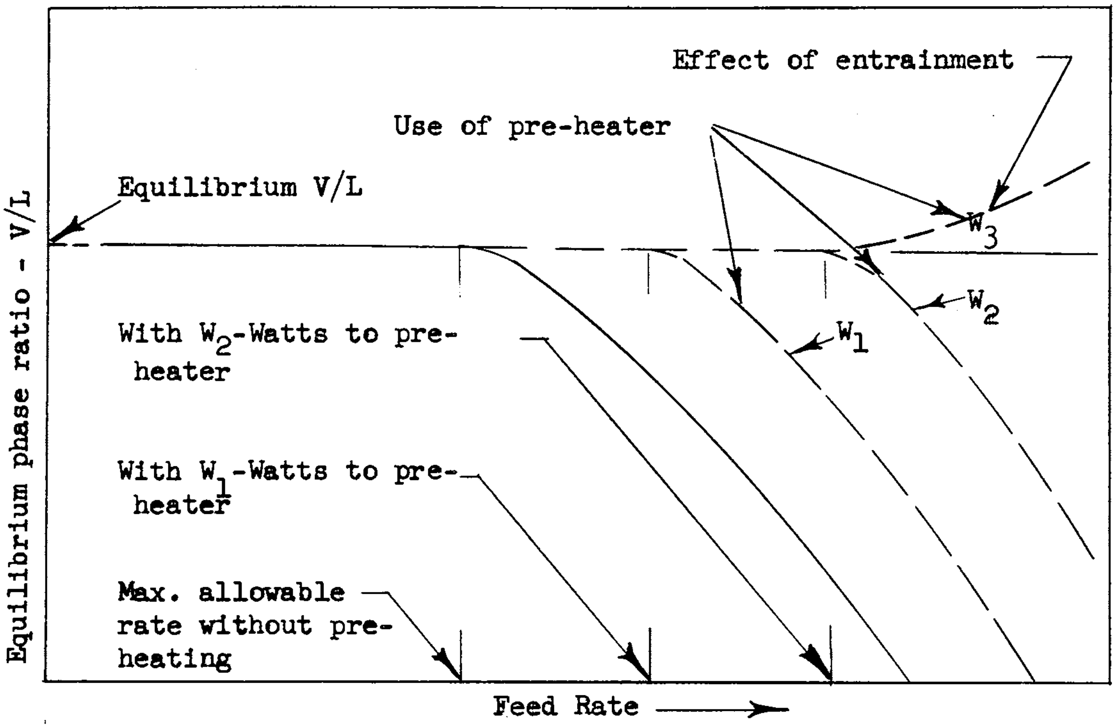


Figure 16 - Condition of Equilibrium for the Thermostatic Equipment.

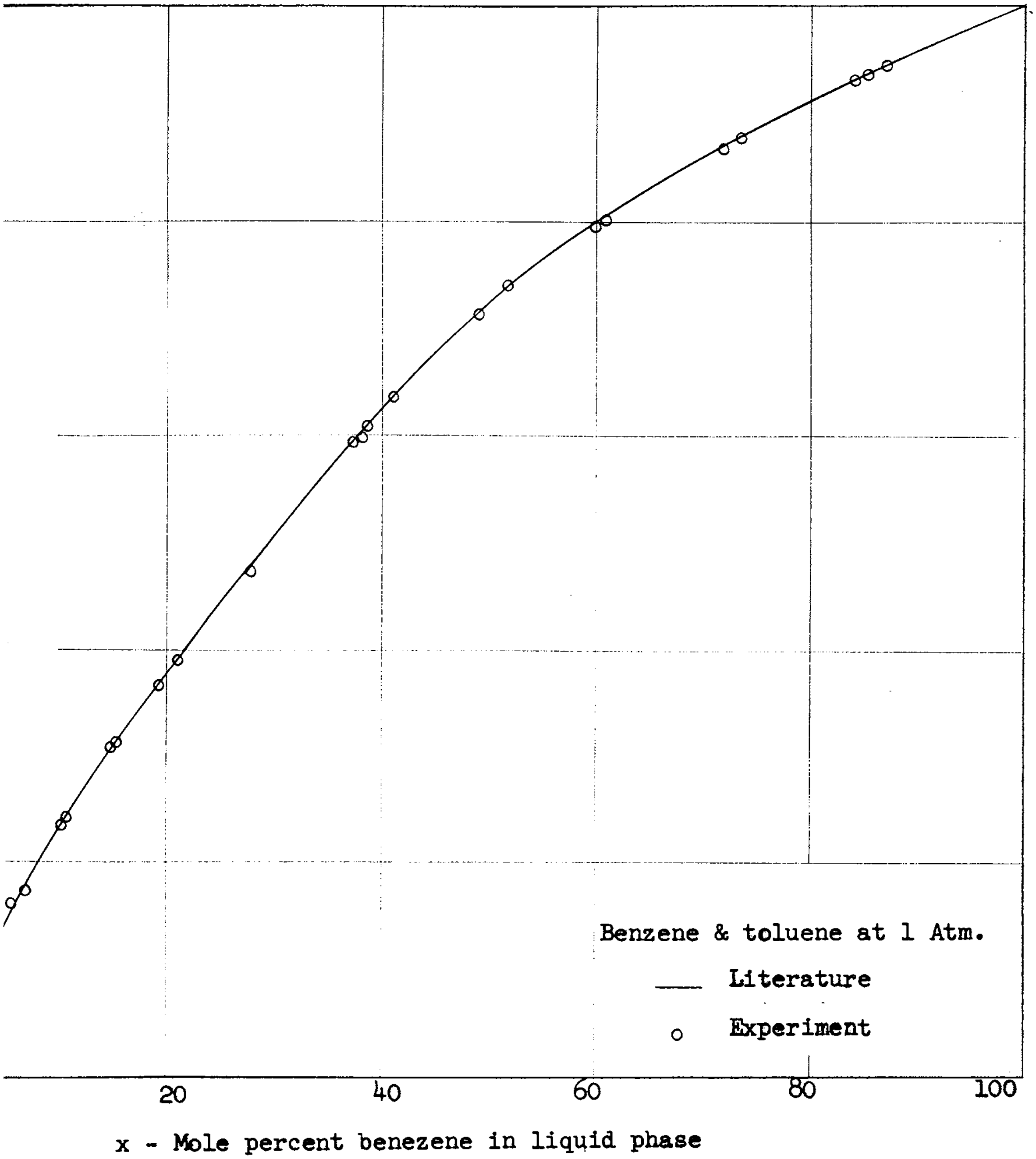
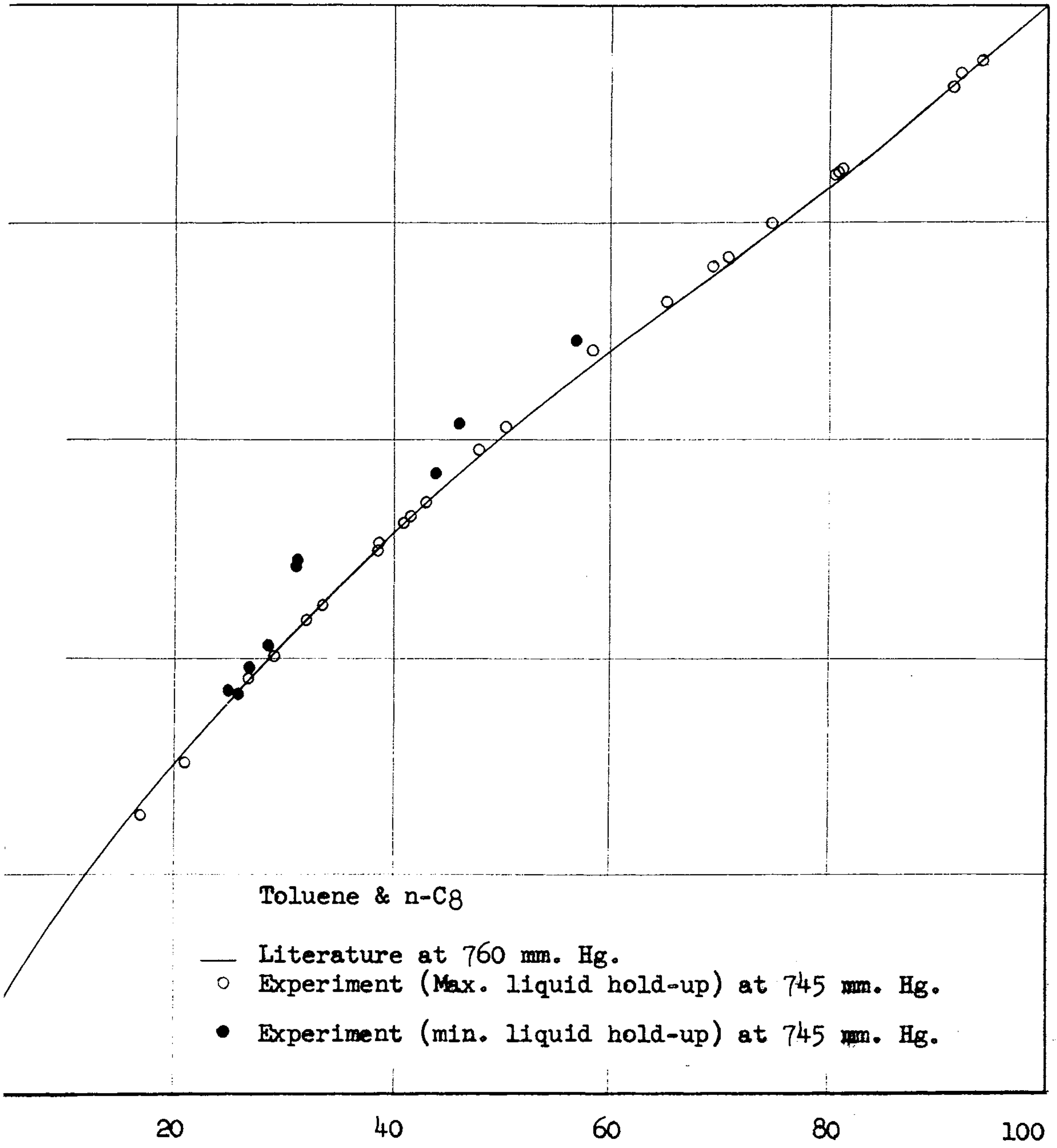


Figure 17 - Equilibrium Test - The New Equilibrium Equipment



x - Mole percent toluene in liquid phase

Figure 18 - Equilibrium Test - The New Flow Equipment

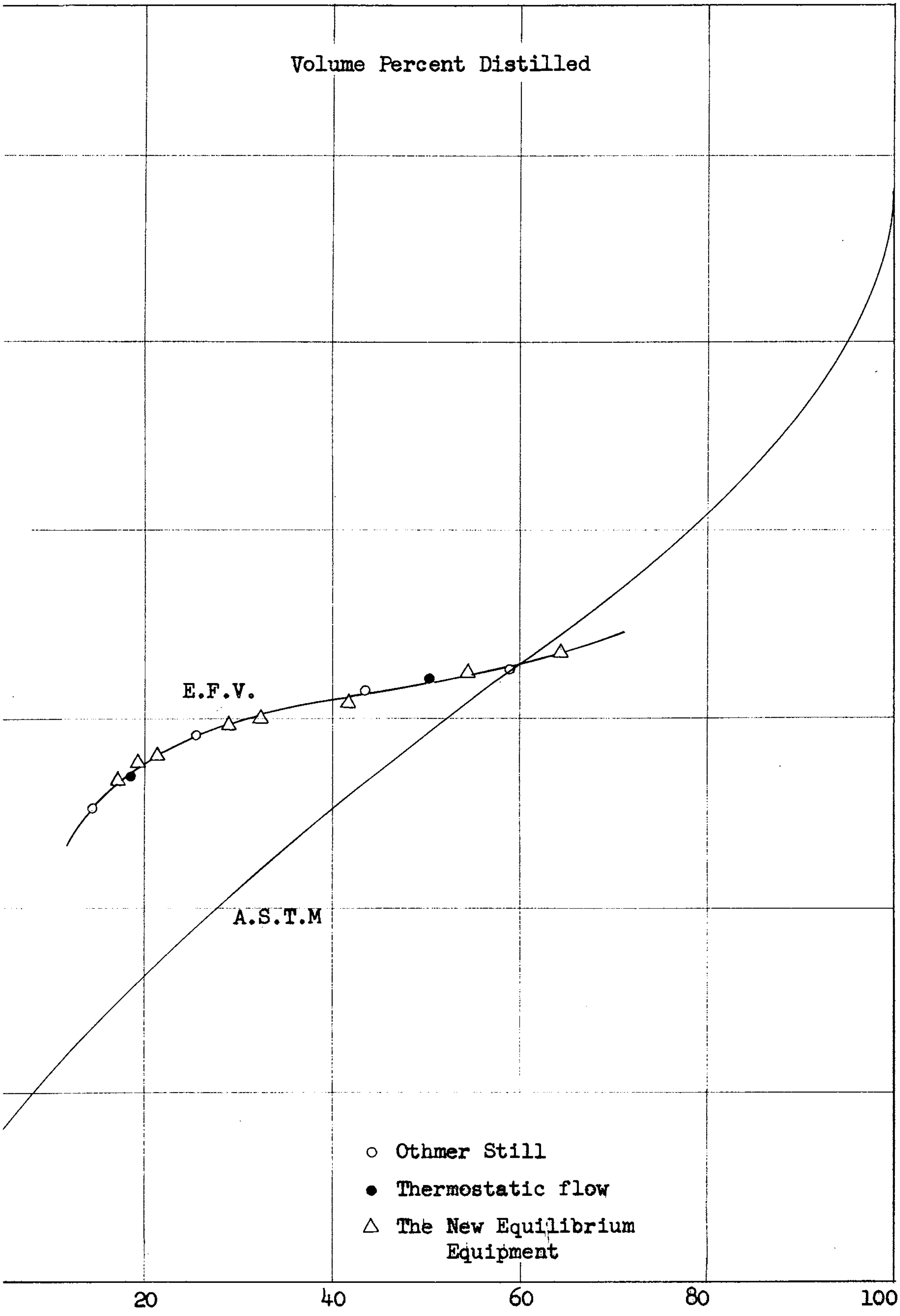


Figure 19 - Comparison of the Equilibrium Apparatus - Oil C

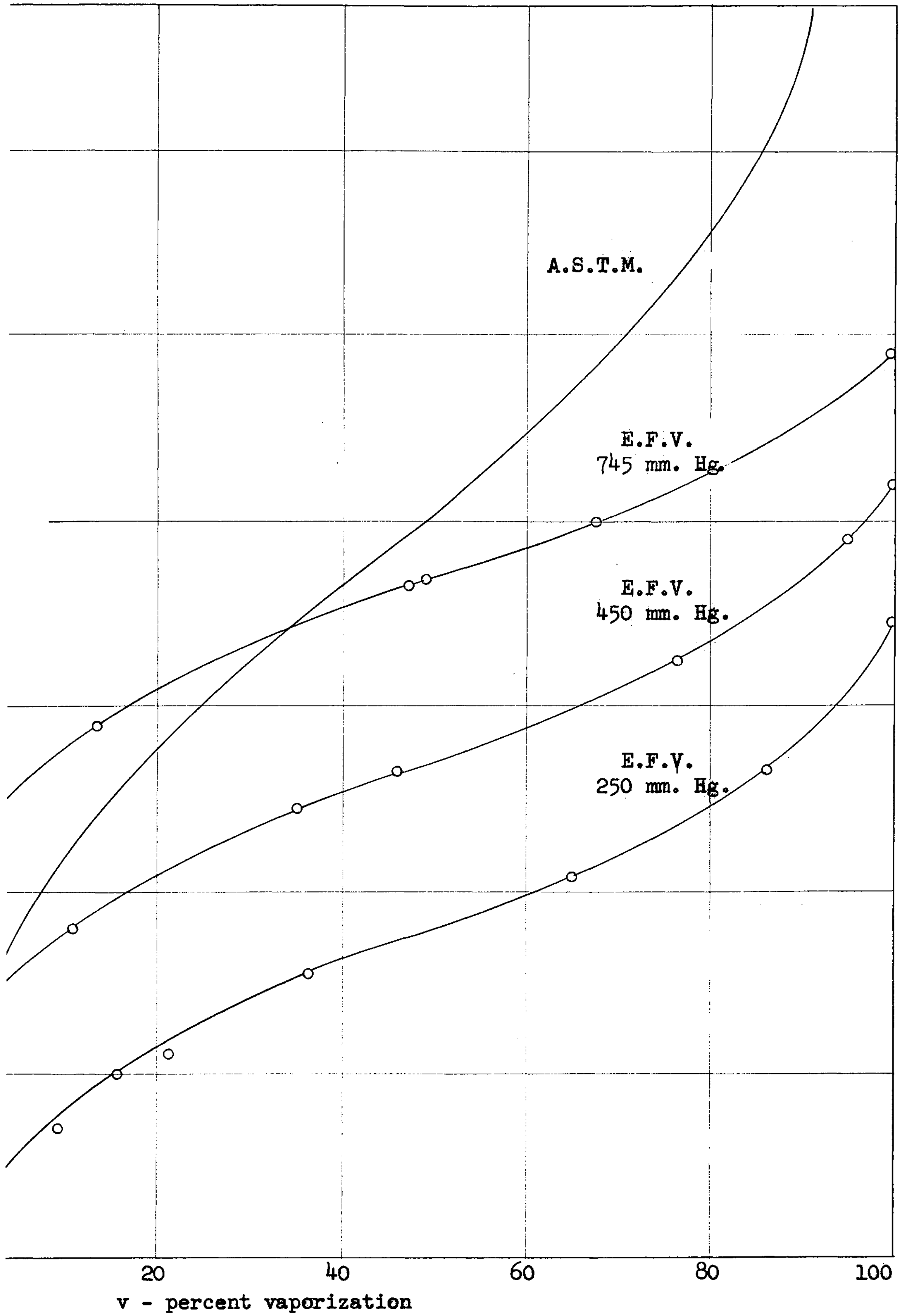


Figure 20 - Vacuum Operation of the New Equilibrium Equipment - Oil E

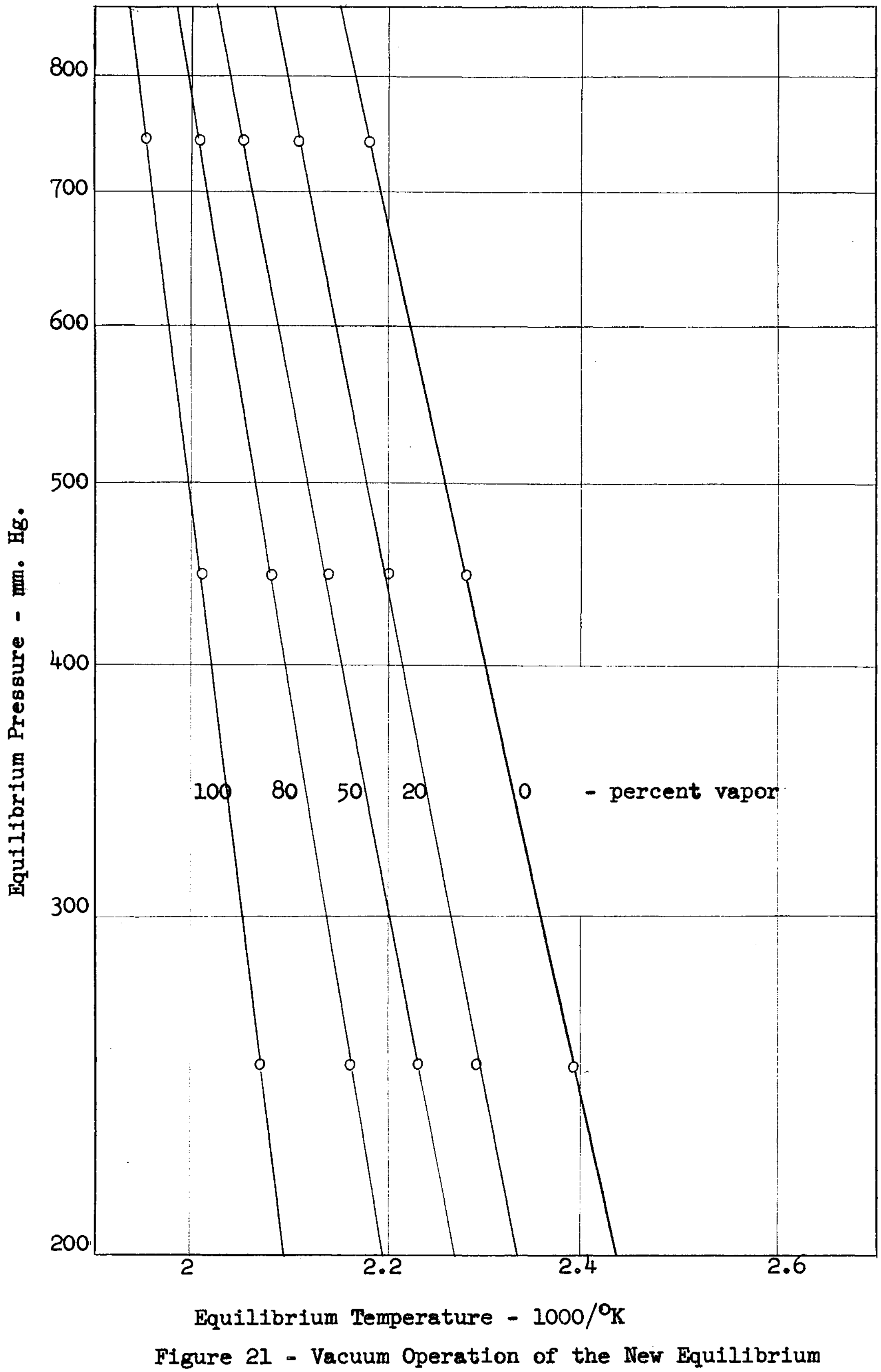


Figure 21 - Vacuum Operation of the New Equilibrium Equipment - Oil E

both flow apparatus. The vacuum receivers and collectors were attached to the condensers, and the manostat was adjusted to produce the desired vacuum. The equipment was then tested for leaks before the test was started. After a sufficient start-up time, the collectors were detached from the unit, cleaned, and placed back for collection of samples. Traps were kept in ice to ensure the collection of any escaping vapors from the condensers. The results of these vacuum operations are shown in Figures (20,21), and are given in the appendix.

Discussion

Because of the complexity of petroleum fractions, the thermodynamic consistency tests (59, 118) can not be applied, therefore it has been the practice of the investigators to operate the apparatus within the limits which produce reliable results for some binary mixtures. For instance Okamoto (96) established a limit for atomization of a binary feed, and applied this to the case of petroleum fractions. Evidently these tests, and also the smoothness of the plot of the fraction of feed vaporized as a function of equilibrium temperature, can be quite misleading in some instances. Here some satisfactory tests have been devised, and presented in this section. It is evident that each apparatus must be investigated independently, and all of the variable factors be studied, before it can be satisfactorily used for equilibrium investigation.

Othmer Still: Othmer recirculating still was the first equilibrium equipment constructed. It was selected because it has been highly recommended by previous workers, and for its simplicity of design. It also appeared to have advantages for the type of investigation in question. In order to meet the large sample requirement, it was decided to construct a 2000 cc. still. Although this did not eliminate the need for repeated operations it nevertheless reduced the number of runs for each case. The equipment because of its great bulk had to be constructed in three separate parts.

Othmer in his similar design used an internal heater and insulated the heated portion with electrical heaters. Here the heat input to the still was regulated by external heaters only. This technique of external heat input, as found in this study, is more advantageous than the other method. An internal heater supplies heat for vaporization of liquid in the pot, and also generates enough heat to compensate for the heat losses from the walls. On the other hand, the external heaters transfer just enough heat to the liquid to cause the desired vaporization. Therefore, for an identical operating condition, an internal heater must transfer more heat to the liquid than the external heaters. Internal heater must be small in size, therefore with a much smaller heat transfer surface than the external heaters, which cover the entire heated section of the equipment. All these necessitate that the surface temperature of the internal heater be much higher than the wall temperature. The conclusion is that an internal heater causes much greater thermal decomposition than when heat is applied externally. Thermal decomposition for each petroleum fraction depends on the equilibrium emperature, and the duration of operation. Studies show that the hermal decomposition, even at an equilibrium temperature as high s 250 °C is not significant.

In all the cases the vapor in the vapor-arm was kept a few egrees superheated. If even a small amount of vapor condenses n the large vapor arm, it would enrich the vapor in a manner similar o that in a wetted wall distillation column. When vapor enters the apor-arm, it can only return to the pot by molecular diffusion, hich is definitely insignificant as compared to the flow transport. herefore the superheating of vapor in the vapor-arm is definitely dvantageous.

Three different return connections, over-flow manifuld, Teflon eedle valve, and a simple regulating cock were compared. It was ound that the regulating cock was inadequate for this type of work, s it did not offer an accurate control of back flow to the pot. lso, it was almost impossible to duplicate an experiment satisfacorily by this technique. The Teflon needle valve gave excellent ontrol of back flow, even though the liquid head was never more han a few inches. The reproducivility of this method was satisfacory, and it needs very little attention.

The over-flow system as would be expected, was the easiest to djust and to reset. It is possible to replace the extensive overlow manifold by a simple inverted 'U' tube with a siphon breaker. he level of liquid in the condenser reservoir can be altered by winging the 'U' tube around the axis of its ball connections to the ot and the vapor reservoir.

Condition of Equilibrium: In order to reflect on what takes place during the equilibrium operation, it would be necessary to consider a sufficiently ideal case for this purpose. Assuming a mixture is to be equilibrium flash vaporized at some temperature and pressure to produce molal vapor to liquid ratio of $\frac{Y_1}{X_1}$. The overflow connection is therefore set for $\frac{Y_1}{X_1}$ condition, and the predetermined power input is such as to cause a constant vaporization rate of b $\frac{\text{Moles}}{\text{hr.}}$ (eg - 1 or 2 drops/sec.). From the time when vaporization starts until the time when over-flow begins, the process is a simple batch distillation. The average composition of liquid in the vapor reservoir, and in the pot may then be calculated as follows:

$$-y_a^* \; d(X+Y) = -d \; (X+Y)\, x_a^* \tag{25}$$

thus

$$\frac{d(X+Y)}{(X+Y)} = \frac{dx_a^*}{y_a^* - x_a^*} \tag{25a}$$

$$\ln \frac{X_1}{(X+Y)} = \int_{x_a^0}^{x'_{1a}} \frac{dx_a^*}{y_a^* - x_a^*} \tag{26}$$

where $(X+Y = X_1 + Y_1)$ is the total moles of feed, and x_a^0 the mole fraction of component A.

x_a^* - mole fraction component A in the pot

y_a^* = mole fraction of vapor in equilibrium with x_a^*,

$$(y_a^*/x_a^* = K_a(x, T_e, P_e))$$

x_{1a} = average mole fraction of component A in the condensate reservoir at the time when over-flow just starts

x'_{1a} = pot composition, corresponding to x_{1a}

Now, the recirculation starts with the same constant rate, and the amount of the most volatile component in the reservoir is higher at this time than during all the recirculation period.

Material balance for component A in the reservoir would result,

$$b\, y^*_a - b\, x_a = \frac{d(Y_1\, x_a)}{d\theta} \qquad (27)$$

$$b\, (y^*_a - x_a) = Y_1 \frac{dx_a}{d\theta} \qquad (27a)$$

x_a = average mole fraction of component A in the reservoir (assuming a complete mixing)

θ = time

For the still pot,

$$b\, (x_a - y^*_a) = X_1 \frac{dx^*_a}{d\theta} \qquad (28)$$

Where the limits are:

x_a from x_{1a} to y^f_a

x^*_a from x'_{1a} to x^{*f}_a

By material balance at equilibrium,

$$(Y_1 + X_1)\, x^{o}_a = Y_1\, y^f_a + X_1\, x^{*f}_a \qquad (29)$$

x_a^{*f}, y_a^{f} are the final composition of component A in the pot and the reservoir respectively.

At the steady state condition, the compositions in the pot and the reservoir remain constant, that is,

$$\frac{dx^{*f}_a}{d\theta} = \frac{dy^{f}_a}{d\theta} = 0 \qquad (30)$$

Also by material balance,

$$by_a^{f} = by_a^{*f} \qquad (31)$$

or

$$y_a^{f} = y_a^{*f} \qquad (32)$$

thus

$$\frac{dy_a^{*f}}{d\Theta} = \frac{dx_a^{*f}}{d\Theta} = 0 \qquad (33)$$

y_a^{*f} is the vapor in equilibrium with x_a^{*f}

Equation (32) shows that at equilibrium the flowing vapor and condensate are of the same composition, and do not change with time. By assuming a satisfactory equilibrium relation, the time required for the operation can be calculated from the given equations.

It is evident, that if the condensate be mixed at all times, a shorter recirculation period is needed. This can be achieved by providing the condensate reservoir with a mixer. Visual observation indicated that diffusion and gravity mixing is inadequate.

It is also quite evident that, during the recirculation time, the composition gradually changes toward equilibrium, without going beyond. Therefore, a plot of composition versus time, at the point where it is independent of time (Equations 30, 33, Figure 10) indicates the true equilibrium condition.

Thermostatic Flow Equilibrium Equipment: The constant temperature flow apparatus has to be operated within the experimentally determined flow range. When the flow rate is higher than the maximum allowable rate, then one of the two following undesirable phenomena will occur: (1). The flow rate may exceed the possible capacity of the heat exchanger, and in such a case the percent vaporization would be less than the true value for the temperature. The pre-heater can effectively improve the range of eration, by aiding the column heat exchanger (2). The second ssibility is that the vapor velocity may become high enough to use an appreciable amount of entrainment. This would of course, rich the vapor with the less volatile components.

The thermostatic materials must be replaced or purified, enever it is necessary. For obvious reasons, the presence of a all quantity of lower boiling components in the thermostatic material very critical. Pressure regulation of the thermostat was found to necessary. The two thermometer wells, one in the middle of the lumn and the other next to the flash chamber were used to avoid y possible error. Because of the heat transfer requirement, the uilibrium temperature is slightly less than the temperature of the cket.

Experiments revealed that when the porous plugs were not sub- rged in liquid, true equilibrium could not be established in many ses. When the plugs are submerged, the vapor and liquid are ought into intimate contact with each other, at a constant tempera- re and pressure.

In order to investigate the working nature of such an equi- brium equipment more systematically, it is advisable to construct column with only one heater-vaporizer coil, which would eliminate e undesirable uncertainty of feed distribution between the two ils.

<u>New Flow Equilibrium Equipment</u>: The need for simple reliable uilibrium equipment motivated the design of this apparatus. this equipment both feed and heat flow must be very closely

egulated, in order to obtain uniform products. The control systems lready discussed served this purpose. This equipment, because of ts small mass can be brought to operating temperature rather quickly. t is very simple in design and easy to construct and operate. The ritted plug can be removed, and easily cleaned with a cleaning olution.

The nature of liquid vaporization in a tubular heat exchanger s such, that even at the best condition true equilibrium can not be xpected. First nucleation at some favorable locations takes place, nd then some of these nuclei grow into large vapor bubbles, as the lugs of vapor and liquid discharge from the exchanger. Because the iquid is not homogeneous, and the slugs of vapor are rather large, n intimate comtact between the two phases is not possible. As a apor bubble moves forward in the vaporizer, the average temperature f fluid increases, and it grows at the interface, becoming enriched n the less volatile components. The main factors which govern the pproach to equilibrium therefore are: the size of heat exchanger nd the rate of heat transfer, the number and the size of vapor ubbles, and the transfer coefficient. The need for a final and omplete contact between the phases, is well known by now, and it an be accomplished easily by porus plugs. The existence of the ritted plug at the end of the vaporizer, and also the crank arrangeent, provide some excellent means for study of the importance of ood contact between the phases. Figure (18) shows that when liquid old-up in the flash chamber is nil, equilibrium is poor, while at igh hold-ups satisfactory results were obtained. The fritted lug breaks the vapor slugs into a great number of infinitely mall bubbles. When the plug is partially or totally submerged in iquid the small vapor bubbles then create a foam, promoting maxi-um contact between the phases. Since both temperature, and pressure re constant, and phases separate immediately after contact, then it s reasonable to expect a true equilibrium between them.

To investigate the uniformity of temperature inside the lash chamber, the thermometer well was replaced by a cork stopper ith a thermometer passed through it. Under various equilibrium onditions, the thermometer was moved up or down to make a complete emperature survey. The results indicated that the flash chamber s completely isothermal at any equilibrium condition.

Figures (20,21) show the equilibrium study of a petroleum raction at various pressures, and the plot is well within the ex-ected limits. In Chapter V, vapor-liquid equilibrium phase distri-ution for some components of a hydroformer product are presented.

The present design is well suitable for atmospheric and acuum studies. Its capacity decreases with the reduction of pres-ure as expected. At high vapor rates, some slugging occurs, and his can be eliminated by placing a deflector in the disengaging ection, or replacing the porous plug with porous disc (fritted isc with solid glass on the upper side). The thermometer well nd the fritted plug can be fixed to the flash chamber if desired. he placement of the glass core in the vaporizer improved the heat ransfer property, as well as causing a better phase mixing.

A high pressure equipment based on this design should be xpected to give satisfactory results (fritted glass can be replaced by sintered metal).

Finally it should be mentioned that from the view-point of equilibrium study of petroleum fractions, the Othmer still requires a long period to come to equilibrium and, moreover, the condition of equilibrium should be investigated by the methods given here. Large samples can only be collected at the expense of repeated runs.

The modified flow equipment (the thermostatic flow equilibrium equipment) is complicated in design and fragile, therefore it has to be handled with great care. It is easy to operate, but its operating range for each equilibrium condition should be determined first by the methods already presented. The equilibrium temperatures are limited to the available thermostatic materials, and this in some instances create a great handicap. The high temperature thermostatic materials are often unstable and costly. The start up time is short, and large samples can be collected without difficulty.

The flow equilibrium equipment, which has been designed as a result of this investigation, is simple and reliable. It can be constructed to be operated at all temperatures and pressures satisfactorily. The start up time is short, and large samples can be collected with ease.

CHAPTER IV

DISTILLATION ASSAYS

In this chapter batch fractional distillation assays, as lated to this work, will be discussed. The components of petroleum actions (continuum) can be separated according to their boiling ints by means of batch fractional distillation.

Both the petroleum feed and the products of equilibrium ash vaporization were analyzed by simple (A.S.T.M.*) and fractional tch distillation, and the results are given in the appendix.

Batch fractionations were performed by means of an efficient eve plate column (Oldershaw), and a comparison was made with a more mmonly used appartus (Sarnia MK II).

Since the apparatus and the procedure for fractional distil- tion of petroleum fractions are not standardized, it therefore be- me necessary to evaluate the fractionator and formulate a reliable erating technique.

THEORY AND SURVEY OF LITERATURE

Petroleum is a complex mixture of various hydrocarbons with ch close physical properties, that complete separation of indivi- ual components is not practical by means of distillation. Even if

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American Society for Testing of Materials e components are separated, the treatment of so many components preent in insignificant quantities is impractical. Therefore, it beame customary to characterize complex petroleum mixtures by their oiling points (distillation curve), density, viscosity, etc.; rather han the amount of each individual components they contain.

Simple or Rayleigh (116) type distillation has been standardzed in petroleum industry (A.S.T.M., D-86, D-158, D-216), and the esult is expressed in the form of volume percent of distillate colected (abscissa) versus distillation temperature (ordinate). The emperature is actually the condensation temperature of the vapor lowing out of the flask, and because of the nonideality of the olution it is not simply related to the volatility of components nvolved. Also in the petroleum industry an efficient batch fractionl distillation is referred to as true boiling point (T.B.P.) distilation, which is an attempt to separate the complex petroleum mixture nto its components according to boiling point. Under the ideal conition of maximum column efficiency, and close to the total reflux peration, it would be conceivable to produce a step-wise distillation urve (T.B.P.), where each step would represent an individual comonent. In practice, these numerous steps are not discrete, and ppear as a continuous curve. The equilibrium flash vaporization E.F.V.), the simple distillation (A.S.T.M.), and the fractional istillation (T.B.P.) curves generally appear in the order of inreasing slopes, and are empirically related to each other. Many nalytical and empirical equations are available for all the three ifferent curves (94,120).

Any fractionating apparatus which accomplishes a good degree f separation is broadly termed T.B.P. equipment. In actuality, for omplex petroleum mixtures, the slight variation in efficiency and perating condition causes no significant change in the position and he shape of T.B.P. curve or properties of distillate when it is perormed in a sufficiently effective column. True boiling point distilation can be conducted at various sub-atmospheric pressures up to 60 mm. Hg., and at constant or variable rates of distillation. The urves obtained by constant distillation rate are more smooth, and re more useful for design purposes.

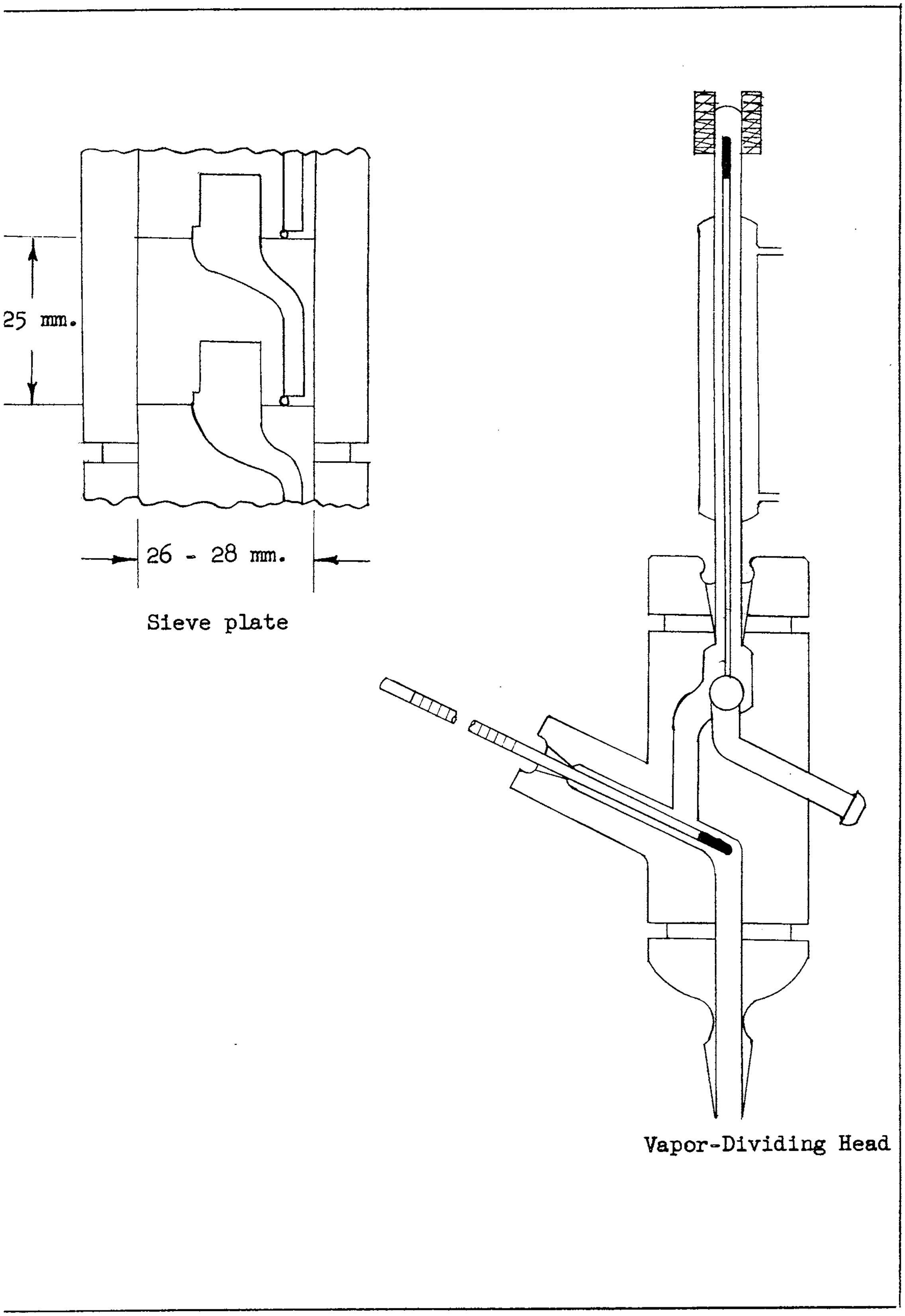
T.B.P. distillation is generally carried out in an efficient nd insulated packed column at a high reflux ratios. There are some ew widely used packed columns (11,86,93,110,112,146), each with some dvantages. Other types, such as sieve plate, spinning band, and wetted wall columns are less common.

APPARATUS

The fractionating equipment (T.B.P. still) selected for this study was an Oldershaw (22,97) column. These columns are made in 30, 20,15,10, and 5-plate sections, and are provided with integral vacuum jacket to approach adiabatic condition. The vacuum jacket is totally silvered with the exception of two narrow longitudinal observation windows on both sides of the column. The column is normally made of Pyrex glass, and sufficient number of expansion bellows are constructed into the outer shell to allow safe operation even up to 300 °C. Each section of the Oldershaw column consists of certain number of ass sieve plates sealed into a glass tube of 26 to 28 mm. in inner ameter.

Figures (22,23,31) show the details of sieve plate, weir and wn-pipe. There are 82 holes in each plate, and they are arranged three circular rows. The holes have low tolerance, and are dril- d with red hot tungstan wire of 0.89 mm. in diameter. The baffle pe which is placed in the center of the plate, is 10 mm. high, and mm. in diameter. A small section (4 mm.) of the baffle is cut f at 1 mm. above the plate to form the weir. The baffle directs e flow of liquid to the weir, which maintains a proper liquid seal the plate. The down-comer or the drain-pipe is bent and tapered om 10 mm. to 3.5 mm. to prevent any vapor-lock. A bead of about 0.5 n. is sealed to the lower section of the drain-pipe to regulate the stance between the end of the drain-pipe and the plate bellow. As- ending vapor passes through the holes in the form of small bubbles, d the descending liquid from the plate above flows over the plate efore it enters the drain-pipe. The lower most plate in any column ection has a uniform weir, and without drain-pipe. Each section can connected to the other parts by means of 29/42 ground tapered joint male joint at the bottom).

Figure (23) shows the details of design of liquid trap used n the operation and the evaluation of the column. The trap is a odification of other commercially available designs. It is basically n integral vacuum jacketed 50 cc. reservoir installed between the istillation flask and the column. Vapor flows through the central ipe, passes around the deflector and enters the column at the base. he liquid from the column drips on the deflector, and finally falls



Sieve plate

Vapor-Dividing Head

Figure 22 - Oldershaw Distillation Column

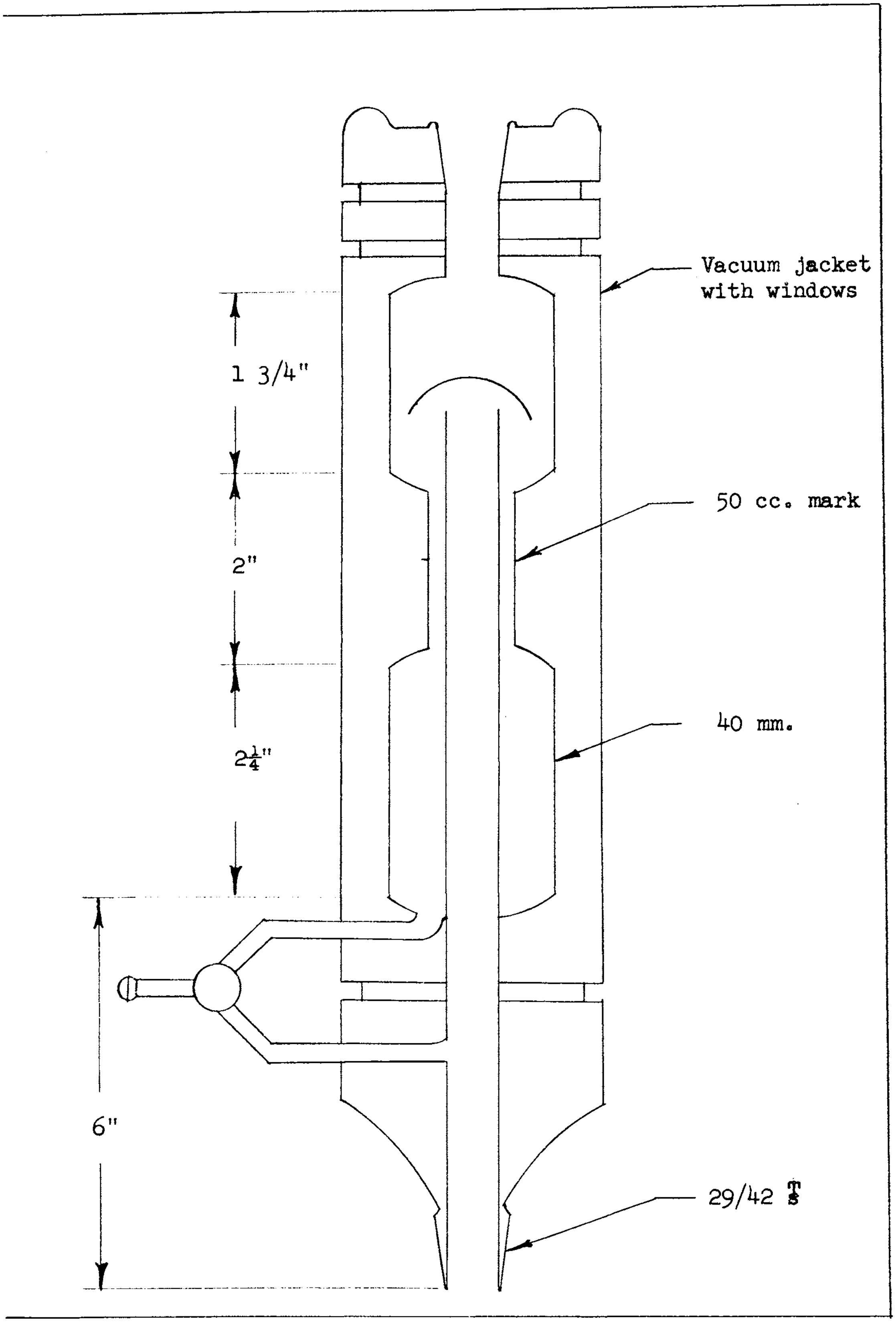


Figure 23 - Reflux Rate Measuring Trap

nto the reservoir which surrounds the vapor pipe. The annular reser-oir has a narrow neck at the top, where the calibration mark is ocated. At the bottom, the reservoir can be connected to the central apor-pipe, or to a sampling line by means of a three-way cock. At he normal operating condition, the column liquid flows from the trap o the vapor-pipe through the cock. When the cock is closed, the iquid collects in the trap till it reaches the 50 cc. mark, and inally over flows to the flask. By proper regulation of the three-ay cock, the vapor going into the column, and the returning liquid an be sampled.

A reflux regulating valve is located between the top of the olumn and the reflux condenser. There are two different designs of eflux dividing heads, vapor-dividing, and liquid-dividing; and of hese the former was found to be more suitable for this work. The till top temperature is measured by a partial immersion thermometer onnected to the lower section of the automatic vapor-dividing still ead with a ground tapered joint (₮ 10/30).

The vapor flowing into the automatic vapor-dividing head rom the column is selectively directed either to the reflux conden-er at the top, or to the product condenser on the side of the column, y means of a glass valve plunger. When the plunger is seated, the apor condenses in the reflux condenser and returns to the column, nd when it is unseated the vapor flows to the product condenser. The alve has a long glass stem, which passes through the reflux condenser, nd at the other end is attached to a soft iron rod enclosed in a glass nvelope. The entire vapor-dividing head is vacuum jacketed.

The selective operation of the valve is by a small solenoid, ich encloses the end of the valve stem. A powerstat controls the wer input to the solenoid, and its operation is regulated by an lectric timer (Flexopulse, Eagle Signal). This time switch is operated a small synchronous motor, with on or off periods from 1 to 120 conds. The time switch can produce reflux ratios from 1/119 to 19/1, with the maximum cycle duration of 120 seconds and a minimum cle duration of 2 seconds.

The reflux condenser is a large (six balls) water cooled ondenser, which is attached to the top of automatic vapor-dividing ead with ground joints ($\mathbb{T}$ 29/42). The product condenser is also an fective one, having a 100 cc. reservoir, and is connected to the apor-dividing head by a ball joint.

Distillation flasks of various sizes, from 1000 to 7000 cc., ith one or three tapered joint necks ($\mathbb{T}$ 29/42) were used.

The heating mantles are hemispherical and metallic, and ere supported by a small automobile scissor-jack. The power input to the heater is through a 1000 W variable powerstat.

OPERATION AND TESTS

Since neither the T.B.P. still nor the operating proceure are standardized, it therefore became necessary to invest some ffort in that direction. Although each individual Oldershaw column ection may have certain inherent characteristics, each section does ave properties that are reproducible. The results of these compreensive tests are given in the appendix, and some are shown in this hapter in the form of plots.

Heat Loss: The column set-up for measuring heat loss conisted of a two neck 2000 cc. flask, the reflux trap, a section or ections of the column to be tested, the vapor-dividing head (valve emoved and a plug used in place of the reflux condenser), product ondenser, and a return line from the product reservoir to the flask. ith this set-up and under steady state operation the liquid hold-up f the column is constant.

Any amount of vapor generated in the flask, (99 mole % pure iquids) should flow to the product condenser, and then return to e flask. But because of the small amount of heat loss from the olumn, a portion of ascending vapor condenses and is collected in e reflux trap. The heat loss can be calculated from the time which equires to collect 50 cc. of condensate in the trap. By this method, eat losses from two 30-plate column sections were measured and comared. Benzene, and toluene were used to compare heat losses from late, and empty packed columns at various boil-up rates. Heat loss aracteristics of 40-plate T.B.P. column (two sections) was investiated at 1000, 2000, and 3000 cc./Hr. boil-up rates. The following re liquids were used for this purpose.

benzene	N-B.P. 80 °C
toluene	111
methylpentane	60
2-2-4 trimethylpentane	99
o-xylene	144
o-ethyl-toluene	165

n-C_{10} 174

re was taken as to eliminate any air draft in the laboratory, and e ambient temperature was measured at close to the middle of the lumn. In order to ascertain the reproducibility of the results, ch test was repeated at least three times. Figure (24) shows the fect of vapor temperature on the heat loss from the T.B.P. column.

By this technique, the thermometer was also checked and librated, as it came in contact with the highly pure and saturated quids at the top of the column.

Start-Up Characteristic: For this test a 7000 cc. flask, a -plate column section, and the condensers were used. A known mixre of benzene and toluene was placed in the flask and then heated some predetermined rate. At the start the distillation column s completely dry and at room temperature. As the vapor mixture peared at the top, a representative sample of it was obtained rough the sampling three-way cock, located at the top of return ne. The samples were taken at various time intervals, from the me when vapor first appeared on the top and to the time when eady state condition was reached. The experiment was carried out r the conditions of: total reflux, total take-off, and one to e reflux ratio. The test for the condition of total take-off was peated to check the reproducibility of the result. In this exriment care was taken to secure representative samples, and they re immediately analyzed by chromatographic technique. The quanties of components in the pot were such as not to be effected the liquid hold-up in the column.

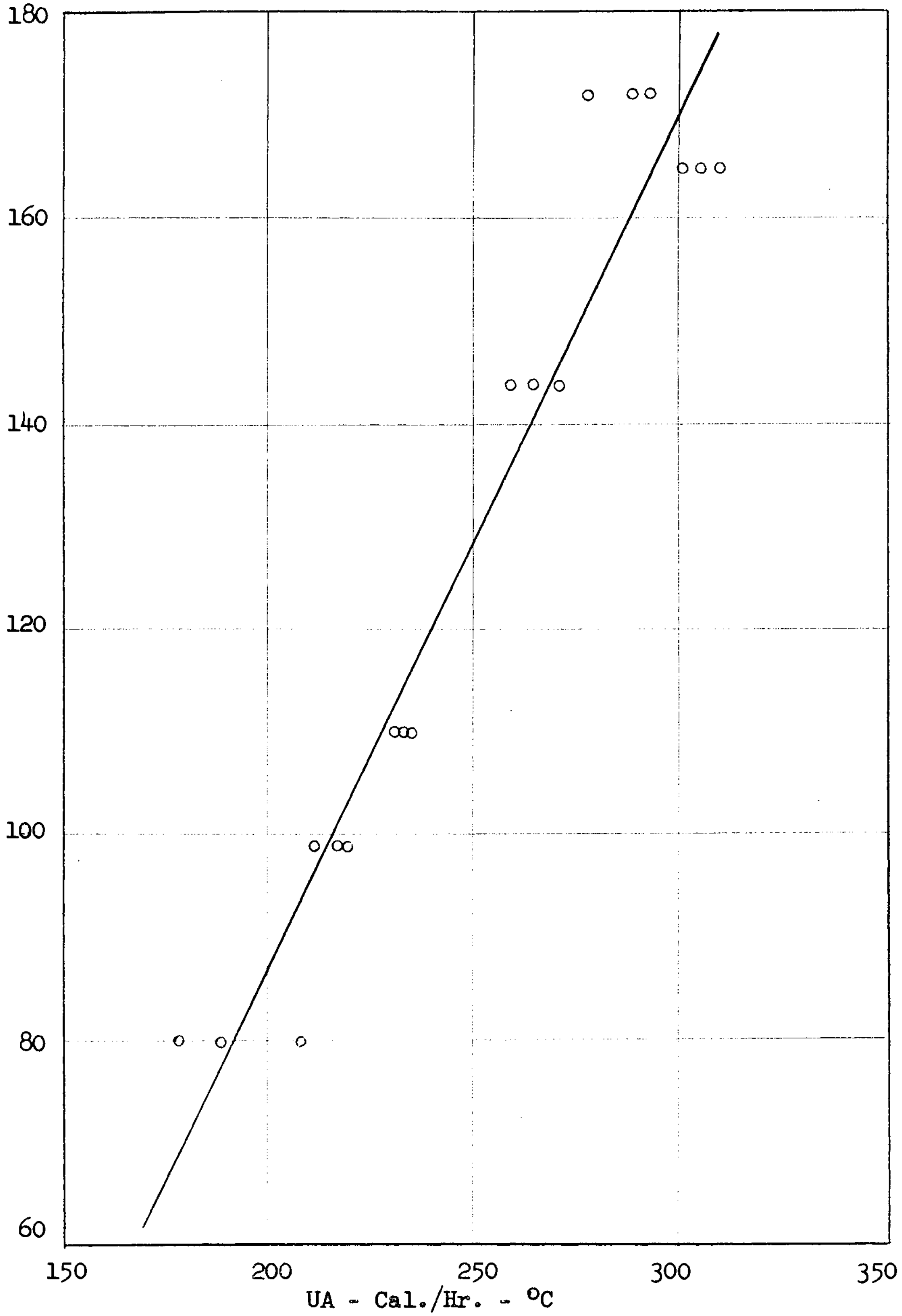


Figure 24 - Influence of Inside Temperature Upon Heat Losses from Oldershaw Column (40 plates)

Pressure Drop: The apparatus set-up for this test is exactly e same as before, with the exception of using pure liquids in a maller flask. The distillation return line, which has a liquid seal op at the bottom, and returns the liquid from the product reservoir the flask, was used as the manometer for measuring pressure drop ross the column. Same liquids and operating conditions as in the irst part were used here.

Hold-Up: Another important characteristic of the column is s capacity for retaining liquid while under operation, and also me times after the completion of operation. The arrangement of the uipment was the same as before, except that heat was supplied to e flask by a Nichrome wire through one of its necks. Because of e negligible heat capacity of the heating wire, the vaporization n be stopped almost instantly in the flask, as soon as the heat is t off.

Pure benezene, n-octane, and toluene were used for this work. e dynamic hold-up of the column at various boil-up rates and reflux atios were measured by suddenly cutting off the heat and at the same ime closing the three-way cock of the trap. The liquid collected in is fashion in the trap was carefully drained and measured as the ynamic hold-up of the column. The static hold-up is that portion of e dynamic hold-up which does not drain even after many hours. The tatic hold-up was measured by placing 200 cc. of some other material a clean flask, and refluxing it for some time, before analyzing e binary mixture for the amount of original liquid in it. Figure 25) shows the effect of boil-up rate on column hold-up.

Effect of Electric Timer on the Actual Reflux Ratio: For his experiment an empty packed column with integral vacuum jacket nstead of plate column was used. The amount of internal reflux and he product for each condition of operation was measured by the reflux rap and the product receiver respectively. Benzene was used for his experiment, and although it produced a small amount of internal ondenstion because of its low boiling temperature, nevertheless his effect was taken into consideration. Reflux ratios from 1/15 o 15/1, and operating cycles from 2 to 120 seconds, with various ower inputs to the solenoid were investigated. The operating naracteristics of A.C. and D.C. solenoids were compared. For each ondition of operation, the actual reflux ratio was compared to the orresponding electric time switch setting. The boil-up rate was bout 2000 cc./Hr. throughout the test.

Column Efficiency: The column set-up for the efficiency easurement consisted of 5000 cc. pot, the reflux trap, a section f the Oldershaw column (10 or 30-plate), the vapor-dividing head, he condenser, and the return line. Benzene-toluene, and toluene-n-ctane systems were used for this purpose, and the analyses were arried out as before. At least three samples for each condition ere obtained and analyzed. The variables for this test were: the oil-up rate and the reflux ratio. The operation consisted of llowing the column to reflux under the desired condition for at east 45 minutes, and then taking samples of the top condensate, the apor flowing into the column from the flask, and the liquid flowing ack to the pot; then the column was operated for another 10 minutes

get the second sample, and the same for the third sample. A
presentative plot is shown in Figure (25).

Effect of the Cycle of Intermittent Operation: This test
nsisted of measuring the effect of cycle of operation on the ef-
ciency of the column. That is, for instance, the efficiency of a
lumn can be measured at reflux ratio of 1/1, but with cycles of
eration from 2 to 120 seconds. The column set-up and the proce-
re was exactly the same as the previous case, but with various
me cycles. In one case the compositions at the beginning and at
e end of each cycle, as well as the average value were measured.
nerally not less than 30 minutes were allowed between each suc-
ssive sampling. Some of the representative plots are shown in
gures (26,27).

T.B.P. Distillation: The operation consisted of charging
e still pot with exactly 1000 cc. of sample, and attaching it to a
-plate Oldershaw column (two sections). The heat input was so
gulated as to produce a boil-up rate of about 2200-2500 cc./Hr.,
d then the column was put under the total reflux for not less
an 45 minutes. At this time the top temperature was constant,
d a reflux condition of 12 parts reflux and one part product was
posed. The top column temperature was recorded at every 25 cc.
oduct take off (2.5% by volume), up to 90% or even 95% over.
e exception to this was, when the top temperature exceeded
0 °C. Each 5% cut was collected for density measurement by
stphal balance. Small samples were taken from every 2.5% cut
d at every 5% over for molecular weight measurement. Generally

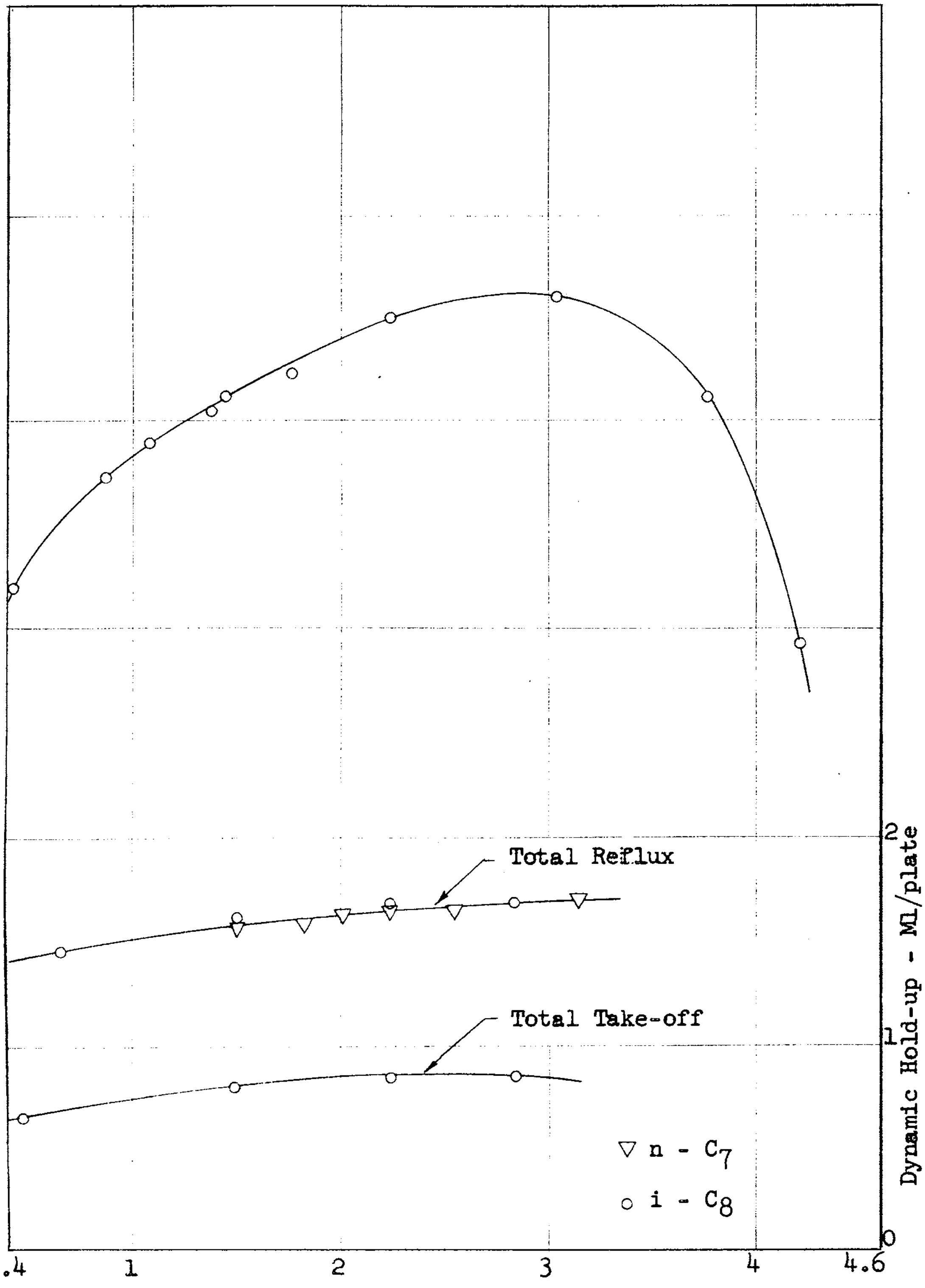


Figure 25 - Effect of Boil-Up Rate upon Efficiency and Dynamic Hold-Up

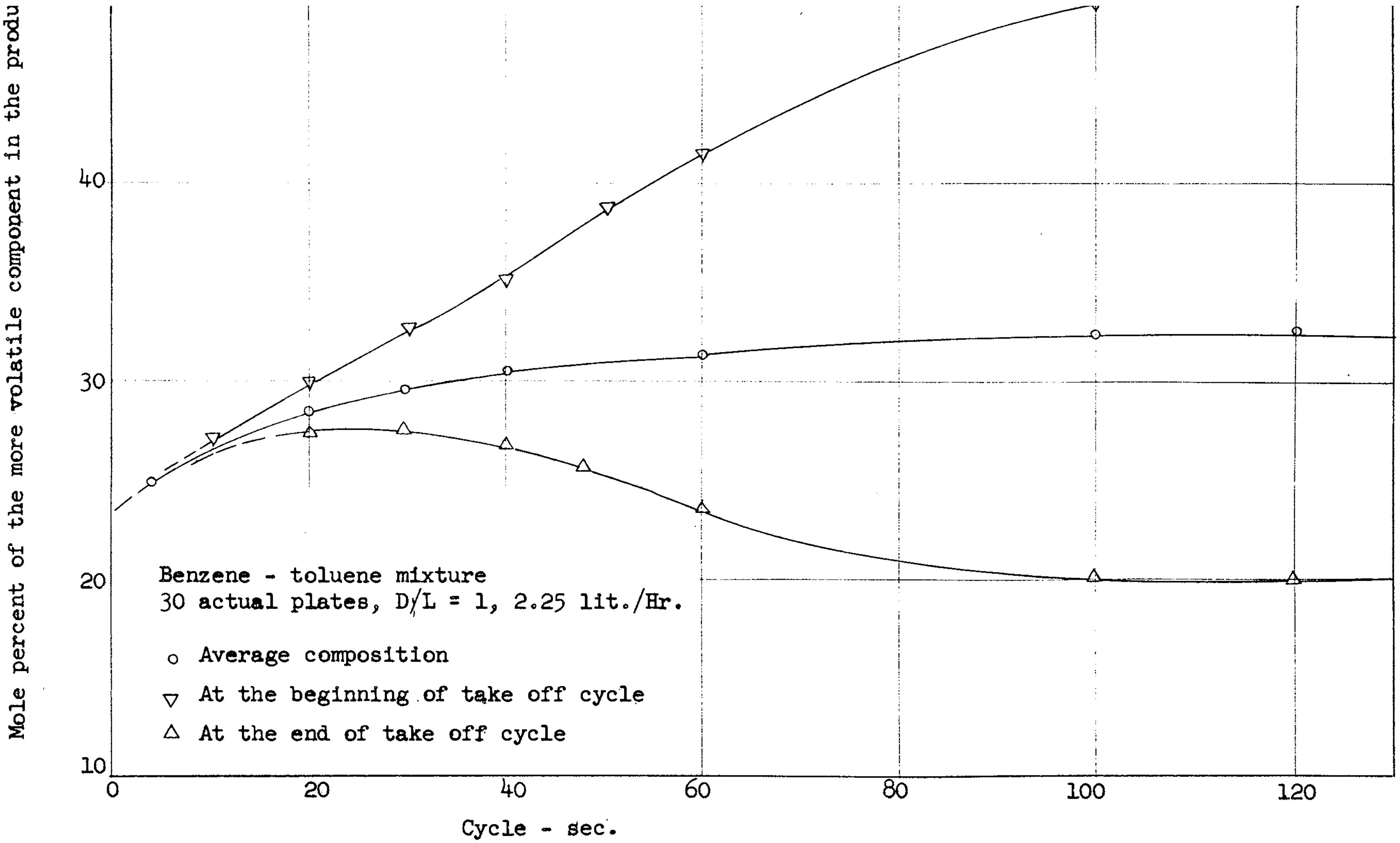


Figure 26 - Effect of Cycle of Operation Upon the Concentration of Product

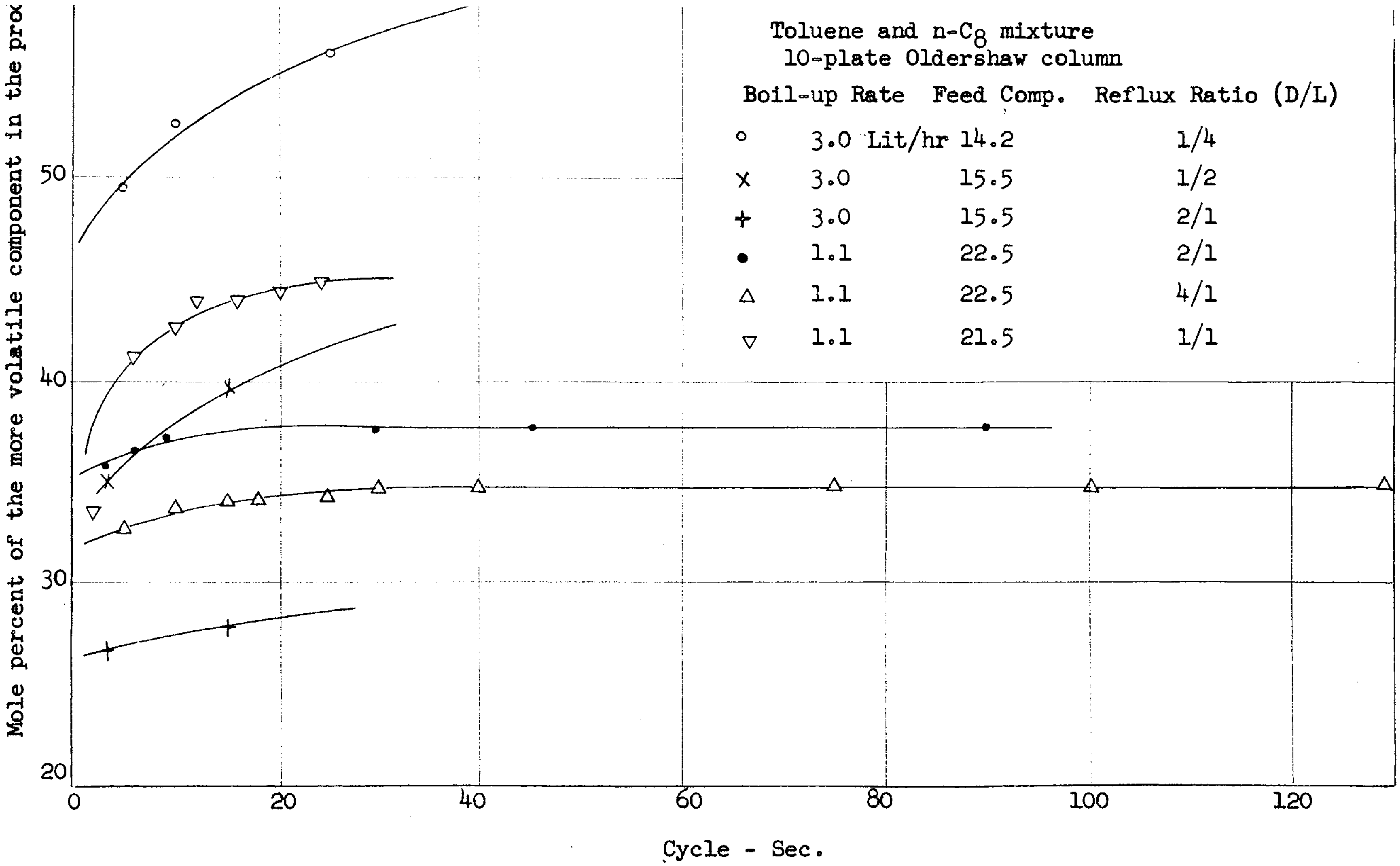


Figure 27 - Effect of Cycle of Operation Upon the Concentration of Product

a trial or duplicating run was found to be useful. The last 10% was distilled in an A.S.T.M. type distillation equipment.

The fractionation equipment was cleaned after each run by refluxing in it either toluene or benzene for at least 10 minutes. When precise analytical work was to be performed, the column was also cleaned with a cleaning solution.

Discussion of Results

Heat transfer from any section of the column can be expressed by the following general equation

$$Q = U \cdot A \cdot \triangle T = \bar{U} \cdot \triangle T \qquad (34)$$

Q = heat loss from column section - $\frac{\text{Cal.}}{\text{Hr.}}$

$\triangle T = T - Ta$ = average column temperature - ambient temperature, °C

Experiment shows that U is some function of tower temperature, therefore,

$$Q = \bar{U}(T) \cdot \triangle T \qquad (35)$$

Equation (35) for the T.B.P. column is,

$$Q = (0.121T - 95.7)(T - Ta) \qquad (36)$$

For each plate, $q = Q/n$ = heat loss in cal./Hr.-plate

So $$q = (.003\ T - 2.39)(T - Ta) \qquad (36a)$$

Equation (36a) can be used to calculate the additional internal reflux caused by heat loss from the vacuum jacket. The above equation also suggests that the over-all heat transfer coefficient is directly related to the column temperature, and at high temperatures the heat loss becomes excessive. When a large column is operated at very high temperature, then the top plate may become dry while the bottom plate may flood.

Start-up characteristics of the column is another factor of importance in the field of batch fractional distillation. Starting with a cold column, at the beginning the product had the highest concentration of the more volatile component (benzene), then it decreased to a minimum and finally the concentration increased with time till it reached the steady state condition. The fact that the concentration of benzene(benzene-toluene) was highest at the start is indeed a logical one. That is, when vapor rises in a cold column it condenses on all surfaces, and therefore it fractionates itself as it moves up in the column.

In other words the efficiency of a column is the highest when it is cold, which is due to its high effective surfaces. As a column approaches its operating temperature the "cold efficiency" decreases, therefore the concentration gradient reduces. Finally the concentration gradient logarithmically increases with time due to increasing reflux and hold-up in the column. This phenomenon is essentially some function of relative volatility of the system, number of plates, hold-up, and boil-up rate of the column. It was for this fact that in T.B.P. distillation, the column was first operated at total reflux till the steady state was attained, and the uncertainty due to the start up condition was eliminated. Figure (28) shows the start-up characteristic of the column.

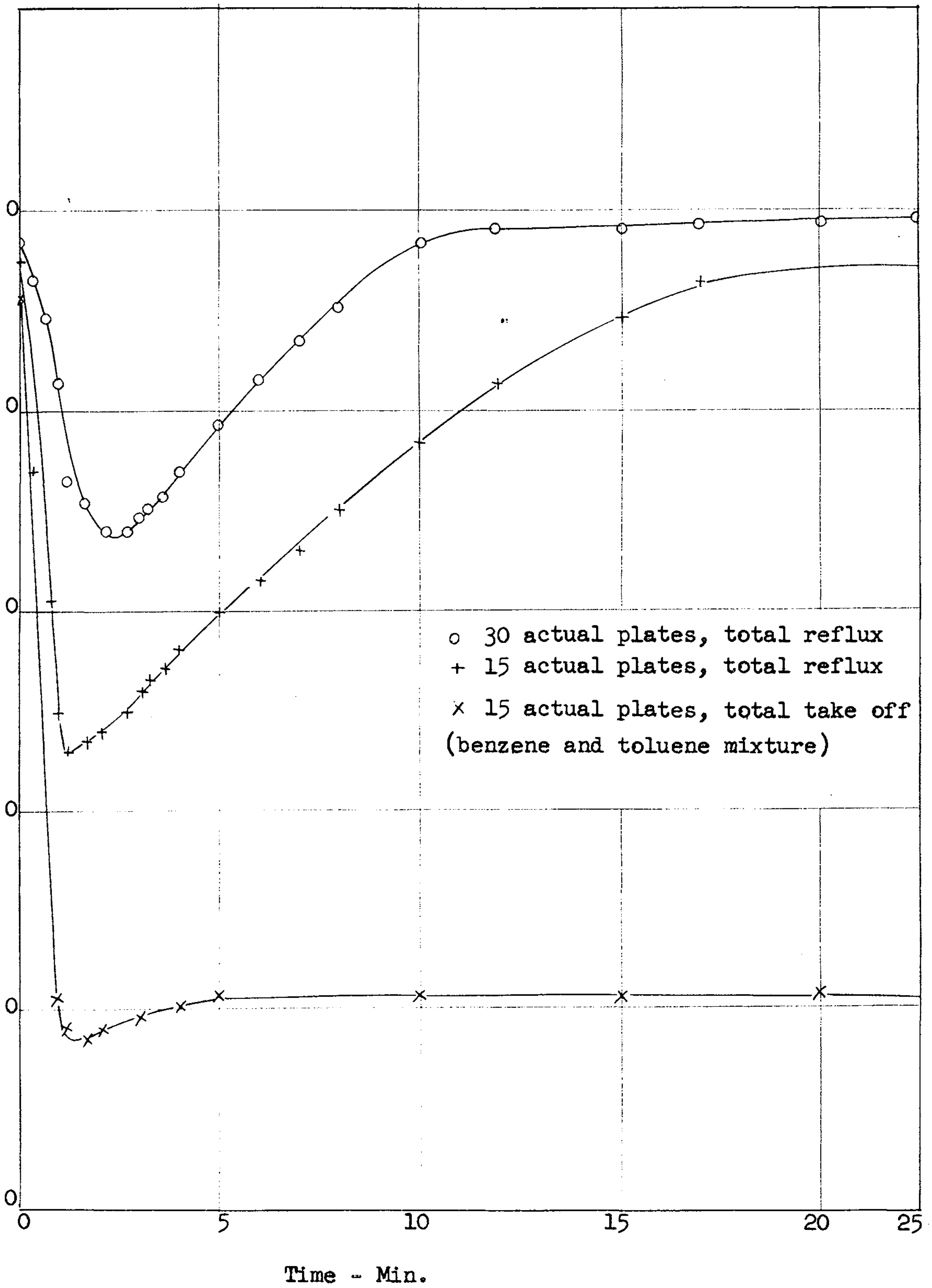


Figure 28 - Start-Up Characteristics of the Oldershaw Column

Pressure drop and dynamic hold-up depend on physical properties of fluid and the boil-up rate. Pressure drop across the column has basically no consequence on T.B.P. distillation, unless it is commenced at very low pressure. High hold-up on the other hand is rather undesirable, firstly for the large feed requirement and secondly for the reduction of efficiency. Static hold-up depends on physical properties of liquid only, and its effect on T.B.P. distillation was found to be insignificant.

The result of comparison of electric reflux timer and the measured reflux is rather capricious. The D.C. solenoid was free from vibrations, and consequently produced better results than the A.C. solenoid. The power input and the position of the solenoid must so be adjusted as to give a quick and firm motion to the vapor dividing valve, and in such a case the reproducibility is very high.

The plate efficiency of Oldershaw column is very high, and almost in all cases is more than 60%. Experimental work shows that efficiency increases with the boil-up rate, till flooding condition occurs. Column efficiency was measured at total reflux, and by use of Fenske (43) equation.

$$n = \frac{\log \left[({x_A}/{x_B})_D \cdot ({x_B}/{x_A})_1 \right]}{\log \alpha \text{ ave.}} \qquad (37)$$

where :

n	is the number of theoretical plates in the column.
$\alpha_{ave.}$	is the average relative volatility of the system.
$({x_A}/{x_B})_D$	is the ratio of mole fraction of the components in distillate.
$({x_B}/{x_A})_1$	is the ratio of mole fraction of the components from the first plate

One of the neglected factor effecting the efficiency of both batch and continuous distillation is intermittent or cyclic product take-off. Since the product take-off of many small industrial and almost all of the analytical columns are done intermittently, therefore it was considered necessary to make some preliminary experimental inquiries. It was ascertained that in all the cases examined, the intermittent product take-off is more advantageous than the continuous operation and an optimum time cycle exists for each condition. Under steady state operation, the concentration gradient in a column depends on D/L, (distillate/reflux). The smaller D/L, the larger would be the gradient or the composition of the most volalile component at the top of the column. Therefore, the greatest concentration gradient exists at the total reflux.

Considering a column operating continuously at some D/L condition, then the concentration gradient throughout the column would remain constant at all times. Now if the column be operated intermittently at the same D/L condition as before, then it has to perform at total reflux for s.L seconds, and at total take-off for s.D seconds (s is a factor, and s.L + s.D is the cycle of intermittency). During the L period, the concentration gradient increases, while it decreases during the D period, and these depend on the rate of approach to steady state. Therefore at the end of sufficiently long L and D periods, the concentration gradient would be the same as in the cases of total reflux or total take-off respectively. When a column is operating intermittently, then at the beginning of the take-off period the concentration of product, which is extracted from the enriched top plates, is the highest.

The effective maximum L period is equal to the time required to create the maximum concentration gradient in the column. The optimum cycle of intermittent operation depends on the column's capacity, rate of approach to equilibrium, and reflux ratio.

T.B.P. distillation was performed most carefully, and in order to avoid any possible mistakes, a duplicate run was also made. In almost all cases the readings were done at every 2.5% cut, although it is more desirable to record the temperature continuously. The duplicate runs showed that the reproducibility is quite high and is within the limits of accuracy of measurements. The operation was so close to the total reflux, that if at any time during the distillation had the column been switched to the total reflux condition, the top temperature would not have had altered noticeably. The T.B.P. distillation curves of the products of flash vaporization operation of each petroleum stock appear on both sides of the feed curve, and in the order of their E.F.V. temperature, as is shown in the representative Figure (29). Figure (29) indicates that the distillation curves of vapor fractions are below, and those of liquid fractions are above the feed curve. As the E.F.V. temperature increases the T.B.P. distillation curve of the vapor approaches the feed curve, while the liquid curve departs from it. When a petroleum fraction is distilled into many product cuts, then the total volume of product is always more than that of the original feed. This, however, did not introduce any difficulty in this work, because ultimately the volumes were converted into moles. One of the main requirements of T.B.P. distillation is to produce a good and

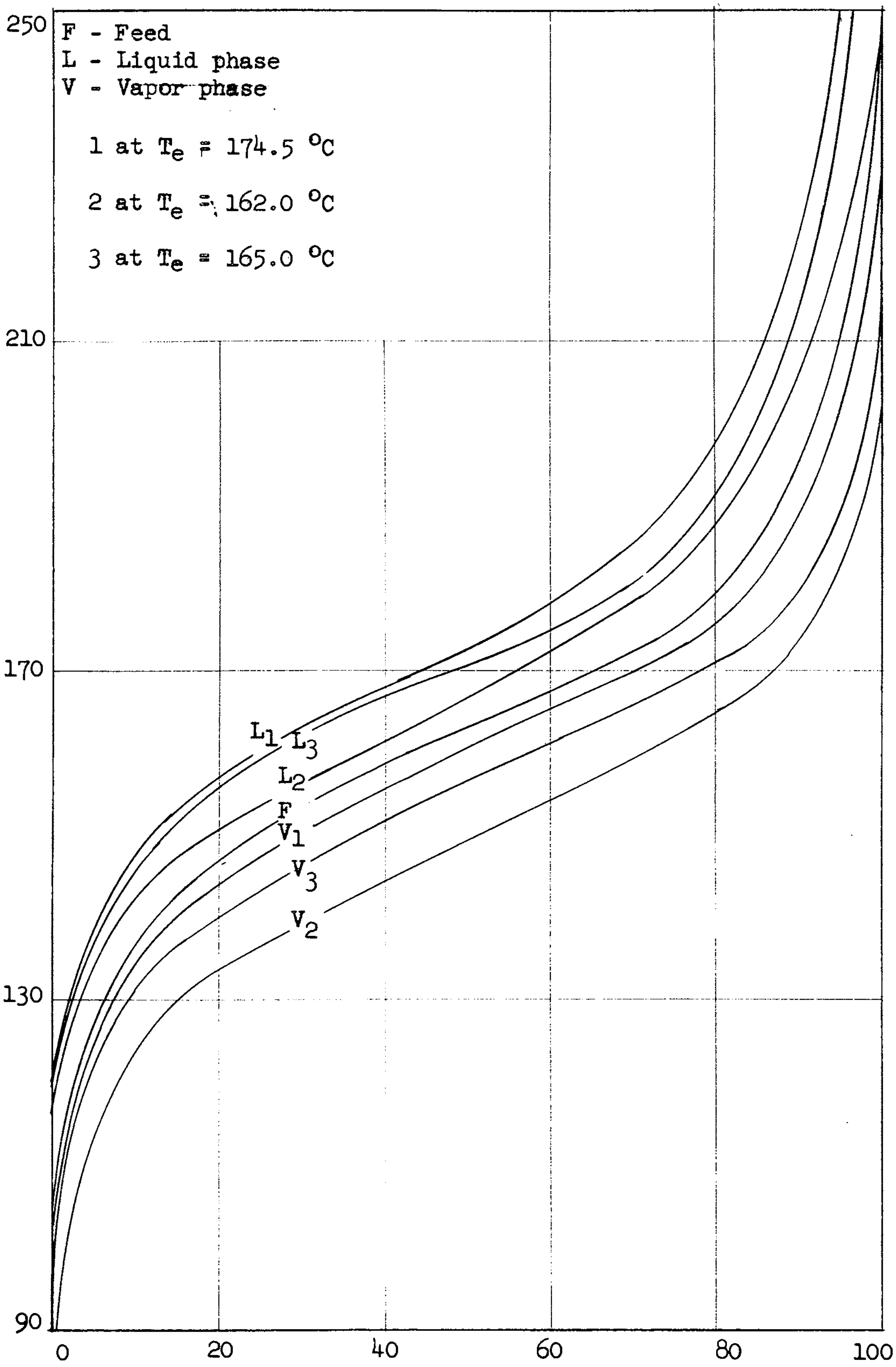


Figure 29 - T.B.P. Distillation of Equilibrium Phases - Oil B

reproducible separation. A rather simple petroleum fraction (a hydroformer product) was used to investigate the sharpness of separation and its reproducibility in both liquid and vapor products of E.F.V. operation. These preliminary trial runs indicated that the sharpness of separation was essentially the same for both vapor and liquid fractions. The T.B.P. distillation curve of this petroleum fraction, as is revealed from its chromatographic analysis (Chapter V), indicates a sharp separation, and small overlapping of the major components. The investigation also indicated that the degrees of separations are fundamentally the same for 60 and 40 plates Oldershaw columns.

This hydroformer product has also been used to compare the performances of the Oldershaw column and a very commonly used packed column (Sarnia MKII, 15 theoretical plates - 86). The results indicate that the separation obtained by the Oldershaw column is superior to that of the Sarnia still (Figure 30).

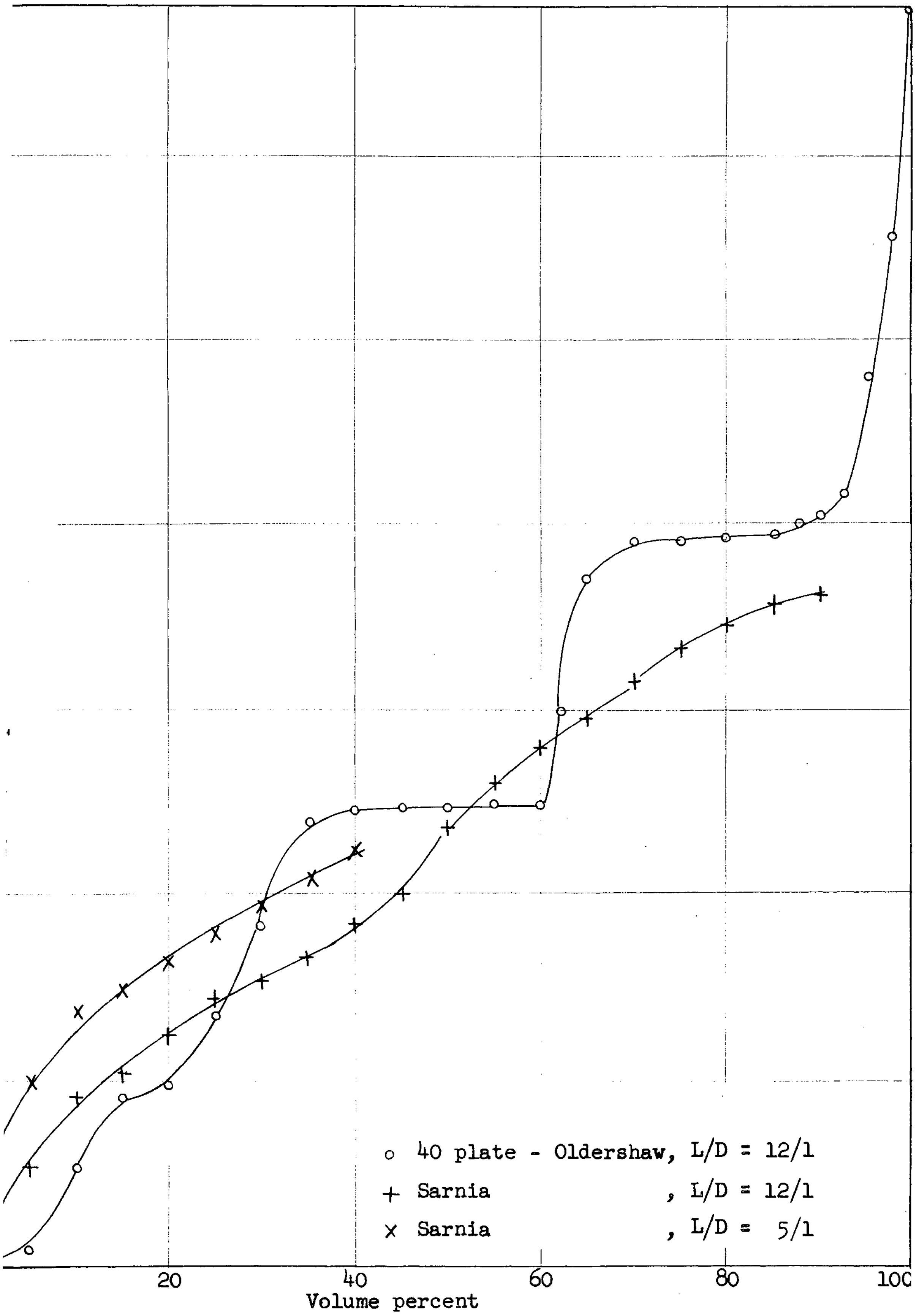


Figure 30 - Comparison of Performances of Distillation Columns

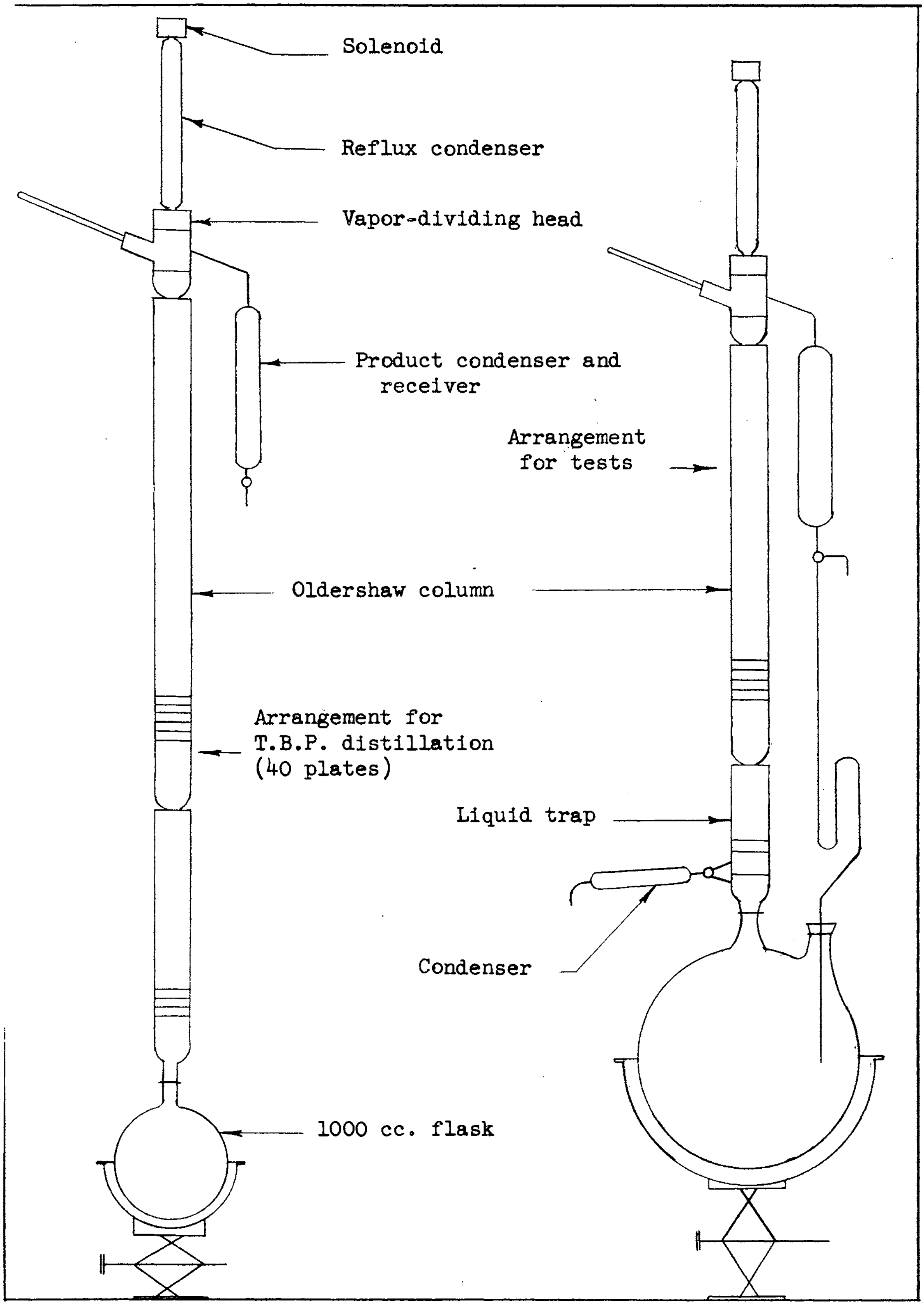


Figure 31 - Arrangement of Fractionating Column

CHAPTER V

CHROMATOGRAPHY

Chromatography is a simple analytical method and produces apid and effective separation leading to exact analyses of complex ixtures of high relative volatilities. Small samples (about one icrogram) may be used for both quantitative and qualitative analyses. relatively large quantity can be separated into its components. he technique can also be used for studying a variety of physico-hemical phenomena, associated with gas, liquid, and solid phase quilibria.

Tswett was credited in 1903 for inventing the chroma-ographic technique, and in 1952 James and Martin (67) introduced he idea of moving gaseous phase, after which several thousand ublications have appeared on the subject.

In this work, gas chromatography was used as an analytical echnique for equilibrium studies of petroleum fractions. The dis-ussion of chromatographic theory and the survey of literature have een kept to a minimum in this chapter. The equipment, procedure, nd finally the discussion of results of this research are presented ere.

Theory

In all the chromatographic techniques, there are two phases, a stationary and a moving one. Gas chromatography covers all those ases where the mobile phase is gaseous. The fixed phase may be an isorbent (gas-adsorption, or gas-solid chromatography, G.S.C.), or n absorbent liquid held on inert supporting substance (gas - liquid artition chromatography, G.L.C.). Gas chromatography can also be lassified according to the means of moving the gas phase through the ixed phase; such as displacement, elution, and frontal methods. All hese three methods can be applied to the gas adsorption, while only lution is used with gas-liquid partition chromatography. The elution nalysis, which was used in this study, consists of passing a carrier as (Hydrogen, helium, nitrogen, · · ·) continuously through the ystem. A gaseous or liquid sample, which will vaporize in the ystem, is introduced into the flowing carrier gas. The carrier gas ransports the sample over the fixed phase, which may either be a iquid or a solid, confined in a suitable container (column).

Each component of the sample distributes itself in a haracteristic fashion between the moving and the stationary phases, s it proceeds through the column. In a favorable condition , the ample components separate and issue from the column in the effluent stream at different retention times. The concentration of each component may be detected in the effluent stream by any one of the many means, such as: automatic PH meter, thermal conductivity cell, infra-red gas analyzer, surface-potential detector, hydrogen flame detector, or gas density balance.

Gas chromatography may be most directly compared with batch fractionation. In both, the separation depends on repeated distribution of each component between the phases. The theoretical late concept, and the height equivalent to a theoretical plate has lso been adopted in chromatography. Therefore, the over-all separaion achieved with a chromatography column depends on the number of lates, and the extent of separation per plate. A gas chromatography olumn may posses many thousand theoretical plates as compared to ess than a hundred plates in a fractionating column.

A temperature gradient must exist in distillation and the eparations are according to the volatilities of components. The olumn temperature in chromatography is normally constant, and the rder of separation depends on many factors. The main difference etween the two may be due to the fact that in gas chromatography ach component is separated and transported individually by the arrier gas, and overlapping of the components can totally be elimiated. It is believed that no molecular rearrangement takes place in gas chromatography, while this is a serious problem in high temperature distillation.

Survey of Literature

There are a number of books (27,79,108,111) on chromatographic technique, which discuss the fundamentals, and give references to more than 2000 publications on the subject.

Attempts have been made to determine vapor-liquid equilibrium phase ratios by chromatographic method, by a few investigators (73,91) and as yet it is far from practical use. Here, the equilibrium phase ratios are measured by detecting the component distribution between the stationary (liquid) phase and the moving phase.

Shively, Morris, and Roberts (137) analyzed a petroleum fraction in the range of gasoline for its components. More than 100 components ranging from C_3 to C_9's were identified, with a maximum deviation of 3.2 percent, when different analytical techniques were applied. The gasoline was first fractionated into seven cuts, and then each cut was analyzed independently.

Apparatus

Figure (32) shows the chromatographic equipment used in this study. It consists of a few standard components, and those which were made to fit the specific needs of this work. The carrier gas, helium, is supplied from a storage cylinder, and it passes through two pressure regulators before it enters the reference thermal conductivity cell. The carrier gas then immerges to the sample injection block, passes through the column, and finally it enters the measuring thermal conductivity cell. Before the effluent gas escapes into the atmosphere, its pressure is regulated by a sensitive needle valve, and its flow may accurately be measured as it passes through a soap-bubble flow meter. The column is constructed from 1/4-inch copper tubing (6 or 8 Ft. long) and packed uniformly with 35 to 80 mesh chromosorb-red coated with liquid (20% T.C.P.). The column is wound in a spiral coil to fit inside the constant temperature bath. A 28-inch long horizontal and well insulated reflux jacket constitutes the main part of the bath. A small distillation flask supplies saturated vapor to the jacket at one end, and a condenser at the other end condenses and returns the thermostatic liquid to the flask. A sensitive thermometer is placed in the condenser, and arrangement is made for manual control of its pressure. The thermal conductivity cells and injection block are also located in the constant temperature jacket. Samples can be injected into the injection chamber through a rubber plug by means of a syringe. The detecting block holds two (8000 ohm) thermistors, one in the reference chamber, and the other in the measuring chamber. The thermistors are heated by a battery, and lose heat mostly by conduction through the carrier and effluent gases. The difference in compositions, therefore thermal conductivities of the two gas streams unbalances the Wheatstone brige, which has these two temperature sensitive thermistors as its components. This electrical unbalance is automatically recorded by a one millivolt Bristol Recorder (Model 560).

Procedure

The bath temperature was regulated by boiling a pure liquid such as water, toluene, or cyclohexane, under a constant pressure (760 mm. Hg.). The flow of the carrier gas was controlled to 50.00 cc./Min., and its outlet pressure was held constant at 760 mm. Hg. The identification of each peak representing each component was made by superposition, that is, by addition of a small amount of a pure material to the sample and noticing the possible growth of one of the peaks representing that component in the mixture. In the case of multi-component mixtures, with wide ranges of volatilities, more than one temperature was found to be necessary for adequate separations.

Calibration graphs based on either the peak height or peak area, depending on the nature of components, were prepared for each constituent. A 10 microliter (μ-liter) syringe with 0.1 μ-liter calibration was used. Since the capacity of the column was limited to about 30 μ-liter of liquid sample, and since some of the multi-component samples contained a small percentage of some of their constituents, it became necessary to extend the charts to the amounts less than 0.1 μ-liter This was realized by injecting a sample consisting of a known mixture of two or more components. For instance, to find the peak height corresponding to 0.01 μ-liter of benzene, 0.1 μ-liter of 10% mixture of benezene and toluene was used.

The attenuator in all cases was set to produce a large peak on the recorder chart.

Discussion of Results

At the present time, the chromatographic technique is not well enough developed to be conveniently used in the exact analysis of complex petroleum fractions; however its future possibilities in this direction should not be questioned.

A petroleum fraction can be fractionated into a few narrow cuts, and each can be divided into groups of hydrocarbons by means of L.S.C. or G.S.C. or both. The results can then be analyzed by some suitable G.L.C.

In Chapter III the use of G.L.C. in connection with equilibrium study of petroleum fractions was discussed. There, only the relative amounts of some of the components of the mixtures, ther than the exact analysis was the objective. In Chapter VI the cessity of G.L.C. analysis of solute oils for possible presence of nzene as a component shall be discussed.

In Appendix B, the approximate G.L.C. analysis of a hydro- rmer-product is given. More than 25 components were identified, and those only 15 occurred in measurable quantities, with aromatics as e prominent portion. Figure (33) shows the results of T.B.P., and e instantaneous G.L.C. analysis of T.B.P. products. The overlap- ng of the components, which is one of the disadvantages of T.B.P. is ll illustrated here. This subject has already been presented in the evious chapter, and also will be discussed from the view point of K lue calculation in Chapter VII.

Equilibrium flash vaporization of the hydroformer-product as studied in both of the flow equilibrium equipments, and the re- lts were analyzed by G.L.C. The consistency of the work for the romatics part of it can be judged from Figure (34), and the complete esults are given in the appendix.

From this exploratory study it is evident, that this techni- ue can be developed to such a state of perfection, where exact analyses f complex petroleum fractions would be possible. The advance of this ethod would assist in the equilibrium investigation of petroleum frac- ions in the following ways:

1. Reduction in size of sample required.
2. Use of small equilibrium stills.
3. More exact and complete analysis of products.
4. Better foundation for theoretical work in complex systems.
5. Much faster, easier, and more reproducible.

technique.

6. Indication of the true equilibrium operating condition of some equilibrium stills.

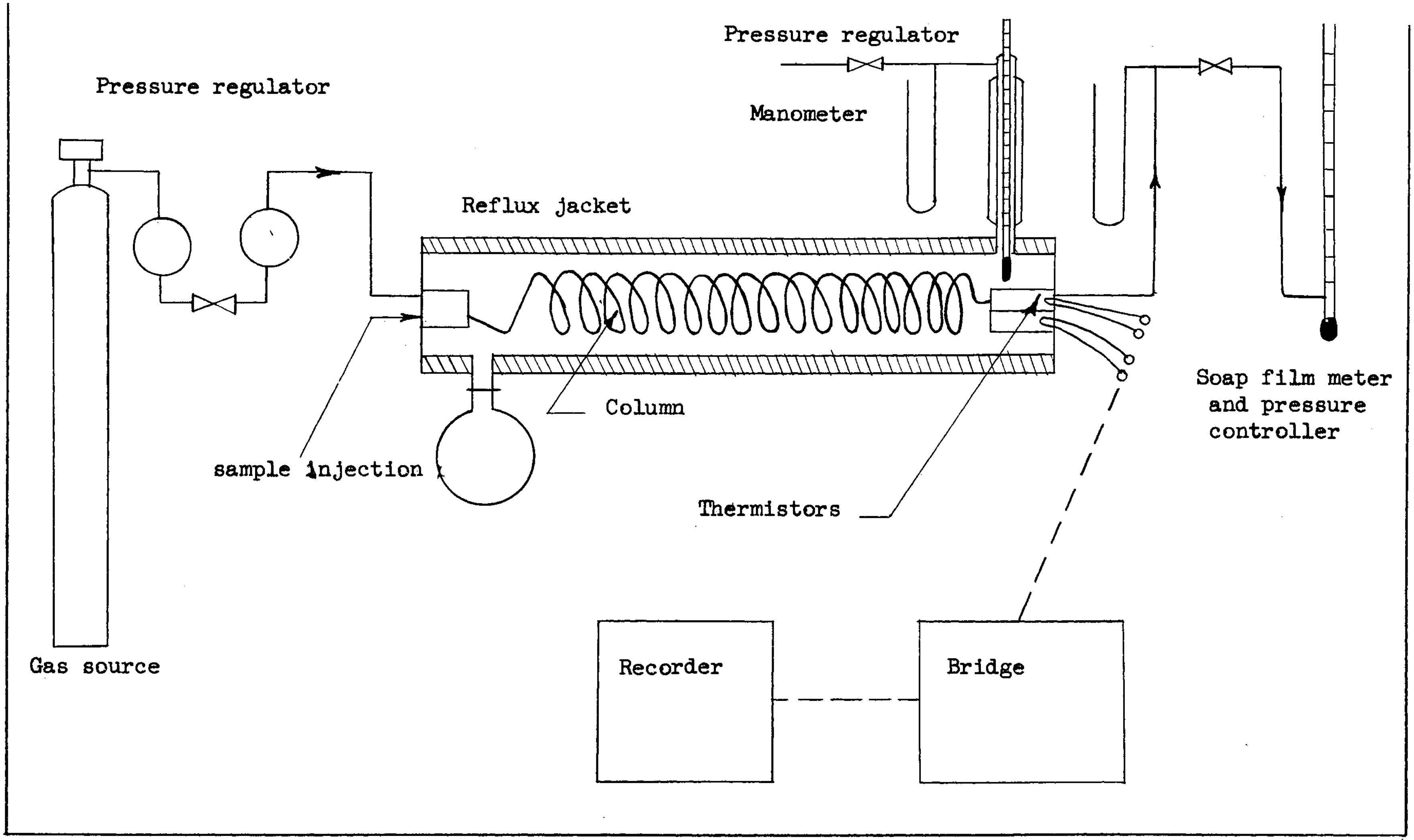


Figure 32 - Cas Chromatograph

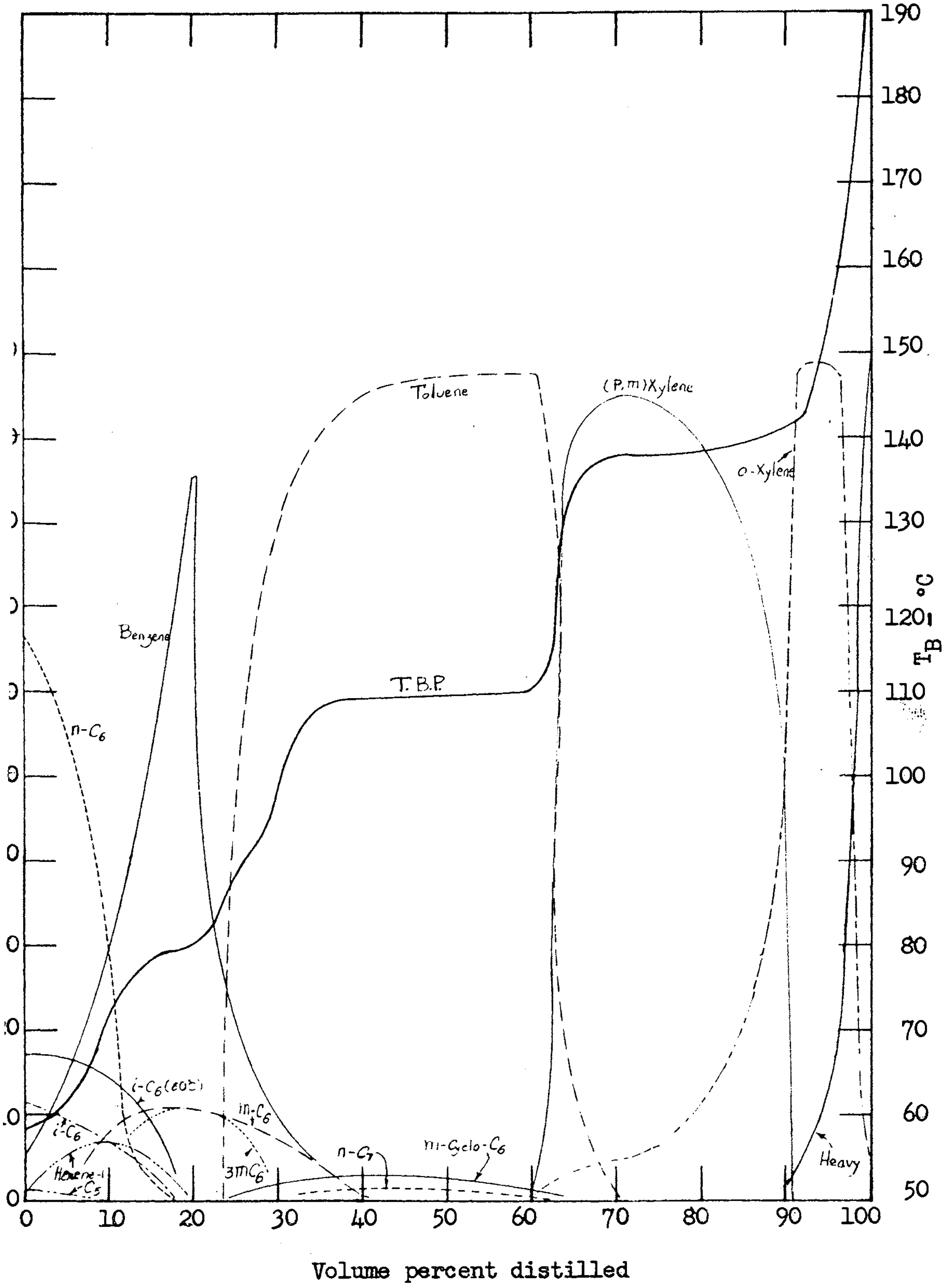


Figure 33 - T.B.P. Distillation and G.L.C. Analyses - Oil D

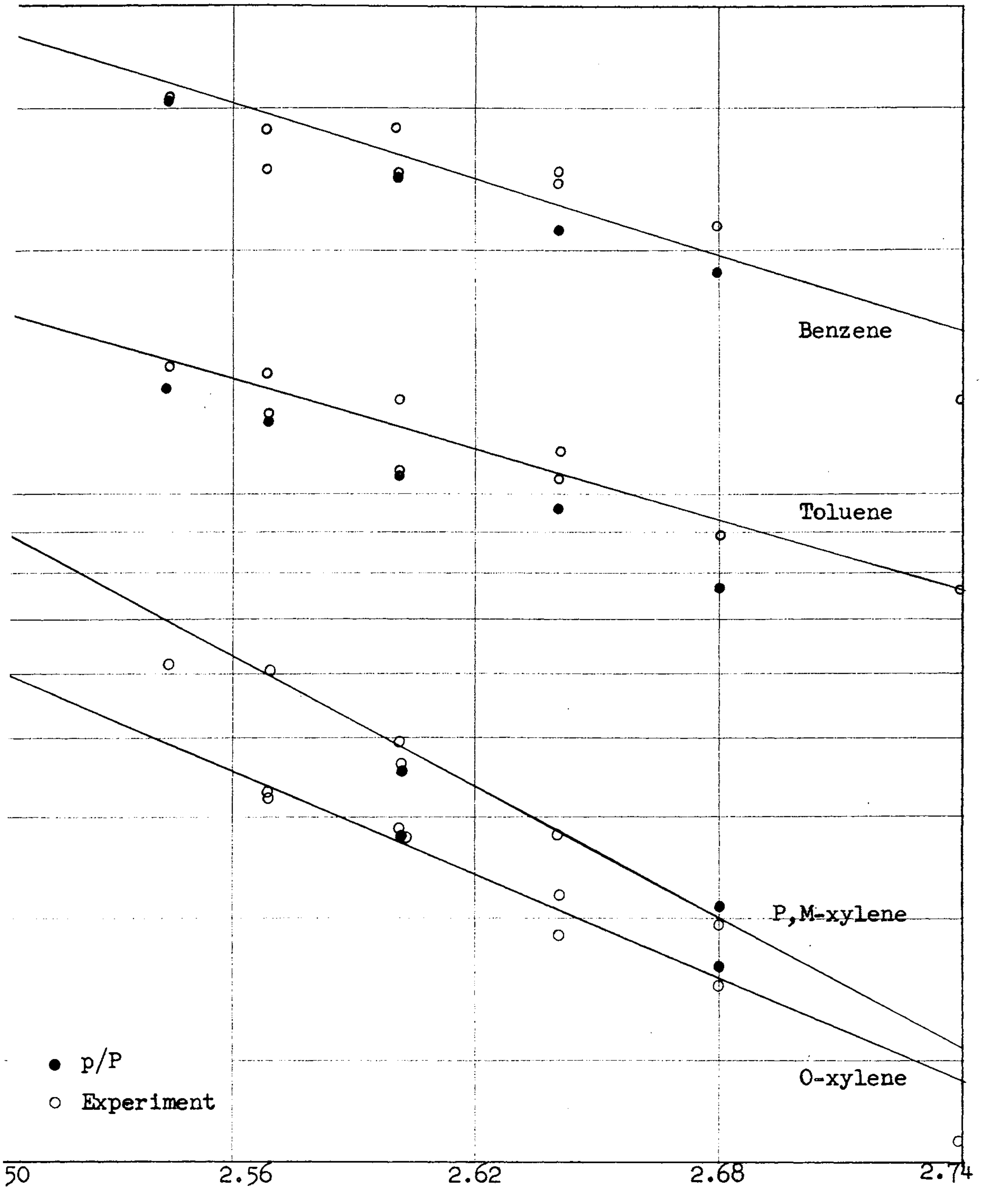


Figure 34 - K-values of Aromatic components of Oil D

CHAPTER VI

MOLECULAR WEIGHT AND MOLAL VOLUME

The molecular weight and molal volume of an oil are physical properties that are interrelated by density. These properties can only be measured indirectly.

Cryscopic technique was chosen for measuring molecular weights of petroleum fractions, which are mixtures of molecules of diversified sizes and kinds existing in some sort of molecular aggregation even at infinite dilution. The measured "apparent average molecular weight at infinite dilution obtained by cryscopic method" was found to be in close agreement with the calculated average molecular weight.

In this chapter, the subject is first treated theoretically. This is followed by a brief account of the research steps. The equipment and the procedure adopted for this study proved to be highly dependable, and are given in detail. The final section of the chapter is devoted to the discussion of results. A few typical graphs are shown to aid the presentation, while the bulk of information is kept in an appendix. Suggestions are made for characterizing petroleum stocks. The usefulness of some of the techniques presented becomes more evident in the next chapter.

Theory

Certain physical properties of liquid solutions are interrelated, without regard to the particular solute or its concentration, the value of any one of these properties can be evaluated, with a high degree of accuracy from the observed value of any one of the others. These "colligative properties" of solutions include: freezing-point depression associated with the presence of a solute that does not enter into solid solution or form a solid compound with the solvent, the boiling-point elevation, the vapor pressure depression associated with the existance of a relatively nonvolatile solute, and the osmatic pressure.

These properties have been predominently used in simplified forms for the purpose of estimating the molecular weight of solute in a dilute solution. Each of these properties is proportional to the molal concentration of the solute in a sufficiently dilute solution. The molecular weight of a substance may either be determined in a gaseous state by the use of Avogadro's law, or in a dilute solution by detecting any of the mentioned colligative properties.

The freezing-point depression method has been selected for estimating molecular weights, because it has the advantages of accuracy and ease of operation over the others. This technique has commonly been used for molecular weight determination of petroleum oils.

The freezing-point is that temperature at which the solid solvent exist in equilibrium with solution. At freezing-point of a liquid (solvent), the solid and liquid phases are in equilibrium, and their vapor pressures are equal. The addition of a nonvolatile, and non-soluble solute in the solid solvent phase to an equilibrium mixture of solid and liquid solvent, would reduce the vapor pressure of liquid solvent, and thus disturb the equilibrium. In order to restore the equilibrium, a part of solid must melt to liquid. This change is accompanied by gain of some heat from the mixture, and consequently lowering the equilibrium temperature.

Figure (35) schematically represents the change of the vapor pressure of pure liquid-solvent, solid-solvent, and a solution. The curves indicated by "liquid-solvent" and "solution" represent the vapor pressures of pure solvent and solution with a fixed concentration, respectively. Points F and F$'$ represent the freezing points of pure solvent, and the solution.

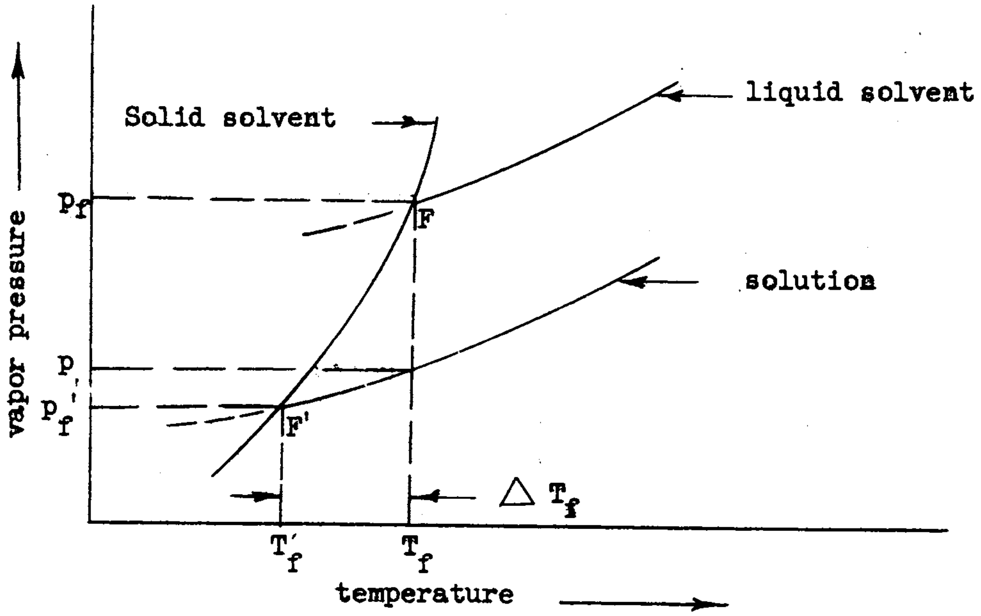


Figure 35

From the geometrical consideration, and for very dilute solution,

$$\frac{P_f - P_f'}{T_f - T_f'} = \frac{d\,P_{solid}}{d\,T}\,, \quad \frac{P - P_f'}{T_f - T_f'} = \frac{d\,P_{solution}}{d\,T} \tag{38}$$

also, $$\frac{d\,P_{solvent}}{d\,T} \cong \frac{d\,P_{solution}}{d\,T} \tag{39}$$

Then $$\frac{P_f - P}{T_f - T_f'} = \frac{d\,P_{solid}}{d\,T} - \frac{d\,P_{solvent}}{d\,T} \tag{40}$$

applying the Clapeyron equation to the case of solid, and solvent,

$$\frac{d\,P_{solid}}{d\,T} = \frac{\Delta H_{(s-v)}\,d\,T}{R\,T_f^2}\,, \quad \frac{d\,P_{solvent}}{d\,T} = \frac{\Delta H_{(l-v)}\,d\,T}{R\,T_f^2} \tag{41}$$

where $\Delta H_{(s-v)} - \Delta H_{(l-v)}$ is the molal heat of fusion of solid solvent, then,

$$\frac{P_f - P}{T_f - T_f'} = \frac{\Delta H_{(s-l)}\,P}{R\,T_f^2} \tag{42}$$

but $$\frac{P_f - P}{P} = x = \frac{\frac{w}{m}}{\frac{W}{M} + \frac{w}{m}} \tag{43}$$

where: x is the mole fraction of solute in solution.

w, m and W, M are the weights and the molecular weights of solute and solvent respectively.

Finally:

$$T_f - T_f' = \frac{R\,T_f^2}{\Delta H_{(s-l)}}\,x = k_f\,x \tag{44}$$

Therefore, the freezing point depression ΔT_f, the cryscopic constant 'k_f', and the mole fraction of solute can be related as follows:

$$\triangle T_f = k_f x \qquad (45)$$

$$\triangle T_f = k_f \frac{w/m}{\frac{W}{\bar{M}} + w/m} \qquad (46)$$

which for very dilute solution, reduces to

$$\triangle T_f = k_f \frac{w/m}{\frac{W}{\bar{M}}} \qquad (47)$$

The freezing point-depression caused by the addition of a small quantity of solute to a solvent is usually detected by a highly sensitive differential thermometer. The exact procedure which was adopted in this investigation will be fully discussed after the presentation of some of the previous pertinent studies.

Previous Works on The Measurement of Molecular Weight of Petroleum: Iwamoto (66), used a miniature Beckman apparatus in which 2 or 3 cc. of solvent and 2 to 10 M.Gr. of solute may be used. Kubata and Yamane (77), introduced a design which uses a sensitive thermocouple instead of a Beckman microthermometer. This equipment gives good results with 5 M.Gr. of solute in 1 cc. of solvent. Wilson and Wylde, (151), determined molecular weight of petroleum fractions by cryoscopic method, using a Beckman equipment and benzene as the solvent. For low concentrations $\triangle T_f = 65.50 \frac{w/m}{W/\bar{M}}$ is suggested. They recommend a $\triangle T_f$ of 0.5 to 2 °C, and a better result may be obtained if $\triangle T_f$ is plotted as the function of observed molecular weight and extrapolated to zero. Fitz Simmons and Bahlke (44,45), measured molecular weight of some petroleum oils by freezing-point depression, Victor Meyer, and Menzies-Wright methods. The results of various method checked well, and they were plotted as the functions of A.P.I. gravity, logarithm of viscosity, and A.S.T.M. distillation midpoint. Steed (144), determined molecular weight of petroleum fractions by freezing-point depression, using nitrobenzene as solvent. Cryscopic constant was found to be a linear function of the temperature depression, and it was taken at infinite dilution. The mean molecular weight of crude oils and their fractions were determined by Gullick (53). Pure nitrobenzene dried insitu by anhydrous sodium sulphate was used as the solvent. The mean molecular weight is expressed as a function of other physical properties.

Epperson and Dunlap (38), measured the molecular weights of ten fractions of lubricating oils by cryscopic method. The results were checked by means of three solvents: benzene, nitrobenzene, and ethylbromide. 25 cc. of dry solvent and enough solute to cause 0.1 to 0.2 ^{o}C freezing-point depression were mixed in a regular Beckman apparatus, and the results were plotted as the function of viscosity. The cryscopic equipment which probably gives the most accurate result for petroleum fractions was developed by Adams (1), and then improved by Kraus and Vingee (75). This apparatus employs two cells, one for pure solvent and the other for solution. The temperature differential may be measured by thermopiles. Rall and Smith (114,115), used a modified Beckman apparatus, with a low temperature flow bath. Four types of dry and wet solvent benzene were used to investigate the effect of moisture and impurities.

Also the results of eleven laboratories for the same oils in benzene solution were compared. They concluded that the deviation of results from different laboratories is greatest for the highest molecular weight oil. A direct relationship is claimed between the slope of molecular weight versus concentration plot, and the value of extrapolated molecular weight for the same solvent. They also suggest that molecular weight of viscous oil be determined by first diluting it with the solvent. Lipkins and Martin (84), and Lipkin and Kurtz (83), present equations which relate molecular weight to other physical properties with a fair degree of accuracy.

Apparatus

Figures (36,37) show the equipment used for measuring the freezing-point depression. It consists of a Beckman thermometer graduated to 1/100 °C, placed inside of a 125 cc. test tube. The thermometer is held in place by a cork stopper, as to be detached from the wall of the test tube. A Nichrome stirring wire with either a ring or a spiral end is placed in the test tube and around the thermometer. This stirrer may be moved up or down without contacting the sides of either the thermometer or the test tube. The other end of the Nichrome wire passes through the cork, and is attached to a small weight and a flexible Nylon cord. The cord passes over two small pulleys, and finally is attached to a wire which is loosely connected to one of the holes of a metal disc. The disc is mounted on the shaft of a small 32 r.p.m. electric motor. The arrangement is such that the rotational motion of the

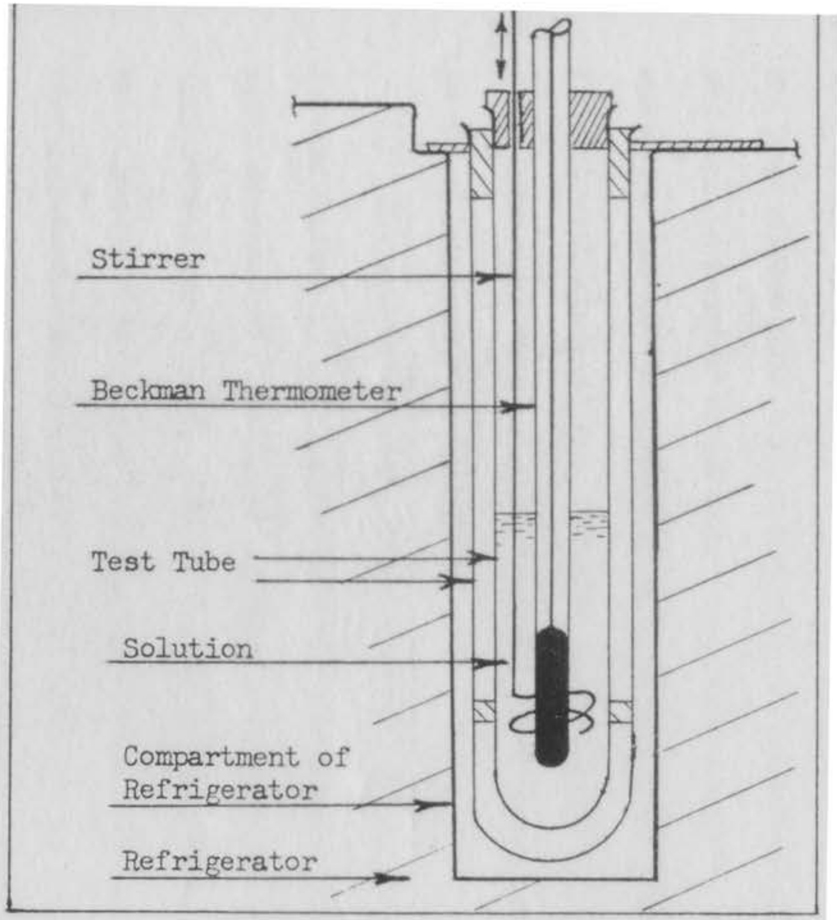


Figure 36 - Molecular Weight Measuring Equipment

Figure 37 - Molecular Weight Measuring Equipment

motor may be transformed into the reciprocating movement of the stirrer. The variously positioned holes in the disc provides a convenient means for adjusting the amplitude of the stirring motion. The test tube is suspended by a cork ring in a larger test tube, with a small air space between the two. These in turn are placed in one of the two cylindrical compartments of a small refrigerating machine. The temperature of this refrigerator can be closely controlled by adjusting the pressure of its evaporator.

Procedure

The solvent, a 99 mole percent pure benzene, was further purified in an efficient fractionating column, and the middle 80 percent cut of each batch was collected over calcium carbonate. This purified benzene was stored in a dark glass container, and was kept closed with a cork stopper. A calibrated 25 cc. pipet was kept in benzene by passing it through the cork, and the other end was connected to a short rubber tubing. The test tubes were cleaned with hot cleaning solution (concentrated H_2 SO_4, K-chromate) after each use, then rinsed with distilled water, and finally dried in a low temperature oven.

The operation started for each series of molecular weight determinations by setting the Beckman thermometer for the freezing point of benezene, and then thoroughly rinsing the thermometer and the stirrer with it. 25.00 cc. of solvent benzene was carefully pipetted in a clean 125 cc. test tube, and then immediately the thermometer and the stirrer were inserted in it. These were placed inside the larger test tube, which was maintained within the refrigerator. The stirring motor was then started, and the temperatures were read to 2/1000 °C with the assistance of a reading lens at every 15 second intervals. 25 cc. of benzene sufficiently covers the thermometer, and the amplitude of the stirring motion was so adjusted to give a full movement inside the liquid.

A plot of temperature versus time shows cooling and supercooling of solution, and then a rapid rise of temperature to the freezing point. The temperature of the evaporator of the machine was kept at 3 °C below the freezing point of benzene. This small temperature differential, plus the arrangement of the test tubes gave a desirable slow cooling rate. The small temperature differential, together with the rather rapid movement of the stirrer, eliminated the possibility of excessive supercooling. During the cooling period the Beckman thermometer was tapped occasionally, and the entire mercury thread of the thermometer was inspected in order to detect any possible discontinuity in it. The accepted freezing temperature of benzene is the average of three readings for each of the three samples used. A maximum deviation of 5/1000 °C was tolarated. The solutions were prepared by adding exactly 0.250 cc. of solute into 25.00 cc. of solvent. The accurate transfer of solute was made possible by a calibrated 0.25 cc. syringe.

The test tube containing the solution was covered with a cork and was placed in one of the compartments of the refrigerator. The solution was removed after total crystallization, and was then melted to a temperature of about 2 or 3 °C above the freezing-point f benzene. The thermometer and the stirrer were swiftly placed in his solution, and the freezing-point was measured as before. While he freezing point of one solution was being measured in one of the ompartments of the refrigerator, another solution was being cooled in he other compartment.

In all the experiments, one solution was investigated for ach sample, and a maximum deviation of 5/1000 °C was accepted for hree readings.

Discussion of Results

It is quite indubitable that petroleum oils do not possess the characteristics of ideal solutes in solvents. Evidently these petroleum solutes have some appreciable vapor pressures at the freezing-point of solution, and may crystallize with solvent, and as well as forming some complex molecular groups in solutions. Although these non-idealities, particularly the latter one, tend to create some discrepancy in the results, nevertheless the "apparent" mean molecular weights have been found to concur with the mean molecular weights in sufficiently dilute solutions. An extremely dilute solution gives a very small freezing-point depression, with a rather large percentage of error.

It has been a common practice for the previous workers to measure solvent volumetrically, and weigh the liquid solute in a sealed glass capsule. In this study, both the solvent and the solute were measured volumetrically with a constant solute to solvent ratio of $\frac{1}{100}$, (0.250, 25.00 cc.). This method essentially eliminates the discrepancy due to thermal expansion of solvent, when both solvent and solute are measured at the same temperature. Moreover this technique is fast and reproducible, and also provides a highly satisfactory method for converting the volume percent T.B.P. into the mole percent.

The cryscopic constant for benzene was calculated from equation (46), by measuring freezing-point depression caused by adding some small quantities of naphthalene to benzene, and it agrees with the values given in literature.

The method of Rall and Smith (115) was used to correct the calculated molecular weight for non-ideality of solution. A plot of uncorrected molecular weight 'm''' as the function of concentration $\frac{'w'}{W}$ gives a straight line for each solute. The general equation of these lines in terms of the extrapolated molecular weight to zero concentration 'm' and the slopes 'S' is:

$$m_i'' = S_i \left(\frac{w}{W}\right) + m_i \qquad (48)$$

Where for solvent benzene $S = 1.150\ m$. The substitution of these two in equation (47) would result the following equation, which has been used in this work.

$$m = \left(\frac{k_f\ M}{\Delta T_f}\right) \frac{w/W}{1 + 1.150\ \frac{w}{W}} \qquad (49)$$

This equation can be simplified for the case of 0.250 cc. solute and 25.00 cc. benzene to:

$$m = \frac{58.838\ \rho_s/\Delta T_f}{1 + 0.0132\ \rho_s} \qquad (50)$$

Where 'ρ_s' is density of the solute.

Some petroleum fractions contain benzene as one of their constituents, which reduces the value of 'w' while increases 'W'. Presence of benzene in solutes were detected and its amounts were measured by chromatographic analysis. Suitable corrections were then applied to the measured values of $\triangle T_f$. It appears that this type of correction has been neglected by the previous investigators.

The experimental technique, the equipment, as well as the validity of the equation, were tested by means of solutes consisting of measured quantities of pure organic compounds (2,2,4, tri-methyl pentane, n-heptane, n-dodecane, n-tridecane, and cyclo-hexane). The average deviation for two different samples, and a total of six determinations was found to be 1.8 percent.

Equation (50) can be simplified without loss of any accuracy to:

$$m = \frac{58.838\ \rho_s/\triangle T_f}{1 + 0.0132(\rho_s)_{ave.}} \qquad (51)$$

where : $(\rho_s)_{ave.}$ is the density of the petroleum stock, and ρ_s is the density of a fraction of it from T.B.P., which its molecular weight is 'm'. Therefore for each stock of petroleum, equation (51) would be

$$m = k_f'\ (\rho_s/\triangle T_f) \qquad (52)$$

or

$$\triangle T_f = k_f'\ (\rho_s/m) \qquad (53)$$

where : k_f' is a constant, and varies insignificantly for different stocks.

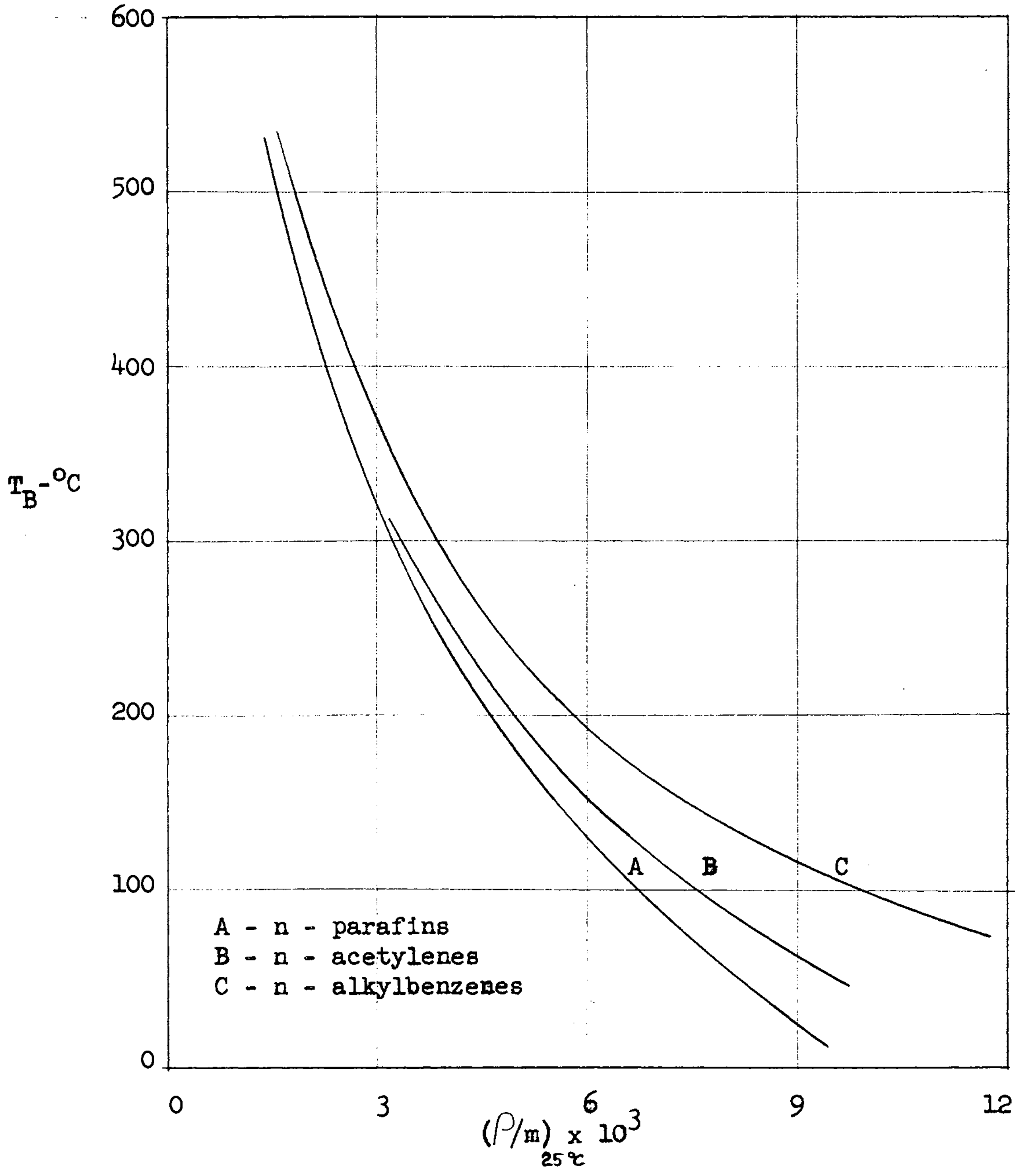


Figure 38 - (ρ/m) as Function of T_B

quation (53), as it will be discussed in the next chapter, is highly ppropriate for transformation of T.B.P. volume percent to the mole ercent. It is also apparent from the above equation that the value f (ρ_s/m) can be measured more readily and accurately than the moleclar weight. It should be recognized at this time that (ρ_s/m) is he reciprocal of molal volume, which is an important physical uantity.

Figure (38) shows the plots of (ρ_s/m) for various homologue series of hydrocarbons as a function of their normal boiling points. Curve 'A' is for n-paraffines and to its left is for branched paraffines. The curve for normal monoolefines runs parallel to 'A' and just to its right, and curve 'B' represents n-acetylenes. Normal alkyl benzenes are represented by curve 'C', where to its right lies the location of branched alkyl benzene depending on the number of branches, and then the other aromatics. I.B.M. 650 computer was used to find the following equations for the mentioned curves, and they are:

The general equation is:

$$(\rho_s/m)_{25\ ^\circ C} = a + bT_B + cT_B^2 + dT_B^3 + eT_B^4 \qquad (54)$$

Where ρ_s is the density at 25 °C in Gr./cc., and T_B is the normal boiling temperature in °C.

Thus, for n-parafines,

$$(\rho_s/m)X1000=9.9132-3.819(T_B/100)+.7635(T_B/100)^2-.08825(T_B/100)^3+ .004495(T_B/100)^4 \qquad (54a)$$

For alkylbenzenes,

$$(\rho_s/m)X1000=18.1534-11.1510({}^{T}B/100)+3.4681({}^{T}B/100)^2-.54389({}^{T}B/100)^3+ .033139({}^{T}B/100)^4 \qquad (54b)$$

for n-monoolefines,

$$(\rho_s/m)X1000=8.6954-3.2153({}^{T}B/100)+.6683({}^{T}B/100)^2-.0\ 7893({}^{T}B/100)^3+ .003811({}^{T}B/100)^4 \qquad (54c)$$

for n-acetylenes,

$$(\rho_s/m)X1000=B.1801-2.6752({}^{T}B/100)+.4655({}^{T}B/100)^2-.04398({}^{T}B/100)^3+ .001664({}^{T}B/100)^4 \qquad (54d)$$

for n-alkylcyclo hexanes and cyclo pentanes,

$$(\rho_s/m)X1000=8.2684-2.5065({}^{T}B/100)+.3901({}^{T}B/100)^2-.03258({}^{T}B/100)^3+ .001087({}^{T}B/100)^4 \qquad (54e)$$

for oil G

$$(\rho_s/m)X1000=8.0721-.7884({}^{T}B/100)-.3794({}^{T}B/100)^2+.08603({}^{T}B/100)^3- .004972({}^{T}B/100)^4 \qquad (54f)$$

for oil A

$$(\rho_s/m)X1000=2.6251+.07469({}^{T}B/100)-.0039455({}^{T}B/100)^2-.01304({}^{T}B/100)^3+ .001130\ ({}^{T}B/100)^4 \qquad (54g)$$

This type of plot can easily be prepared for a petroleum sock by simply measuring $(\triangle T_f)$'s of its fractions at various T.B.P. temperatures. Such a plot not only furnishes the molecular weight information, but it can serve as an excellent and yet a facile technique for characterization of petroleum stocks over their entire boiling range. The utility of equations similar to (54) for petroleum stocks will be mentioned in the next chapter.

Figure (39) shows a representative plot, relating together

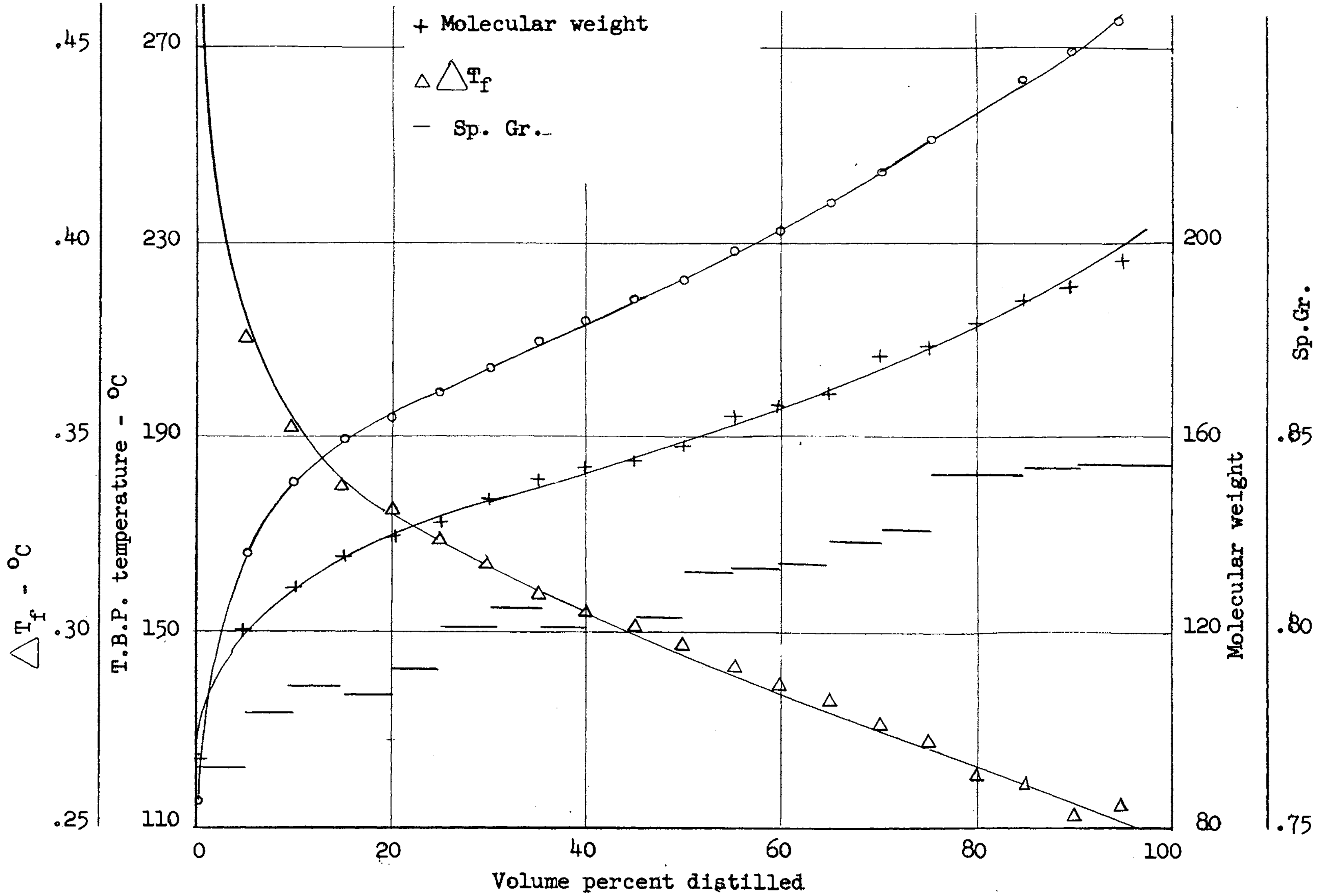


Figure 39 - $\triangle T_f$, M. Wt., Sp. Gr., and T.B.P. Distillation Curves for Oil G

molecular weight, T.B.P. temperature, and the volume percent distilled-off for one of the petroleum stocks investigated. Similar information for the other stocks are given in the appendix.

In Figure (40), $(\triangle T_f)$'s of each of the twenty equal volume (5%) T.B.P. cuts are plotted in the step-wise fashion, as the function of their T.B.P. temperatures and volume percent. A smooth curve is passed through these steps, in a fashion as to balance the area on both sides of each one. The $(\triangle T_f)$'s of very small samples taken at various T.B.P. temperatures are also plotted on the same curve. From this and the similar graphs for the other stocks (with 20 or 40 T.B.P. cuts), it becomes quite evident, that the mean $(\triangle T_f)$'s of fractions can be satisfactorily obtained from the corresponding point $\triangle T_f$ plot, or vice-versa.

Figure (41) is a representative plot, which clearly indicates that $\triangle T_f$ vs. T.B.P. temperature curves for various flash vaporization cuts of the same petroleum stock plot into a single curve.

These experimental results coincide well with the theoretical reasoning, and therefore, evidently for each petroleum stock a single plot of $\triangle T_f$ as a function of its T.B.P. temperature would be sufficient to characterize it.

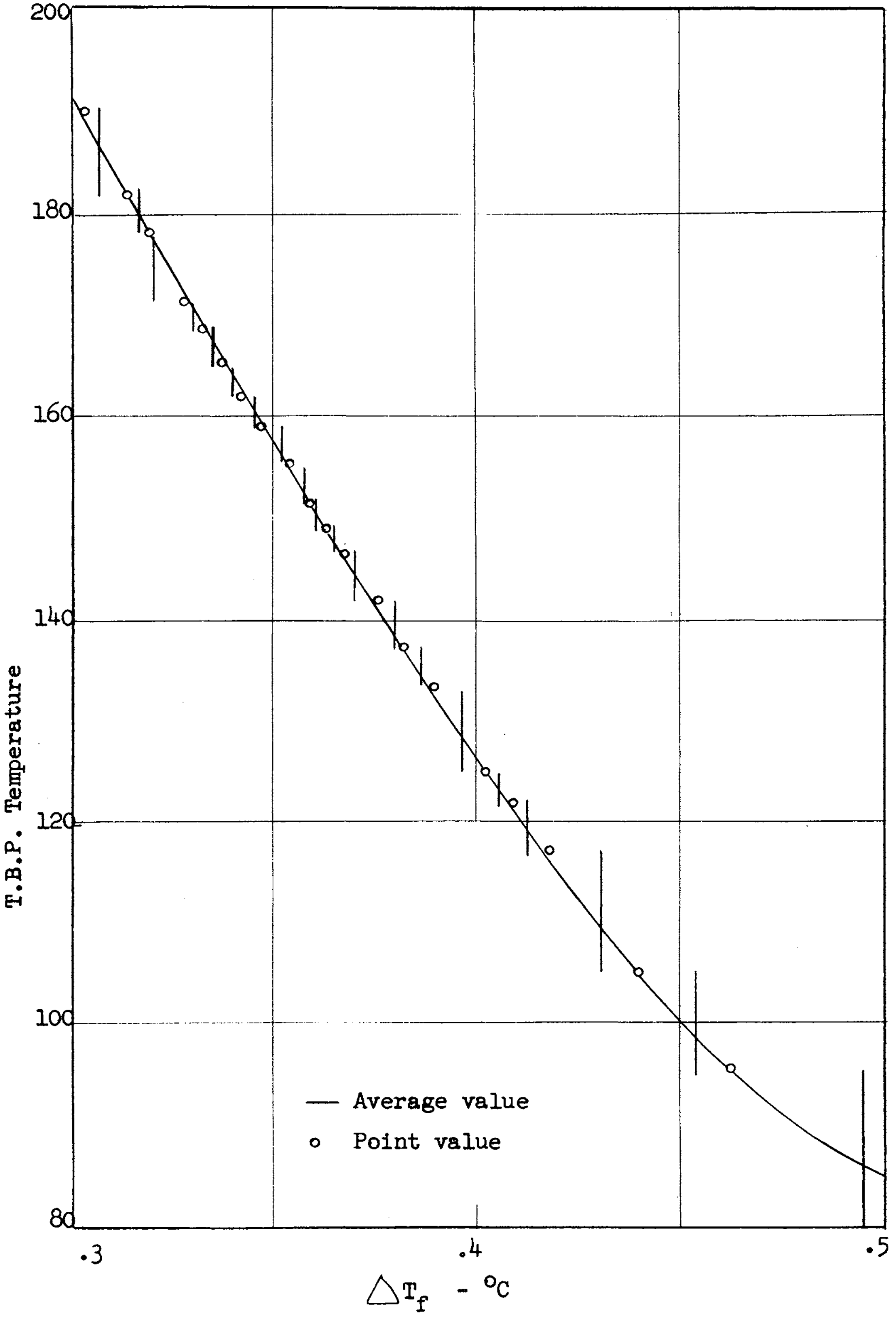


Figure 40 - $\triangle T_f$ as the Function of T_B, for Oil A

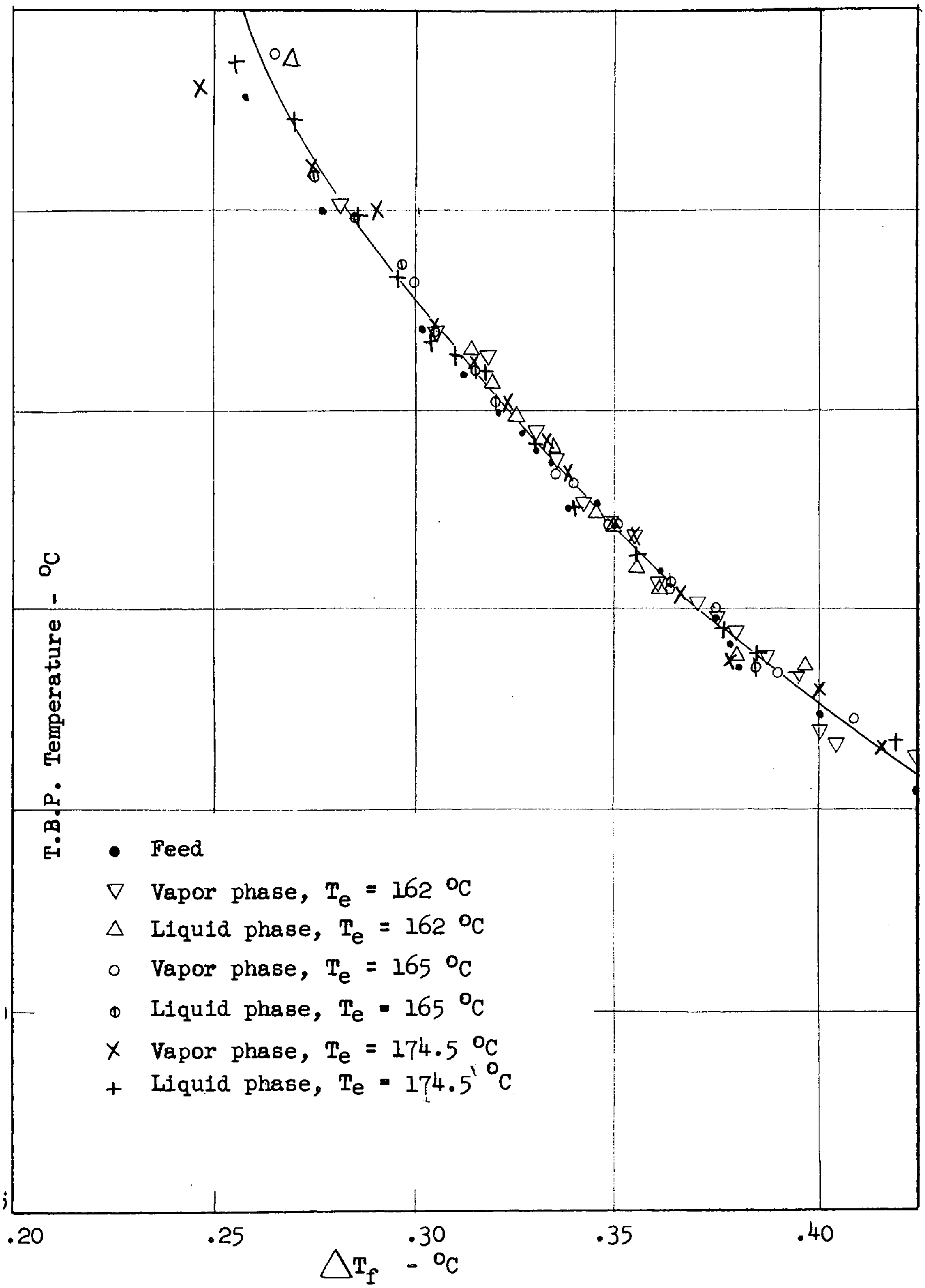


Figure 41 - ΔT_f as the Function of T_B and T_e for Oil B

CHAPTER VII

EXPERIMENTAL K-VALUES AND DISCUSSION

In the previous chapters the apparatus and the experimental techniques for obtaining the equilibrium vapor and liquid, the T.B.P. distillation curves, chromatographic analysis, density, and molecular weight of petroleum fractions have been fully discussed. This chapter deals with the calculation of vapor-liquid phase distribution coefficients (K-values) of petroleum fractions. As has been stated earlier, the proper design and operation of any vapor-liquid contacting equipment require accurate knowledge of equilibrium phase distribution coefficients. The technique presented through this investigation is sufficiently easy and realiable to be used for design purposes.

K-Values of Petroleum Fractions: For convenience in presenting the method, a hypothetical petroleum mixture composed of six components, 1, 2, 3, 4, 5, and 6 with normal boiling points T_{B1}, T_{B2}, $\cdot \cdot \cdot$, T_{B6} are assumed. It is further assumed that this hypothetical petroleum fraction is batch fractionated in a highly efficient column, giving a plateau for each component and with no overlapping. The result is converted from the volume percent into mole percent, as is shown by the distillation curve in Figure (42). This petroleum fraction is equilibrium flash vaporized at some pressure (e.g. 1 Atm.), and some temperature (e.g. $T_e = T_{B3}$), to produce equilibrium vapor-iquid phases with distillation curves as shown in Figure (42). The .B.P. distillation curves of these phases indicate that the mole ercent of the components are y_1, y_2, $\cdot\ \cdot\ \cdot$, y_6, and x_1, x_2, $\cdot\ \cdot\ \cdot$, $_6$ in vapor and liquid phases respectively. Then the vapor-liquid quilibrium phase distribution coefficient of each component of the ixture at the condition of equilibrium $(P_e = 1,\ T_e = T_{B_3})$ would be,

Component	Normal-B.P.	$K_{(T_e,P_e)}$
1	T_{B_1}	$K_1 = {}^{y_1}/x_1$
2	T_{B_2}	$K_2 = {}^{y_2}/x_2$
3	T_{B_3}	$K_3 = {}^{y_3}/x_3 = 1$
.	.	.
.	.	.
6	T_{B_6}	$K_6 = {}^{y_6}/x_6$

To this point two assumptions have been made, the complete absence of over-lapping in the distillation analysis, and the small number of components present in the petroleum fraction. In general the physical properties of the components existing in most petroleum fractions change gradually with boiling temperature. Therefore, for example, the physical properties of component 3 in the former example is close and in between those of components 2 and 4. Then consequently, K_3 is close and in between K_2 and K_4. This condition is more true when the petroleum mixture is composed of nearly the same type of hydrocarbons, and of very close boiling constituents. Figure (43) shows T.B.P. distillation curves of equilibrium phases, but for a less hypothetical condition then the former example. Here the number of constituents are more, and some over-lapping of components exist.

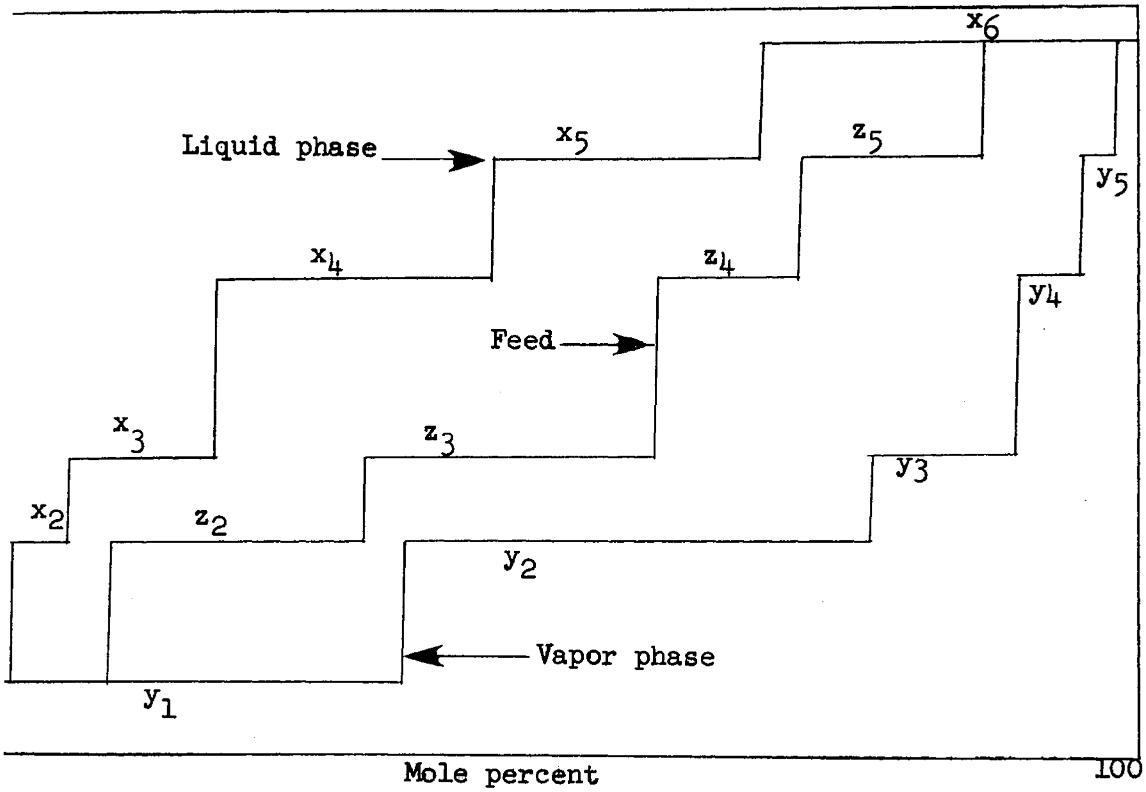


Figure 42 - Hypothetical T.B.P. for Feed and Equilibrium Phases

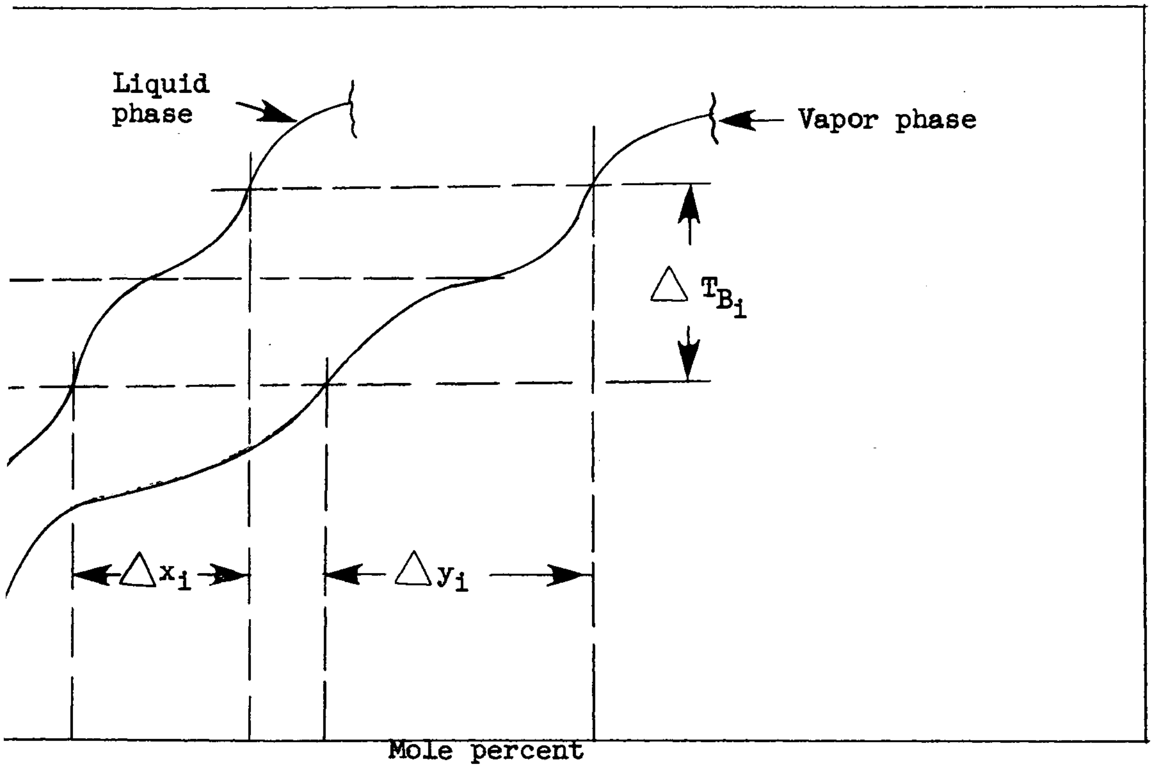


Figure 43 - T.B.P. Curves for Equilibrium Phases

herefore, the K-value for a component of the mixture, such as the ne which boils between T_B and $(T + \Delta T)_B$ would be

$$(K^{P_e}_{T_e})_{T_{B_i}} = \frac{y_{(T+\Delta T)_B} - y_{T_B}}{x_{(T+\Delta T)_B} - x_{T_B}} = (\frac{\Delta y_i}{\Delta x_i}) \qquad (55)$$

$$(K^{P_e}_{T_e})_{T_{B_i}} = (\frac{\Delta y_i/\Delta T_{B_i}}{\Delta x_i/\Delta T_{B_i}}) \qquad (56)$$

In actual cases the number of these distillation steps or the number of components are so high, that the T.B.P. plots appear as smooth curves. Then equation (56) takes the following form:

$$(K^{P_e}_{T_e})_{T_{B_i}} = (\frac{\partial y/\partial T_B}{\partial x/\partial T_B})_{P_e,\ T_e,\ x} \quad \text{at } T_{B_i} \qquad (57)$$

For a constant equilibrium condition (P_e, T_e, x), equation (57) can be simplified to,

$$(K)_{T_{B_i}} = (\frac{dy/dT_B}{dx/dT_B}) \quad \text{at } T_{B_i} \qquad (58)$$

or

$$(K)_{T_{B_i}} = (\frac{dT_B/dx}{dT_B/dy}) =$$

$$\frac{\text{slope of T.B.P. distillation curve (temperature-VS-mole percent) of liquid phase}}{\text{slope of T.B.P. distillation curve of vapor phase in equilibrium with liquid at } P_e,\ T_e.}$$

both slopes are taken at the distillation temperature T_{B_i}. (58a)

The transformation of T.B.P. volume percent into mole percent, can either be done by analytical technique or by incremental method. In the case of the former technique, the experimental data must be expressed in analytical form, which is often unsatisfactory and with reduction of accuracy. The latter method, however, has been found to be more reliable, when sufficiently small increments are used.

Conversion of T.B.P. Volume% to Mole% (with 40 cuts)

Volume% off (1)	T.B.P. Temp. (2)	Ave. Density (3)	Ave. M.Wt. (4)	Moles (5)	Mole% (6)	Mole% off (7)
0	T_{B_0}					0
		ρ_1	m_1	$2.5\rho_1/m_1$	$\frac{2.5\rho_1/m_1}{100\sum\rho_i/m_i}$	
2.5	T_{B_1}					$\frac{2.5}{100}\frac{\rho_1/m_1}{\sum\rho_i/m_i}$
		ρ_2	m_2	$2.5\rho_2/m_2$	$\frac{2.5\rho_2/m_2}{100\sum\rho_i/m_i}$	
5.0	T_{B_2}					$\frac{2.5}{100}\frac{(\rho_1/m_1+\rho_2/m_2)}{\sum\rho_i/m_i}$
		ρ_3	m_3	$2.5\rho_3/m_3$	$\frac{2.5\rho_3/m_3}{100\sum\rho_i/m_i}$	
7.5	T_{B_3}					$\frac{2.5}{100}\frac{(\rho_1/m_1+\ldots.)}{\sum\rho_i/m_i}$
.	.	ρ_4	m_4	$2.5\rho_4/m_4$	. . .	
.	.			.	.	. . . .
.	.	.		.	.	
.	.	.		.	.	.
.	.	.		.	.	.
.	.	ρ_{40}	m_{40}	$2.5\rho_{40}/m_{40}$	$\frac{2.5\rho_{40}/m_{40}}{100\sum\rho_i/m_i}$	
100	$T_{B_{40}}$					100
				$100\sum_{1}^{40}\rho_i/m_i$	100	

Columns (1), (2), (3), and (4) are results of the experimental measurements, and plot of (2) versus (7) gives T.B.P. mole percent distillation curve. All the T.B.P. readings were done at equal volumetric intervals, and the M. Wt's were measured with a constant volumetric ratio of 1/100, then the following simplification can be applied for the conversion of T.B.P. curves.

The molecular weight of each cut of a petroleum fraction can be calculated from equation (52),

$$m_i = k_f' \left(\frac{\rho}{\Delta T_f}\right)_i \qquad (52a)$$

To convert volume quantity to mole quantity,

$$\left(\frac{v\rho}{m}\right)_i = \left[\frac{v\rho}{k_f'(\rho/\Delta T_f)}\right]_i = \left(\frac{v}{k_f'}\right)(\Delta T_f)_i \qquad (59)$$

where v is volume percent T.B.P. cut, and $\frac{v}{k_f'}$ is the same for all volume fractions. Thus, the general T.B.P. conversion formula is,

$$\frac{(v\rho)_i/k_f' \left(\frac{\rho}{\Delta T_f}\right)_i}{\sum_{i=1}^{i=n} \left[(v\rho)_i/k_f' \left(\frac{\rho}{\Delta T_f}\right)_i\right]} = \frac{(\Delta T_f)_i}{\sum_{i=1}^{i=n} (\Delta T_f)_i} \qquad (60)$$

So, the previous table can be reduced to the following form:

Volume% off (1)	T.B.P. Temp. (2)	Ave. ΔT_f of each cut (3)	Mole Fraction (4)	Mole % off. (5)
0	T_{B_0}			0
		$(\Delta T_f)_1$	$(\Delta T_f)_1/\sum(\Delta T_f)_i$	
2.5	T_{B_1}			$100\frac{(\Delta T_f)_1}{\sum(\Delta T_f)_i}$
		$(\Delta T_f)_2$	$(\Delta T_f)_2/\sum(\Delta T_f)_i$	
5.0	T_{B_2}			$100\frac{(\Delta T_f)_1+(\Delta T_f)_2}{\sum(\Delta T_f)_i}$
		$(\Delta T_f)_3$	$(\Delta T_f)_3/\sum(\Delta T_f)_i$	
7.5	T_{B_3}			$100\frac{(\Delta T_f)_1+(\Delta T_f)_2+(\Delta T_f)_3}{\sum(\Delta T_f)_i}$
⋮	⋮	⋮	⋮	⋮

⋮	⋮	⋮	⋮	⋮	
100	T_B	$\frac{(\Delta T_f)_{40}}{\sum_{1}^{40}(\Delta T_f)_i}$	$(\Delta T_f)_{40}/\sum(\Delta T_f)_i$		100

The advantages of this technique are,

1. No need for density measurement of each cut
2. No need for calculation of average molecular weight of each cut
3. Ease of computation
4. $(\Delta T_f)_i$, can be obtained from the general equation or the plot (Chapter V) with a minimum of experimentation.

The T.B.P. distillation curves on the mole percent basis for both vapor and liquid equilibrium phases were plotted on large graph papers for obtaining the proper slopes.

K-Value Calculation From T.B.P. Temperatures vs. Volume Percent Curves: Assuming an equilibrium flash vaporization of a known mixture at some T_e and P_e to produce volumetric phase ratio $\frac{V}{L}$, then the K-value for each individual component would be

$$K_i = \frac{\dfrac{\Delta V_i \rho_i/m_i}{\sum \Delta V_i \rho_i/m_i}}{\dfrac{\Delta L_i \rho_i/m'_i}{\sum \Delta L_i \rho'_i/m'_i}} \qquad (61)$$

Where: ΔV_i is the volume of the ith component in the vapor phase;

ρ_i, m_i are the respective density and molecular weight

ΔL_i is the volume of the ith component in the liquid phase;

ρ'_i, m'_i are the respective density and molecular weight

Equation (61) can be rearranged to,

$$K_i = \frac{\left(\frac{\Delta V_i}{V}\right)\frac{\rho_i/m_i}{\rho/m}}{\left(\frac{\Delta L_i}{L}\right)\frac{\rho'_i/m'_i}{\rho'/m'}} = \frac{\Delta v_i\left(\frac{\rho_i/m_i}{\rho/m}\right)}{\Delta l_i\left(\frac{\rho'_i/m'_i}{\rho'/m'}\right)} \qquad (62)$$

where: Δv_i is the volume fraction of the ith component in the vapor phase;

ρ, m are the average properties of that phase

Δl_i is the volume fraction of the ith component in the liquid phase;

ρ', m' are the average properties of that phase

But $m'_i = m_i, \rho'_i = \rho_i$; and using equation (52a), then

$$K_i = \frac{\Delta v_i}{\Delta l_i}\left(\frac{\Delta T_f'}{\Delta T_f}\right)_P \qquad (63)$$

where: $\Delta T_f, \Delta T_f'$ are the freezing point depression of the equilibrium vapor and liquid phases respectively, and are proportional to the corresponding molal volumes.

When the number of components increases to infinity, then equation (63) would be,

$$K_i = \left(\frac{dv}{dl}\right)_{T_{B_i}}\left(\frac{\Delta T_f'}{\Delta T_f}\right)_P \qquad (64)$$

Thus

$$K_i = \left(\frac{dv/dT_B}{dl/dT_B}\right)_{T_{B_i}}\left(\frac{\Delta T_f'}{\Delta T_f}\right)_P \qquad (65)$$

Where: dT_B/dv, dT_B/dl are the slopes of the volumetric T.B.P. curves of equilibrium vapor and liquid phases respectively.

Figures (62,63,64) show the comparison between the K-value curves calculated by equation (65), and the previous method. Some of the advantages of this method are:

1. No need for measurement of density and molecular weight of each cut.
2. Ease of calculation
3. Temperature-volume recorder chart can be used directly.

Other Techniques: Edmister(34) suggests that appropriate horizontal lines be drawn on the graph of molar T.B.P. curves of equilibrium phases, and the ratio of the corresponding mole percent of phases be taken as the average K-value for that cut. If the T.B.P. curves consist of plateaux, then the horizontal should be placed about halfway between each two succeeding ones. Evidently, the method presents a sound technique for the cases where T.B.P. curves have plateaux. For smooth T.B.P. curves, this method is basically the same as those presented here, and at the limit they are identical. Figure (63) shows the K-values obtained by this method with small temperature increments of 2.5 °C, and those obtained by the use of equation (58).

White and Brown (152) calculated K-values for pentanes, hexanes, heptanes, and a few higher boiling cuts, with an average boiling range of 50 °F. As it has been stated in Chapter II, the method failed in the case of light hydrocarbons - furnace oil mixture, while it produced consistent results for light naphtha. Pentanes, hexanes, and heptanes made up the major portion of the feed, and the heavier hydrocarbons constituted the rest. The results were presented as a straight line, with log K and average boiling temperature as the coordinates. The K-values calculated from White and Brown's experimental data by the use of equation (58) are compared with their K-values in figure (47). Evidently

White and Brown's technique has the following disadvantages:

1. More experimental and calculational work is required
2. It is highly dependent on the accuracy of molecular weight and density measurements
3. The technique may fail when one cut or more contains a large percent of the total quantity
4. The K-values are the average values for the cuts, rather than the instantaneous quantities; and therefore are less theoretically sound
5. A very limited number of experimental K-values can be obtained
6. The presentation of results in graphical form, because of the above limitations and the spread of points, is quite difficult.

Measurement of Slopes: In general the errors of differentiation of a function from tabulation of experimental or calculated values, are exaggerated, whereas integration improves them. Differentiation is concerned with a limit process carried out on the quantity $\left[f(T+\triangle T)-f(T)\right] / \triangle T$, and as the magnitude of $\triangle T$ gets smaller, the uncertainty in the result gets greater. Experimental data may be differentiated analytically, numerically or graphically, and some of the techniques are briefly indicated here.

The experimental T.B.P. data can be represented by an equation (polynominal) fit to the data points by a suitable computer, and then differentiated. In general the curve fitting of T.B.P. data is a complex operation, and yet this method may not have any added accuracy.

The differentiation by numerical method (113,153) is often very time consuming, and not desirable for this type of work.

The graphical differentiation of this type of experimental data is usually more satisfactory, if the applied technique is sufficiently sound. Evans (39), and Lipka (82) describe mechanical devices for performing differentiation with a good degree of accuracy. Evans' seems to be more exact, while Lipka's gives a continuous curve.

One of the reliable graphical method is by connecting the equal-distance near-by points P_1, P_2 · · · etc. on both sides of (x, T) and as P approaches T, the slopes $\frac{\Delta_1 x}{\Delta_1 T}, \frac{\Delta_2 x}{\Delta_2 T}$ · · · etc. may then be plotted as a function of ΔT. The value of $(\frac{\Delta x}{\Delta T})_{\Delta T \to 0}$ obtained from $\frac{\Delta x}{\Delta T} = f(\Delta T)$ is equal to $(\frac{dx}{dT})_T$. This method is very reliable but rather time consuming. Figure (64) shows the close comparison between the K-values calculated by this technique and the following one.

Graphical Differentiation: A small flat mirror was mounted on wood in such a way that it can be placed on the graph paper with its surface precisely perpendicular to the paper and extend right down to it (Figure 44). The instrument was set so as to intersect the curve at the point at which the slope was desired. The mirror was then rotated around the point until there appeared no discontinuity in the direction between the curve and its immage in the mirror. At this condition the mirror is perpendicular to the curve at the point. The slopes were then determined directly from the intersection of the plane of mirror with the grid lines of the graph paper. The slope of each point was checked from both sides of the curve, by just turning the face of the mirror 180 degrees. In this fashion slopes of T.B.P. curves were measured at every 5° or 10 °C intervals. With great care and experience these settings were made with an accuracy higher than that to which the curves could be drawn. Trial tests of this technique with relatively large circles indicated that with this simple device an experienced operator can measure slopes with deviation of about two parts per one hundred. Throughout the work this technique has been applied for differentiating of T.B.P. curves.

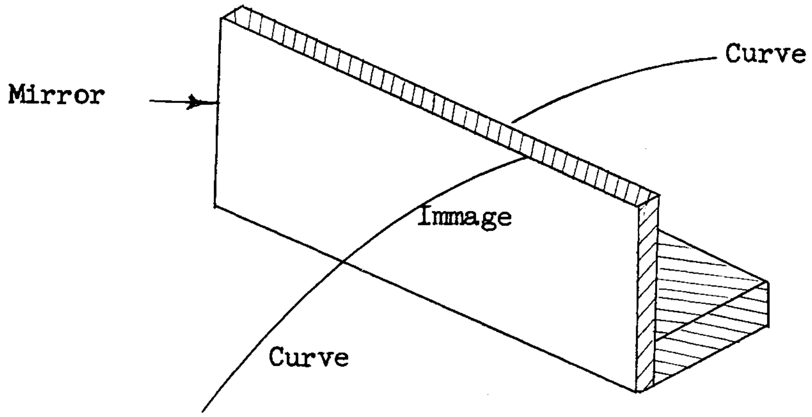


Figure 44. Mirror Differentiator

The values of $\frac{dy}{dT_B}$, $\frac{dx}{dT_B}$ or $\frac{dv}{dT_B}$, $\frac{dl}{dT_B}$, so obtained were plotted as functions of their corresponding T.B.P. distillation temperature (T_B). In the case of all normal petroleum fractions, the plot gradually increases to a maximum and then decreases. The curves $\frac{dy}{dT_B} = f(T_B)$, $\frac{dx}{dT_B} = f'(T_B)$ of vapor and liquid phases in equilibrium with each other intersect at only one point, and that temperature should be the same as the equilibrium temperature. These curves can serve to smooth the values of measured T.B.P. slopes, and therefore improve the consistency of K-values.

Presentation of K-values: With a few exceptions, equations (58) or (65) or both were used for calculation of K-values throughout this work. Because of the existance of many accumulated experimental and calculational discrepancies, the results are somewhat scattered. Therefore, the smoothing of data is desirable. Moreover, the result would be more useful, if correlated in the form of equations as well as charts. Equations serve as a satisfactory means for interpolation and extrapolation of the experimental data, which is often necessary.

Although the empirical presentation of experimental information is often unreliable, a semi-empirical correlation is most suitable for the present problem of petroleum fractions. The problem is to present the K-values of each component as a function of equilibrium temperature, and the normal boiling temperature (here equilibrium pressure is not a factor, since all measurements were made at atmospheric pressure).

In order to achieve the above objective, it is necessary to start from the basic equations. For low pressures and ideal solutions, the K-value of each component can be found as the ratio of its vapor pressure p_i and the equilibrium pressure P. Therefore,

$$(K_i)_{Raoult} = \frac{p_i}{P} \tag{66}$$

From the integration of the Clausius-Clapeyron equation $\left(\frac{dp_i}{dT} = \frac{\triangle H_i}{TV_i}\right)$, the vapor pressure of any substance can be related to the saturation temperature as follows:

$$\log p_i = Ai - \frac{Bi}{T} \tag{67}$$

Where A and B are constants, and T is the absolute saturation temperature. It is evident from the assumptions made in deducting the above equation from the Clausius-Clapeyron equation, that (67) would be limited to short temperature intervals at low pressures.

Contrary to expectations, the experimental data show that the equation is applicable to a much wider range of pressure and temperature. Equation (67) can better be adapted to the real conditions as follows:

$$\log p_i = Ai - \frac{Bi}{T + C} \tag{68}$$

Where C is a constant with small variations for all hydrocarbons. By combining equations (66) and (67),

$$Ki = ai\ 10^{\frac{bi}{Te}} \tag{69}$$

Equation (69) suggests, that the vapor-liquid equilibrium constant of each component of a mixture can be expressed by log K as a function of $\frac{1}{Te}$.

Also, an attempt should be made for correlating Ai and Bi as some functions of normal boiling temperature, T_{B_i}, of all the components of the mixture. Figures (45,46) show the plot of Ai and Bi of equation (68) as functions of T_B for various groups of hydrocarbons. These values are taken from the A.P.I. tables (5). As can be judged from the graphs, B can be successfully presented as a direct function of the normal boiling temperature. A can be approximately expressed as a direct function of the normal boiling point up to moderate temperature ranges, or in form of some exponential function for higher temperature ranges.

Thus

$$B = B_o + S_B T_B \tag{70}$$

$$A = A_o + S_A T_B \tag{71}$$

or

$$A = A_o + A_1 T_B + A_2 T_B^2 + \cdot \cdot \cdot \tag{72}$$

Combining equations (66), (67), (70), and (71), the following general equation would result.

$$K = (\frac{1}{P})\ 10^{(A_o + S_A T_B - \frac{B_o + S_B T_B}{Te})} \tag{73}$$

Using equation (73) for a more general case, then

$$K = (\frac{1}{P})\ 10^{(A_o + A_1 T_B + A_2 T_B^2 + \cdot \cdot \cdot \cdot - \frac{B_o + S_B T_B}{Te})} \tag{74}$$

Equation (74) can be written in a more useful form as follow,

$$\log(PK) = A_o + S_A T_B - \frac{B_o}{Te} - \frac{S_B}{Te} T_B \tag{75}$$

For a constant equilibrium temperature T_e, equation (75) can be simplified to,

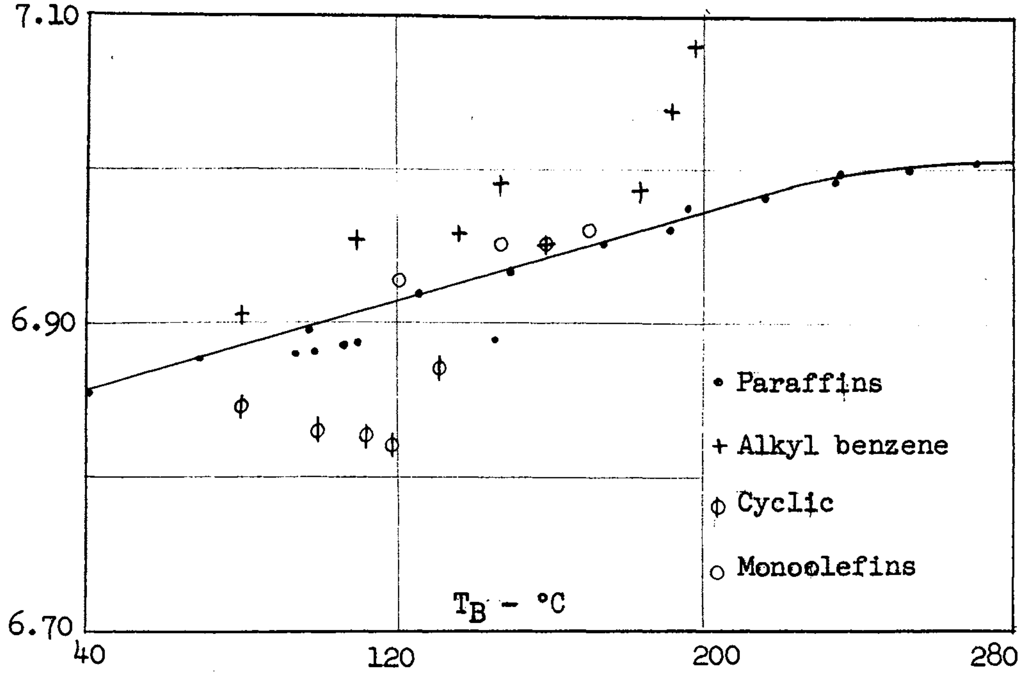


Figure 45 - Constant of Equation (68)

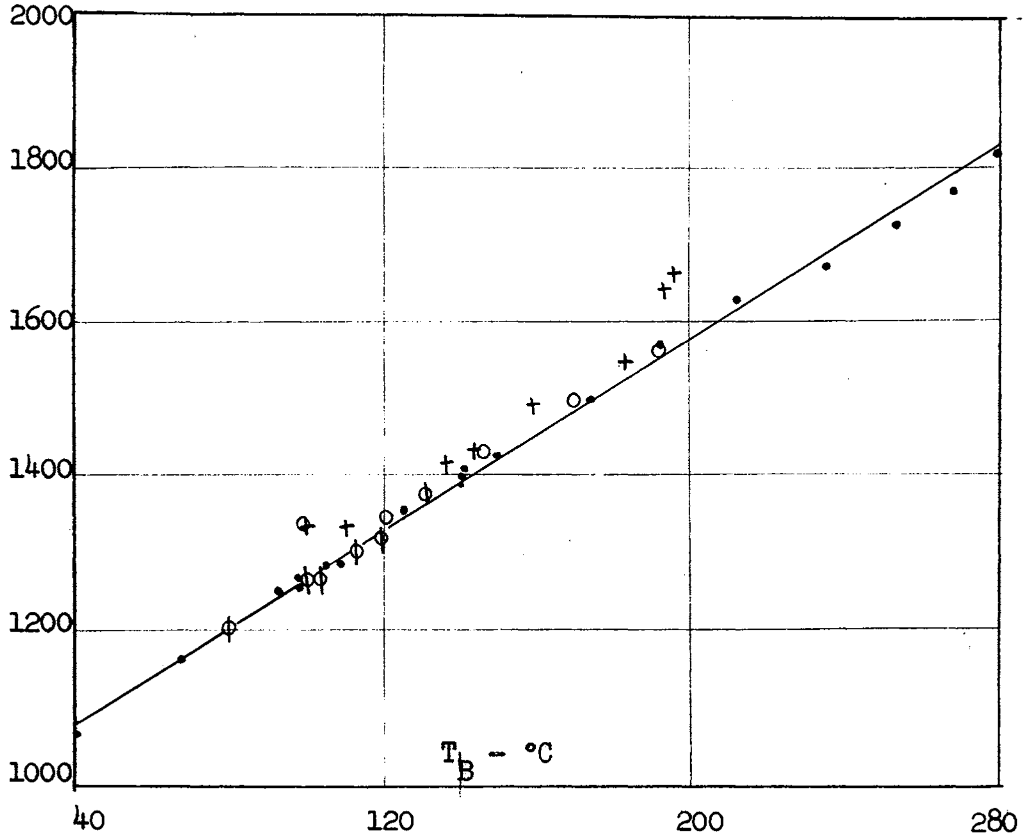


Figure 46 - Constant of Equation (68)

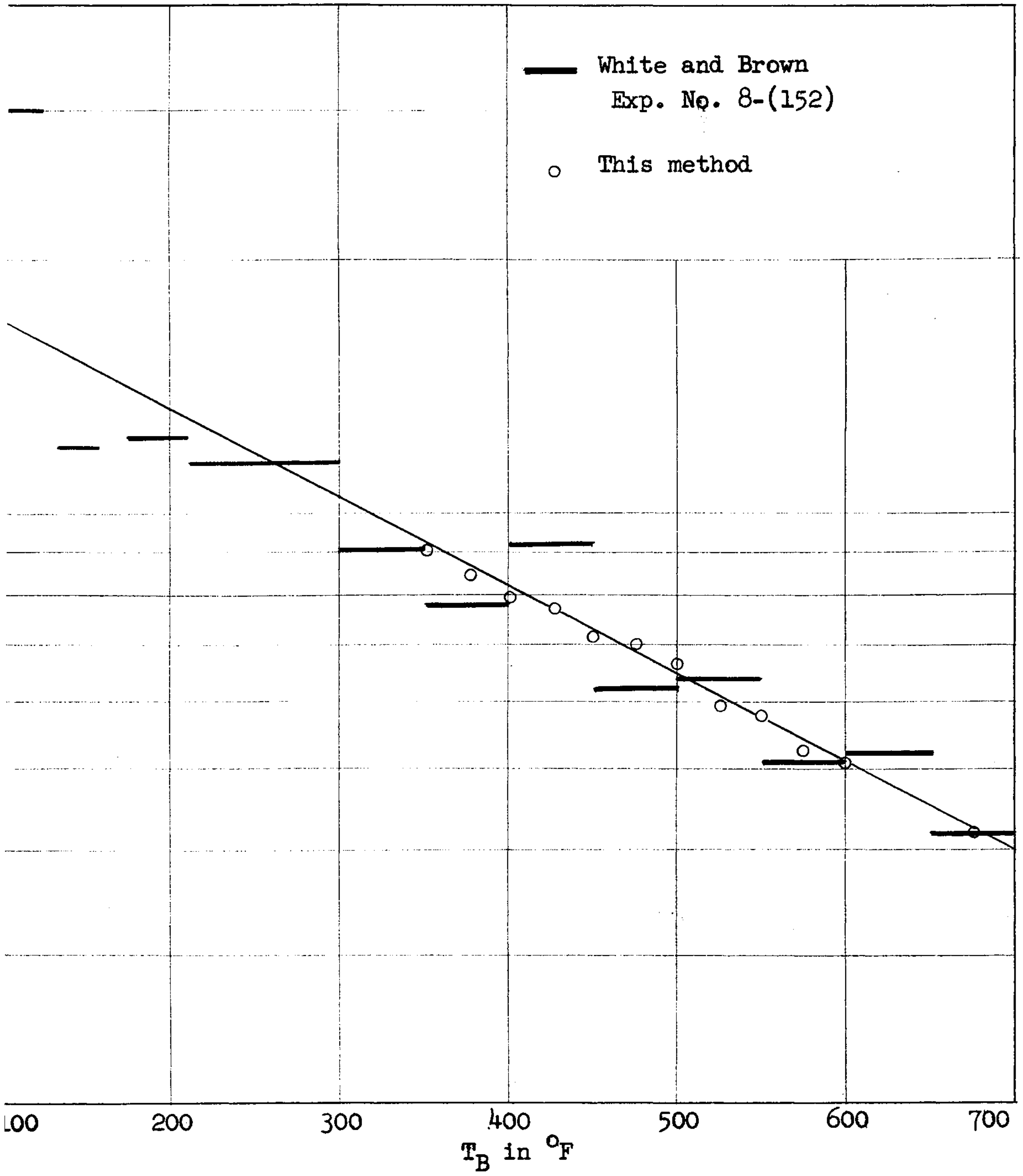


Figure 47 - K-Values calculated From Experimental Work of White and Brown

$$\log (PK) = (A_o - \frac{B_o}{T_e}) - (\frac{S_B}{T_e} - S_A)\ T_B \qquad (76)$$

or
$$\log K_{T_e}^{P_e} = C_1 - C_2\ T_B \qquad (76)$$

Equation (77) suggests that, for any fixed condition of equilibrium. $\log K$ of all the components of a mixture can be expressed as a direct function of the normal boiling temperature. For computer utility equation (77) can be expressed as follows:

$$\log K_{T_e}^{P_e} = C_5 + C_6\ T_B + C_7\ T_B^2 + C_8\ T_B^3 + \cdot\ \cdot\ \cdot \qquad (77a)$$

From equation (75a), the K-value of any component of the mixture represented by its normal boiling temperature T_{B_i}, can be expressed as a function of the absolute equilibrium temperature T_e. Thus,

$$\log(PK)_i = (A_{o_i} + S_{A_i} T_{B_i}) - (B_{o_i} + S_{B_i} T_{B_i}) \frac{1}{T_e} \qquad (75a)$$

or

$$\log(K^{P_e})_i = C_3 - \frac{C_4}{T_e} \qquad (78)$$

where C's are constants.

Equations (77) and (78) were satisfactorily used for the analysis and the presentation of the experimental results. Figures (48) through (71) show the physical properties curve, the equilibrium T.B.P. curves, and the K-values plots for some of the petroleum fractions tested in this work.

Experimental K-Values: The first set of curves belong to oil A, which its physical properties are presented by appropriate plots. The recirculating still was used to prepare the equilibrium phases at atmospheric pressure in this case.

The K-values calculated from the experimental results (by the use of equation 58), are presented as plots of log K versus T.B.P. temperature for each equilibrium temperature T_e. The plots indicate that the experimental results can well be expressed by equation (77). The graphs also show that the deviations of the points over the T.B.P. temperature range of 70^{o} to 180 ^{o}C are very meager. A small equilibrium temperature change of 2.5 ^{o}C has caused a definite variation in K-values. This clearly indicates that for such a low boiling petroleum fraction, the presented method for K-values calculation is very sensitive to small equilibrium temperature variations.

Log K for various T.B.P. temperatures are plotted as the functions of $\frac{1}{T_e}$ in figure (53). This plot shows a good agreement between the experimental data and equation (78). Finally the extrapolated and the interpolated values of log K as the functions of T.B.P. temperature are given in figure (54). These curves are obtained by cross plotting the experimental results (equations 77 and 78), and are useful for engineering applications.

The experimental K-values can best be expressed by the following equations (Figures 49, 50, 51, 52):

Oil A, P_e = 1 Atm.

$\log K = -1.038 \times 10^{-2} T_B + 1.383 \quad ; \quad T_e = 134.0\ ^{o}C$

$\log K = -1.038 \times 10^{-2} T_B + 1.463 \quad ; \quad T_e = 141.2\ ^{o}C$

$\log K = -1.038 \times 10^{-2} T_B + 1.150 \quad ; \quad T_e = 144.5\ ^{o}C$

$\log K = -1.038 \times 10^{-2} T_B + 1.517 \quad ; \quad T_e = 147.0\ ^{o}C$

where T_B is the T.B.P. temperature in ^{o}C.

The slopes of these lines changed insignificantly and capriciously (1.045×10^{-2} to 1.032×10^{-2}) over the entire range of T_e; therefore, the average value was selected as a better representative quantity. Evidently a definite trend in variation of these slopes with T_e should be expected over a much wider range of equilibrium temperature.

Oil B, which is a higher boiling cut than Oil A, was vaporized in the Othmer equilibrium still. The physical properties of this oil are also presented in graphical form (Figure 55). Figures (56,57,58) show plots of log K vs. T.B.P. temperature for this oil. The curves indicate that the experimental data well follow the trend of equation (77) over the entire boiling range. Figure (59) shows plot of log K as the function of $\frac{1}{T_e}$, which is the graphical representation of equation (78). Each line on the graph indicates a material boiling at a constant T.B.P. temperature. These lines have negative slopes, which increase with T.B.P. temperature. The experimental K-value equations for this oil are,

Oil B, P_e = 1 Atm.

$$\log K = -1.693 \times 10^{-2}\, T_B + 2.660 \quad ; \quad T_e = 162.0\ ^{\circ}\mathrm{C}$$

$$\log K = -1.625 \times 10^{-2}\, T_B + 2.608 \quad ; \quad T_e = 165.0\ ^{\circ}\mathrm{C}$$

$$\log K = -1.465 \times 10^{-2}\, T_B + 2.488 \quad ; \quad T_e = 174.5\ ^{\circ}\mathrm{C}$$

Both slope and intercept decrease with increase in T_e, and they can be related to $\frac{1}{T_e}$ as should be suspected from equation (75a).

Oil B_1, is a blend of Oil B, and has essentially the same physical properties. The experimental K-values of this oil are expressed as before. The results are rather scattered, and do not coincide with those of Oil B (Figures 60,61).

Oil B_1 ; $P_e = 1$ Atm.

$\log K = -0.880 \times 10^{-2}\, T_B + 1.425$; $T_e = 169.5\ ^{\circ}C$

$\log K = -0.560 \times 10^{-2}\, T_B + 0.783$; $T_e = 176.0\ ^{\circ}C$

These equations for no obvious experimental reasons have dubious values of slopes and intercepts. The data as it may be observed from the plots, are uniformly scattered throughout the boiling range.

Figures (39 and 62 through 71) show the physical properties and K-value curves for heavy boiling kerosenes (oils G and F), and their blend (oil F-G, 50/50 by volume). The thermostatic flow equipment was used to flash vaporize these oils at atmospheric pressure. Here the various methods of obtaining slopes of T.B.P. curves, therefore K-values such as $\frac{dy}{dT_B} / \frac{dx}{dT_B}$, $\left[\frac{\Delta y}{\Delta T_B} / \frac{\Delta x}{\Delta T_B}\right]_{\Delta T_B = 2.5'}$ $\left[\frac{\Delta y}{\Delta T_B} / \frac{\Delta x}{\Delta T_B}\right]_{\Delta T_B \to 0}$ are compared with $\left(\frac{dv}{dT_B} / \frac{dl}{dT_B}\right)(\Delta T_f' / \Delta T_f)_p$. The results indicate that the accuracy of the techniques are basically the same, with $\left(\frac{dv}{dT_B} / \frac{dl}{dT_B}\right)(\Delta T_f' / \Delta T_f)_p$ method being favored for its greater ease of application and higher consistency.

Oils G and F have basically the same characteristics, and their vapor-liquid equilibrium constants differ but little from each other. The K-values of the blend, as it should be expected, are in between those of oils G and F. The scattering of data is noticeably greater for these high boiling oils, as compared to the previous fractions. The results indicate that equations (77,78) also apply to these oils over their entire large boiling ranges. Contrary to the first case, a difference of 3.5 °C in T_e produced no noticeable changes in T.B.P. curves of equilibrium phases, therefore the K-values.

The experimental K-values of these oils can be expressed by the following equations:

Oil G, 1 Atm.

$\log K = -1.554 \times 10^{-2}\, T_B + 3.230 \quad ; \quad T_e = 218.0\ ^{\circ}C$

$\log K = -1.500 \times 10^{-2}\, T_B + 3.300 \quad ; \quad T_e = 234.0\ ^{\circ}C$

$\log K = -1.395 \times 10^{-2}\, T_B + 3.253 \quad ; \quad T_e = 244.0\ ^{\circ}C$

Oil F, 1 Atm.

$\log K = -1.550 \times 10^{-2}\, T_B + 3.340 \quad ; \quad T_e = 218.0\ ^{\circ}C$

Oil F-G, 1 Atm.

$\log K = -1.563 \times 10^{-2}\, T_B + 3.250 \quad ; \quad T_e = 218.0\ ^{\circ}C$

$\log K = -1.610 \times 10^{-2}\, T_B + 3.640 \quad ; \quad T_e = 234.0\ ^{\circ}C$

In the cases investigated, the T.B.P. boiling temperatures corresponding to $K = 1$ are less than their respective equilibrium temperatures. These temperature differences are higher (about 10 °C) for high boiling oils, and are lower (about 1 °C) for low boiling oils.

K-values of a hydroformer product (oil D) were obtained by the use of both flow equilibrium apparatus. The equilibrium phases were directly analyzed by G.L.C., and the results are presented in Chapter V and Appendix B.

K-values obtained by the methods of this chapter, although in reality somewhat differ from the original concept, but have greater engineering applications, as will be shown in the next chapter

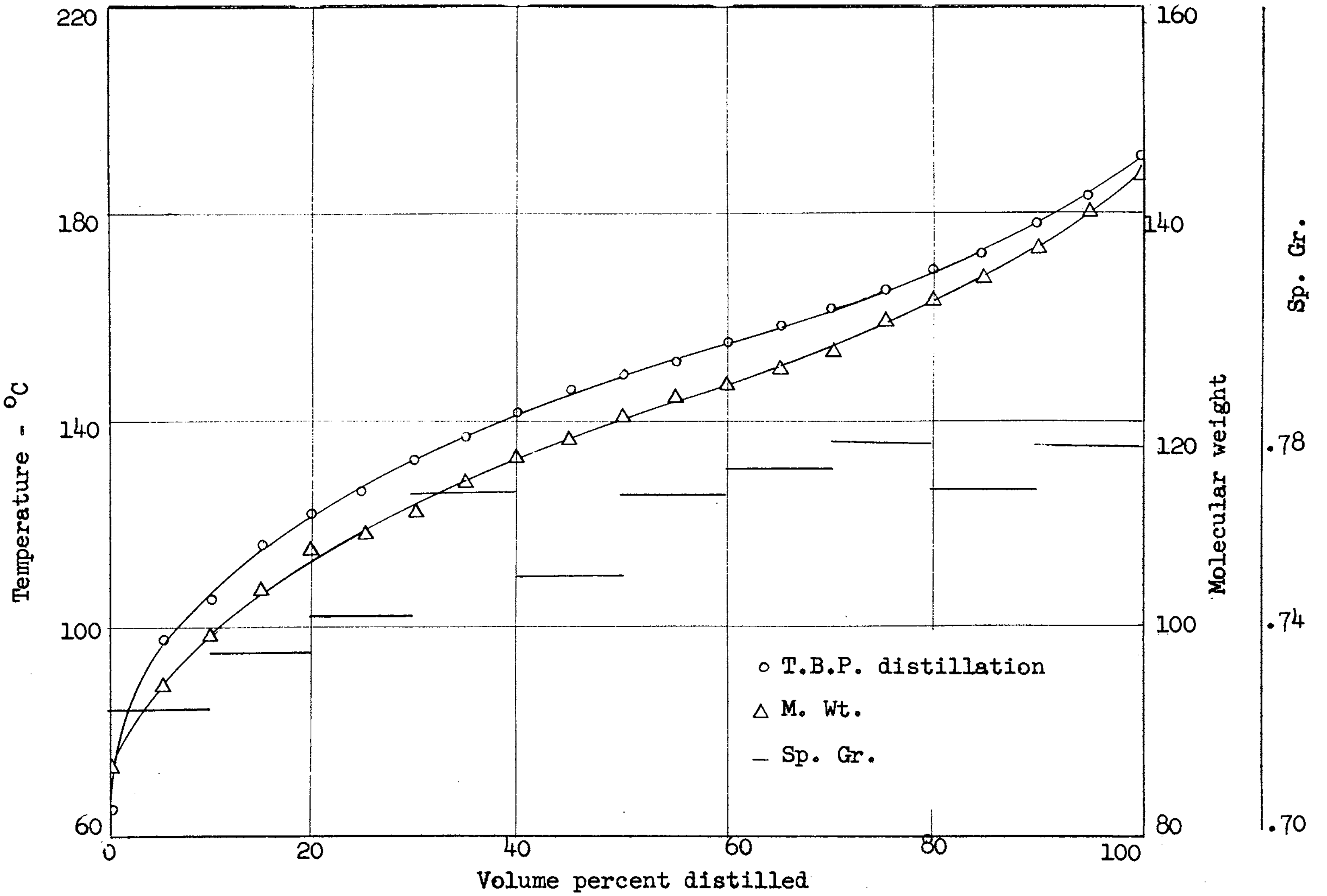


Figure 48 - Physical Properties of Oil A

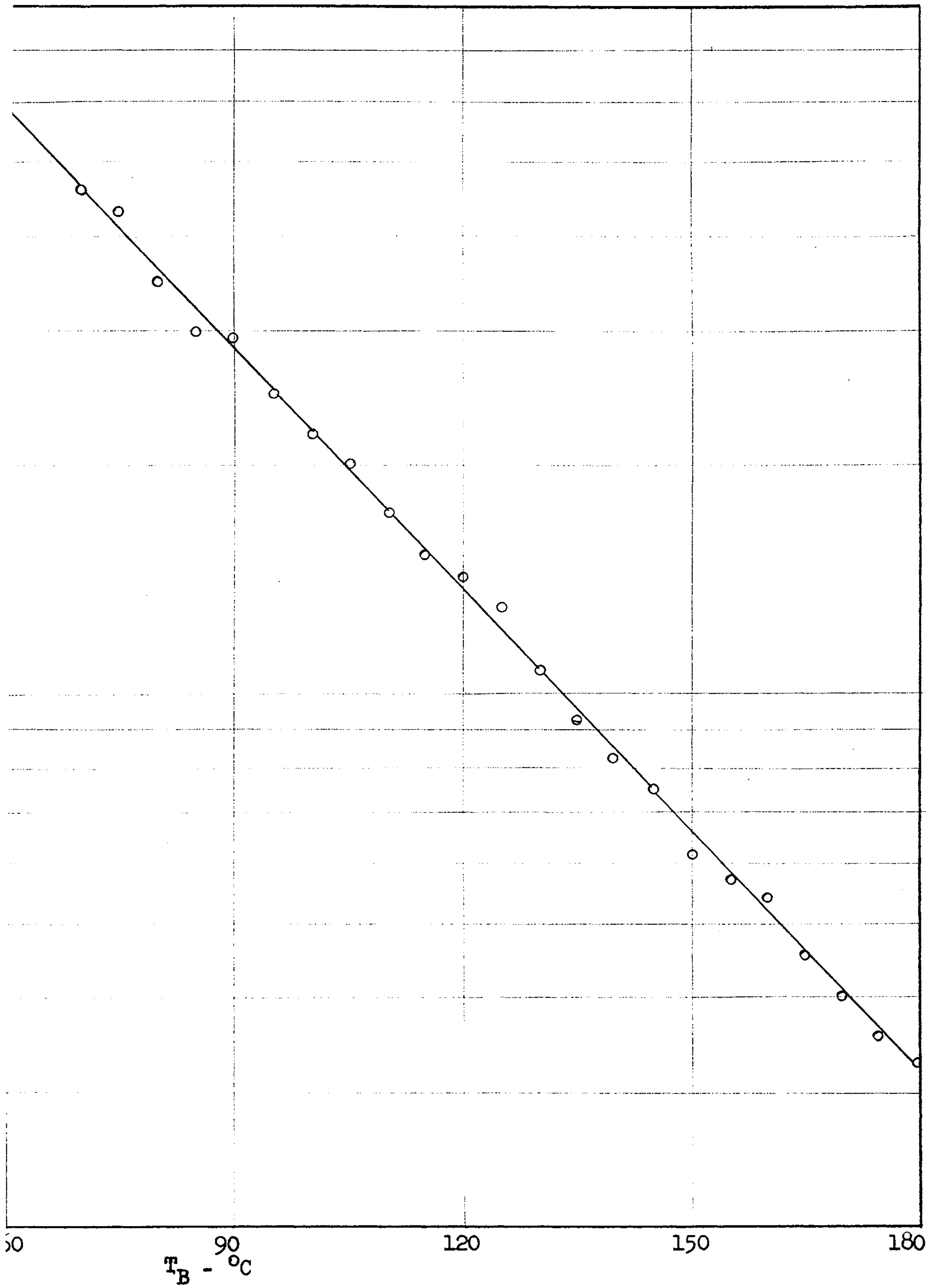


Figure 49 - Log K as the Function of T_B at T_e = 134 ^oC - Oil A

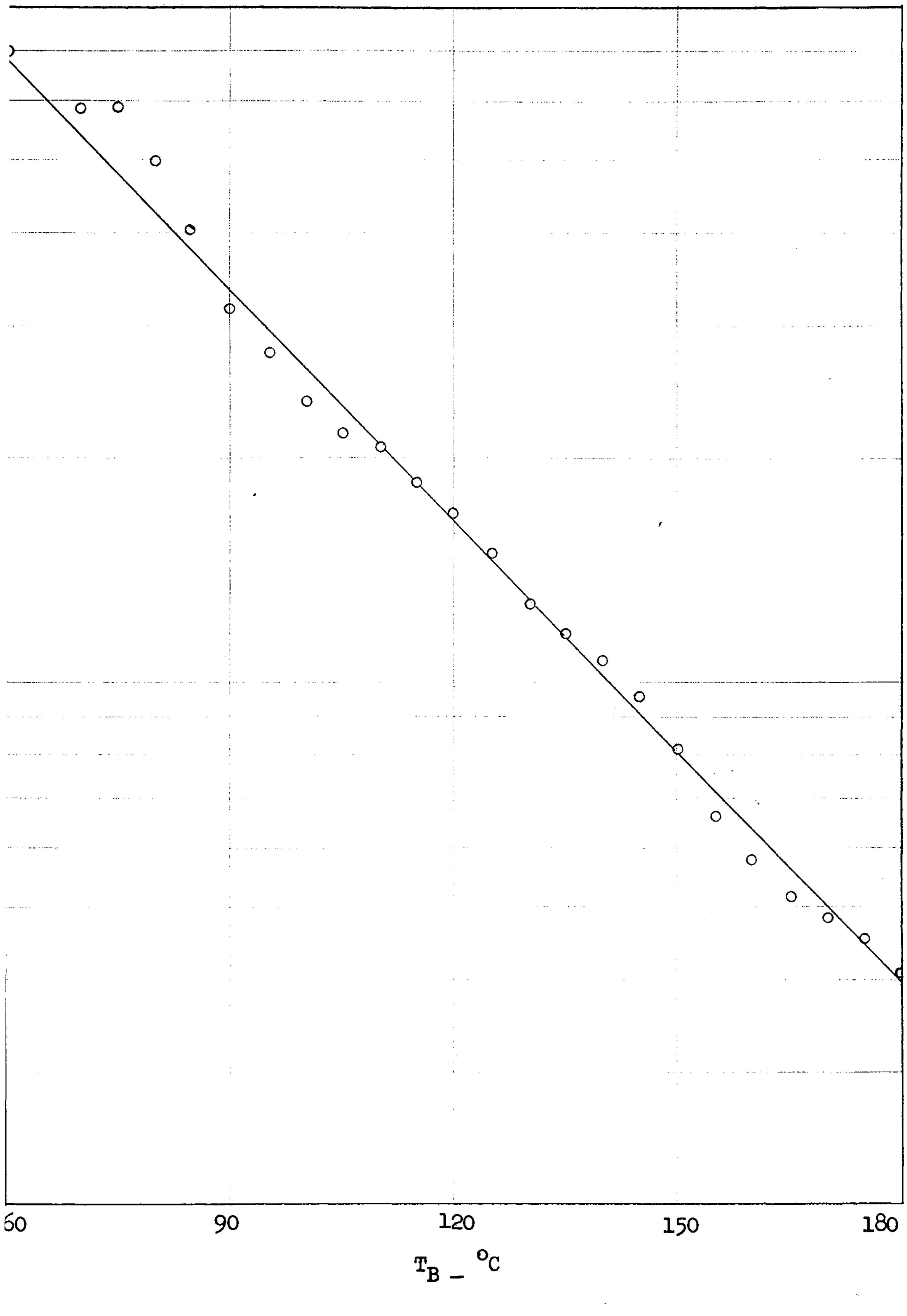


Figure 50 - Log K as the Function of T_B at T_e = 141.2 °C - Oil A

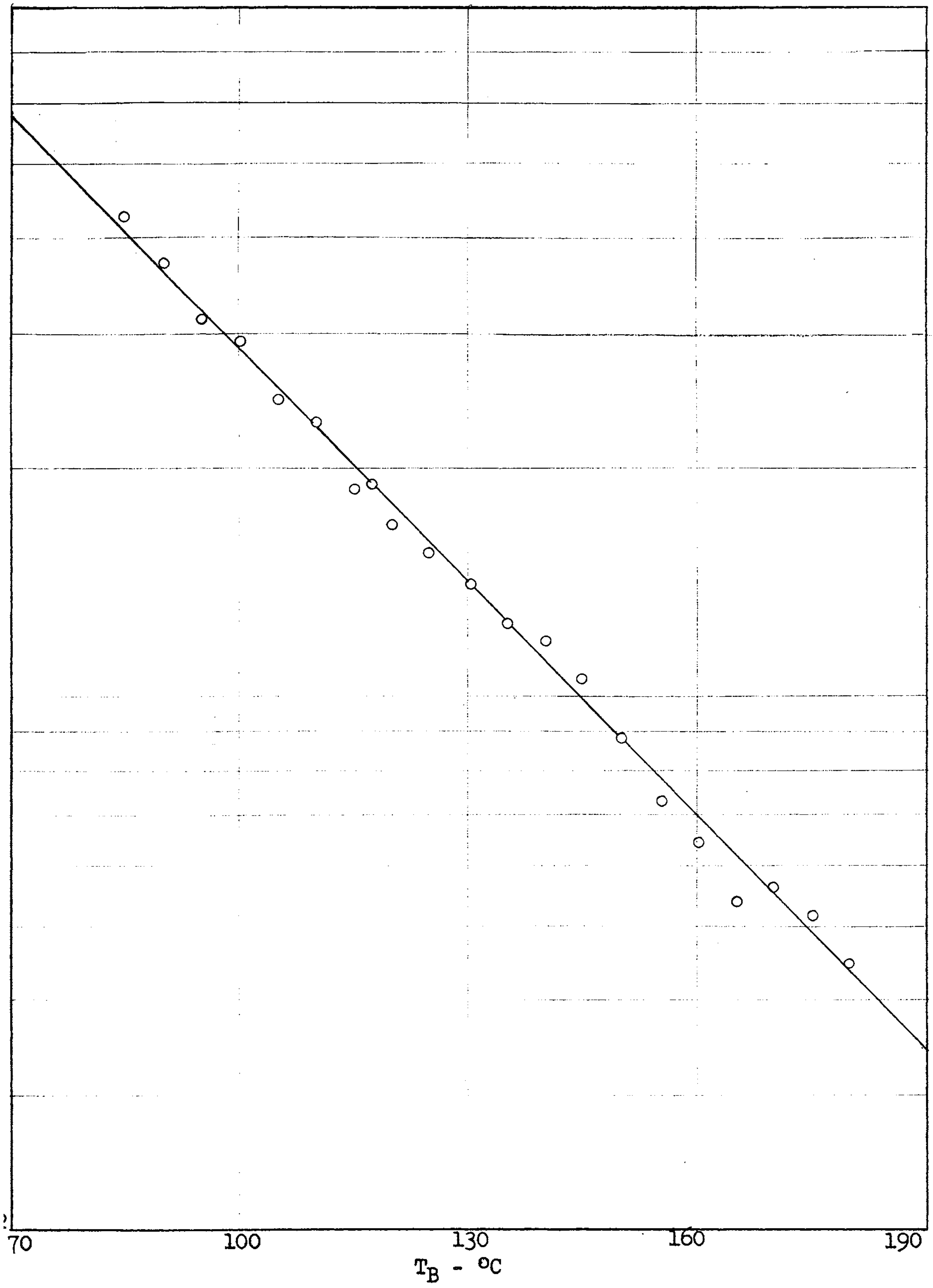


Figure 51 - Log K as the Function of T_B at T_e = 144.5 °C - Oil A

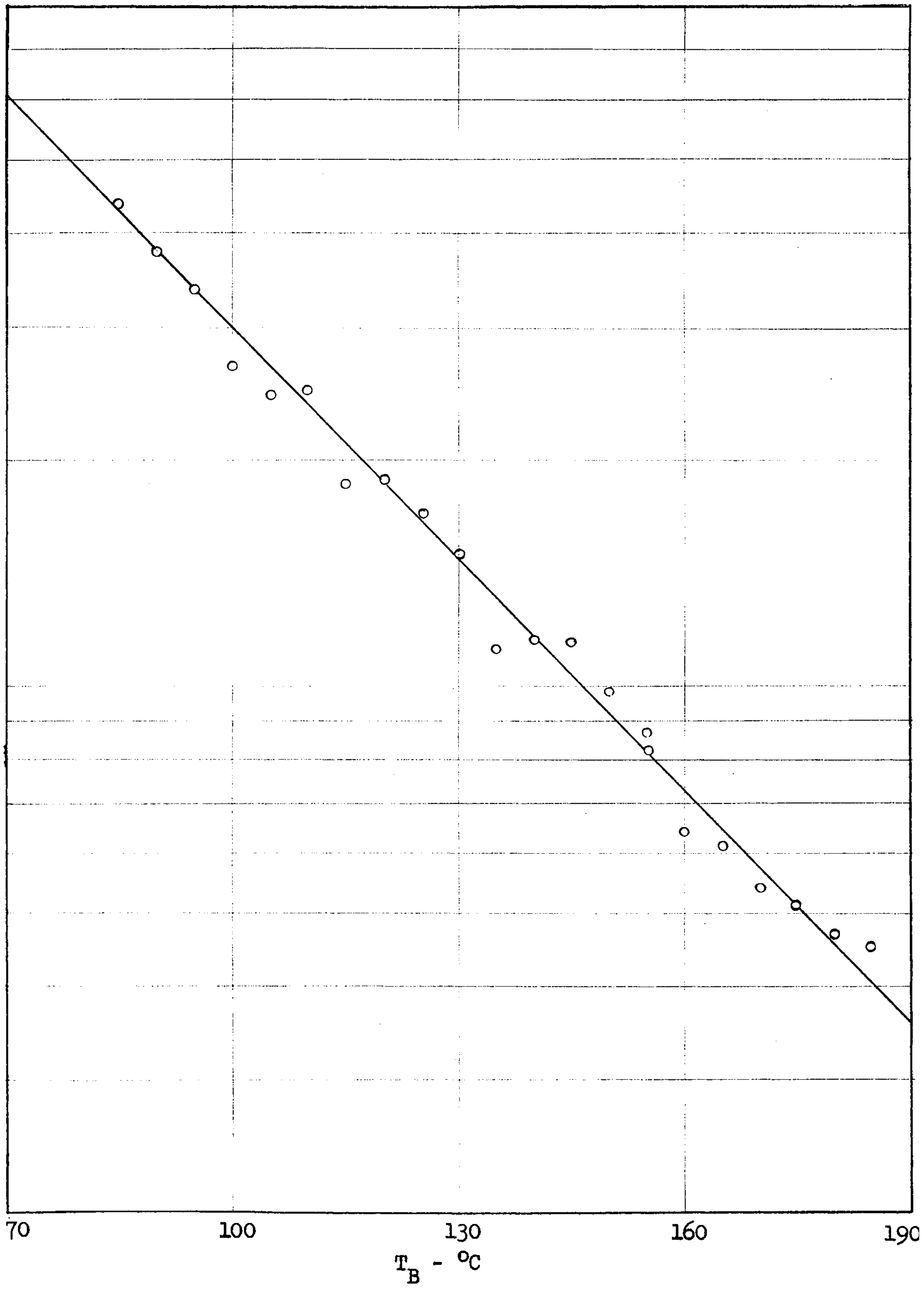


Figure 52 - Log K as the Function of T_B at T_e = 147 °C - Oil A

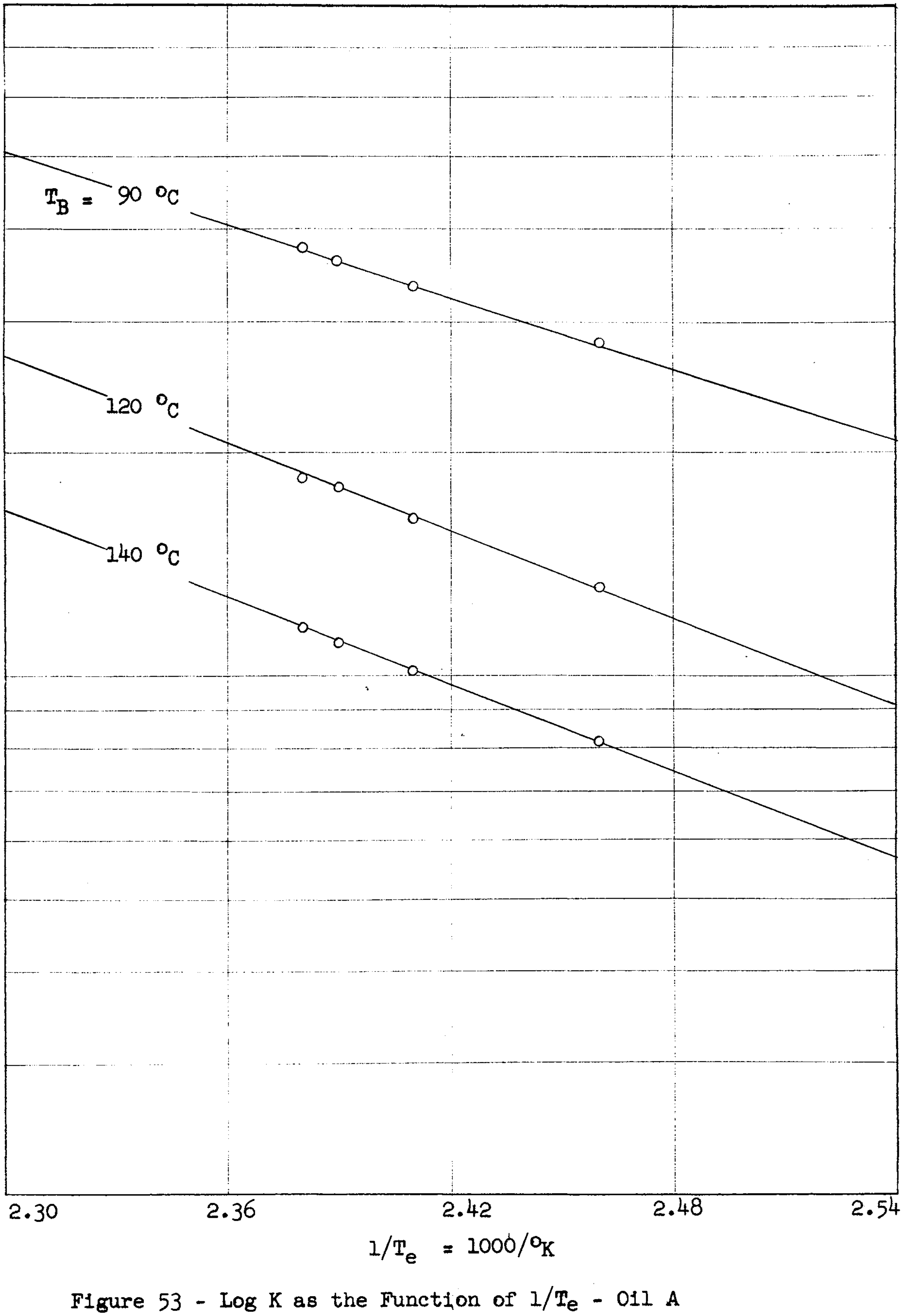


Figure 53 - Log K as the Function of 1/T_e - Oil A

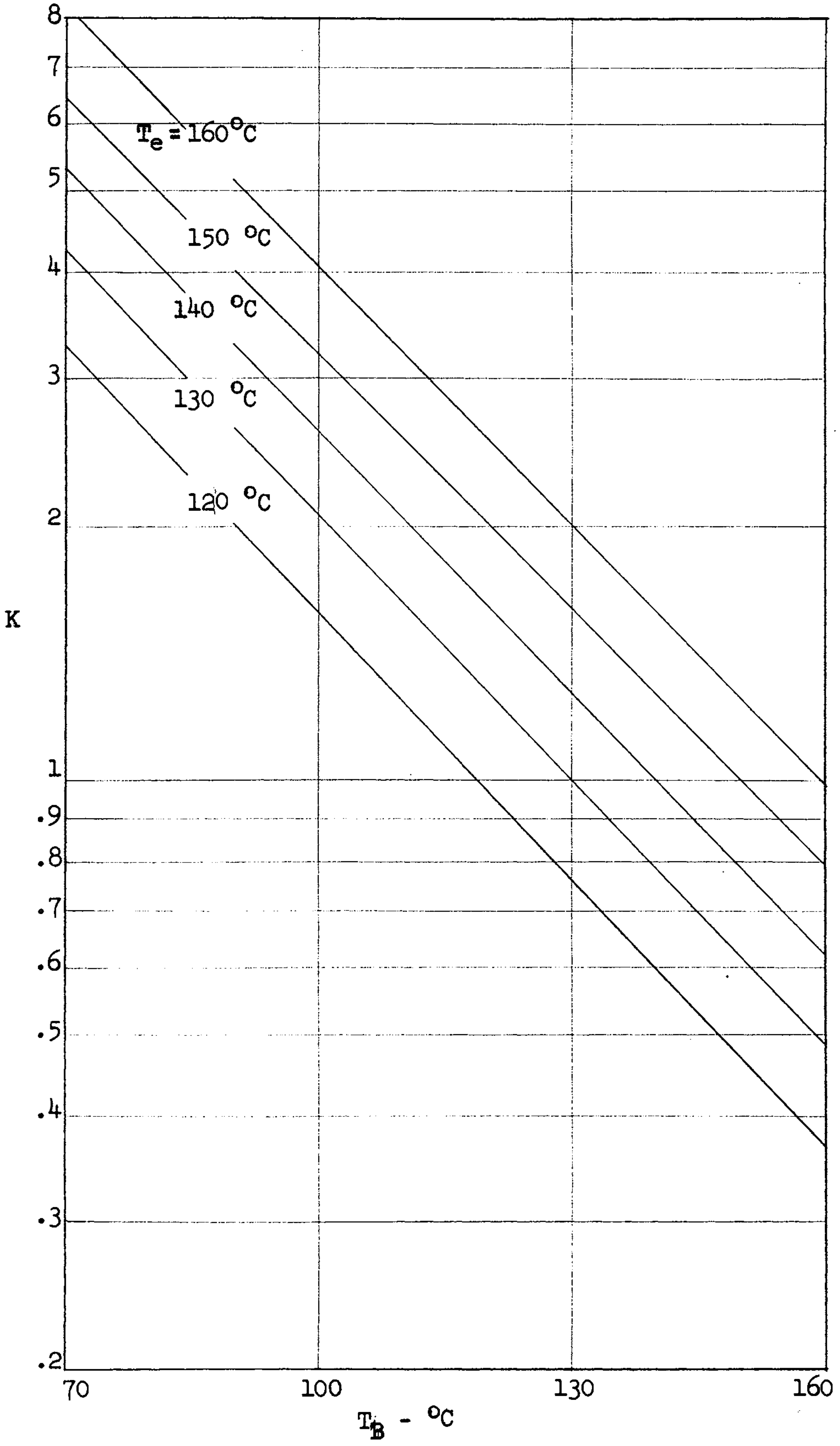


Figure 54 - Interpolated and Extrapolated K-Values as the Function of T_B - Oil A at 1 Atm.

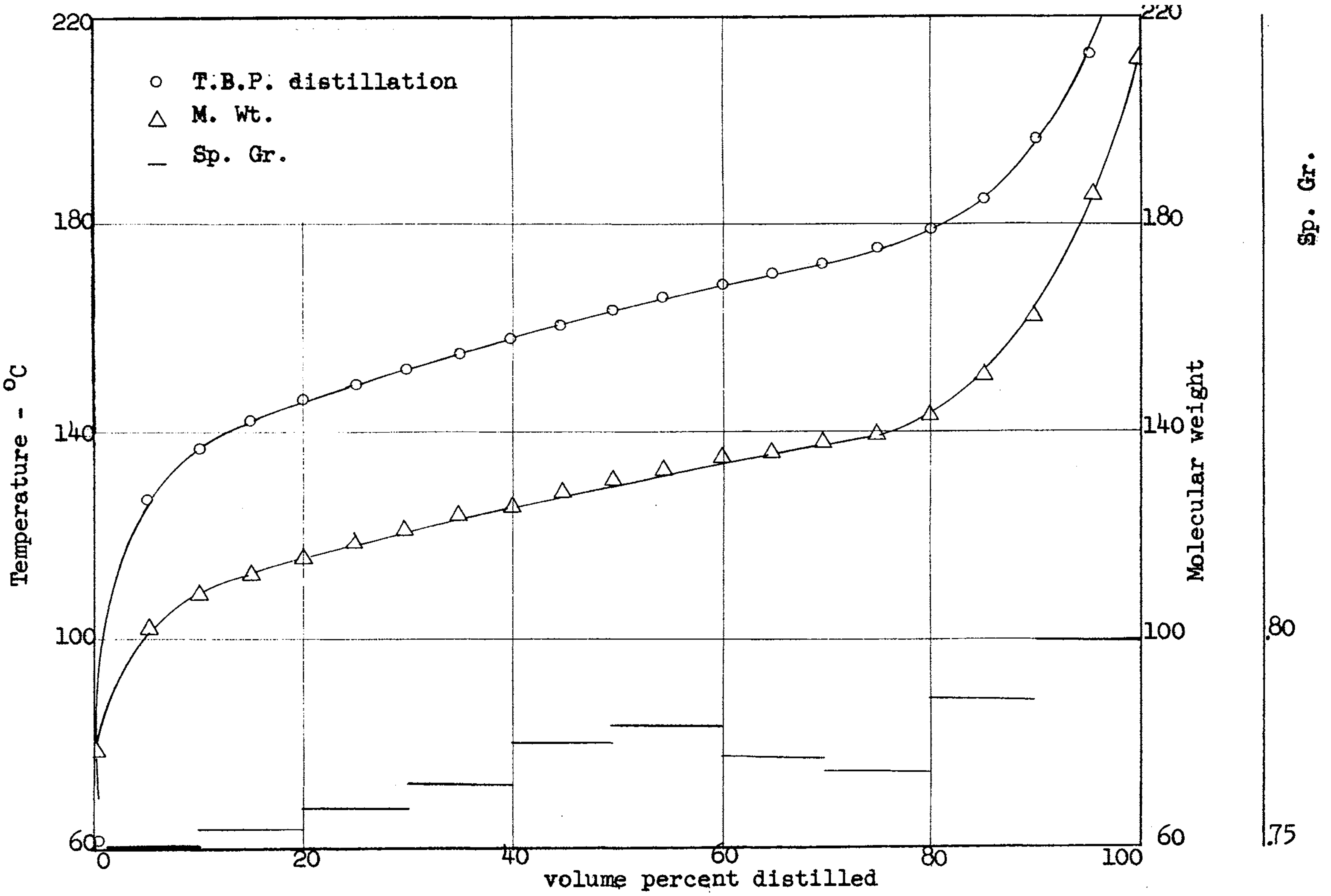


Figure 55 - Physical Properties of Oil B

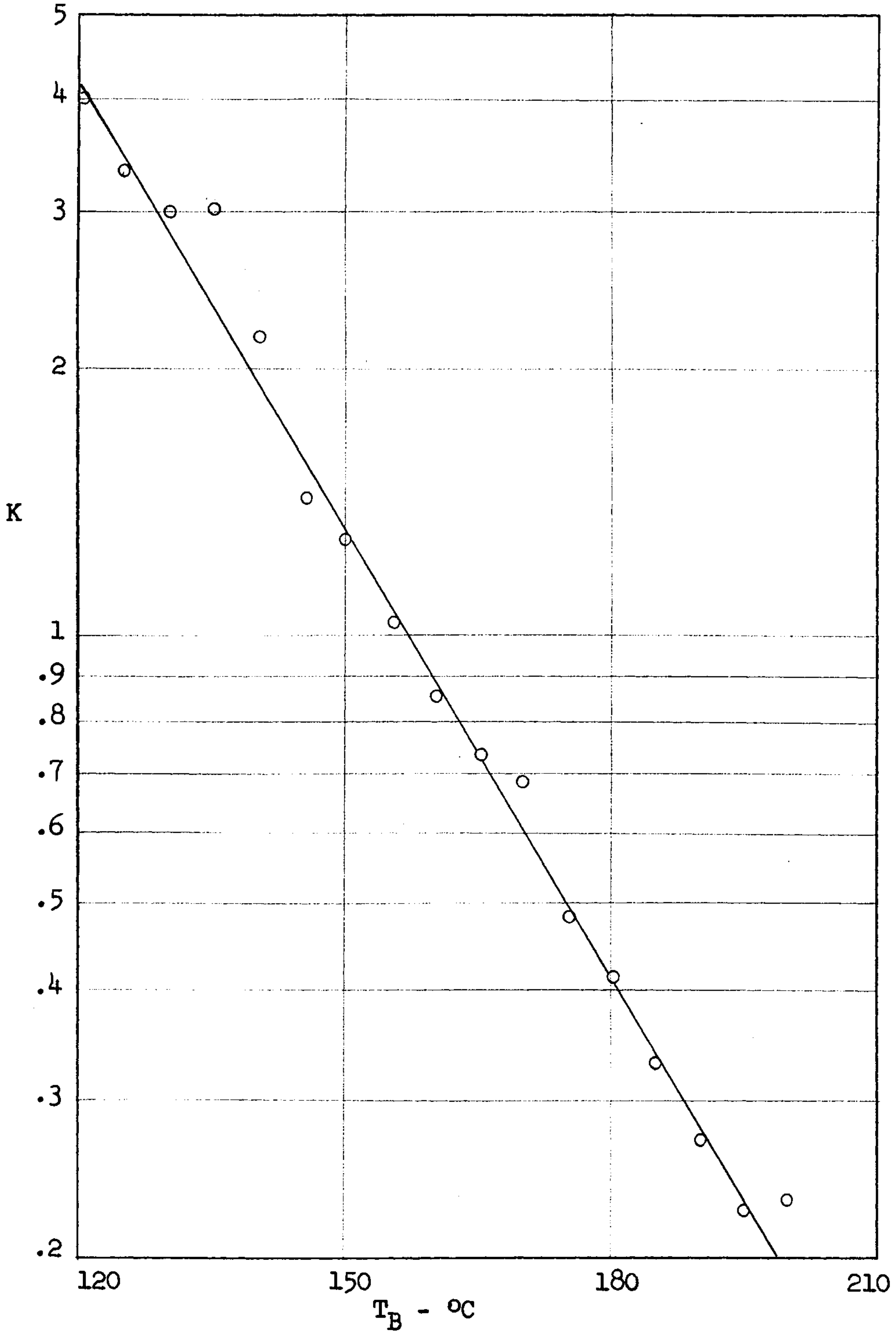


Figure 56 - Log K as the Function of T_B at T_e = 162 °C - Oil B

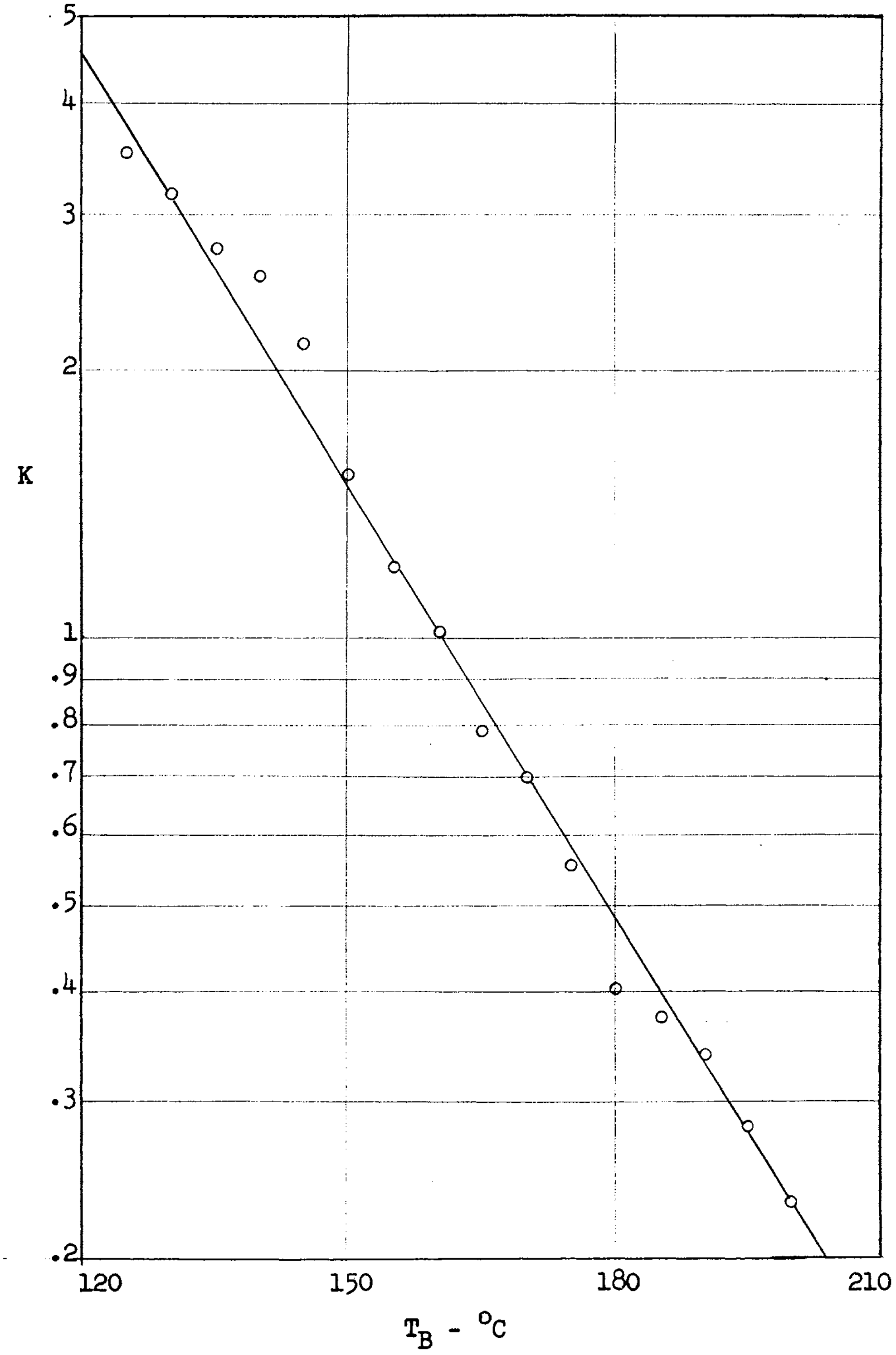


Figure 57 - Log K as the Function of T_B at T_e = 165 °C - Oil B

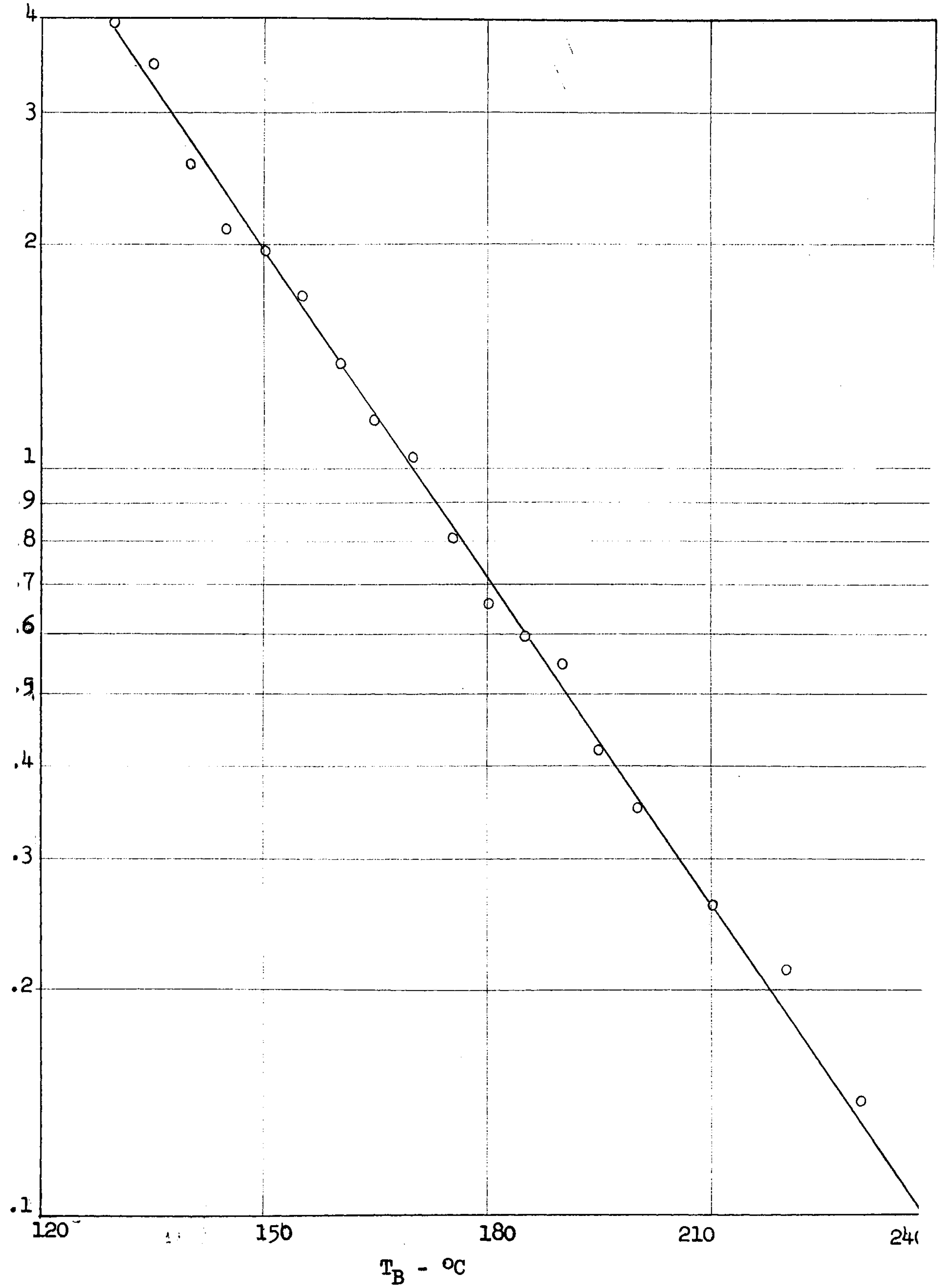


Figure 58 - Log K as the Function of T_B at T_e = 174.5 °C - Oil B

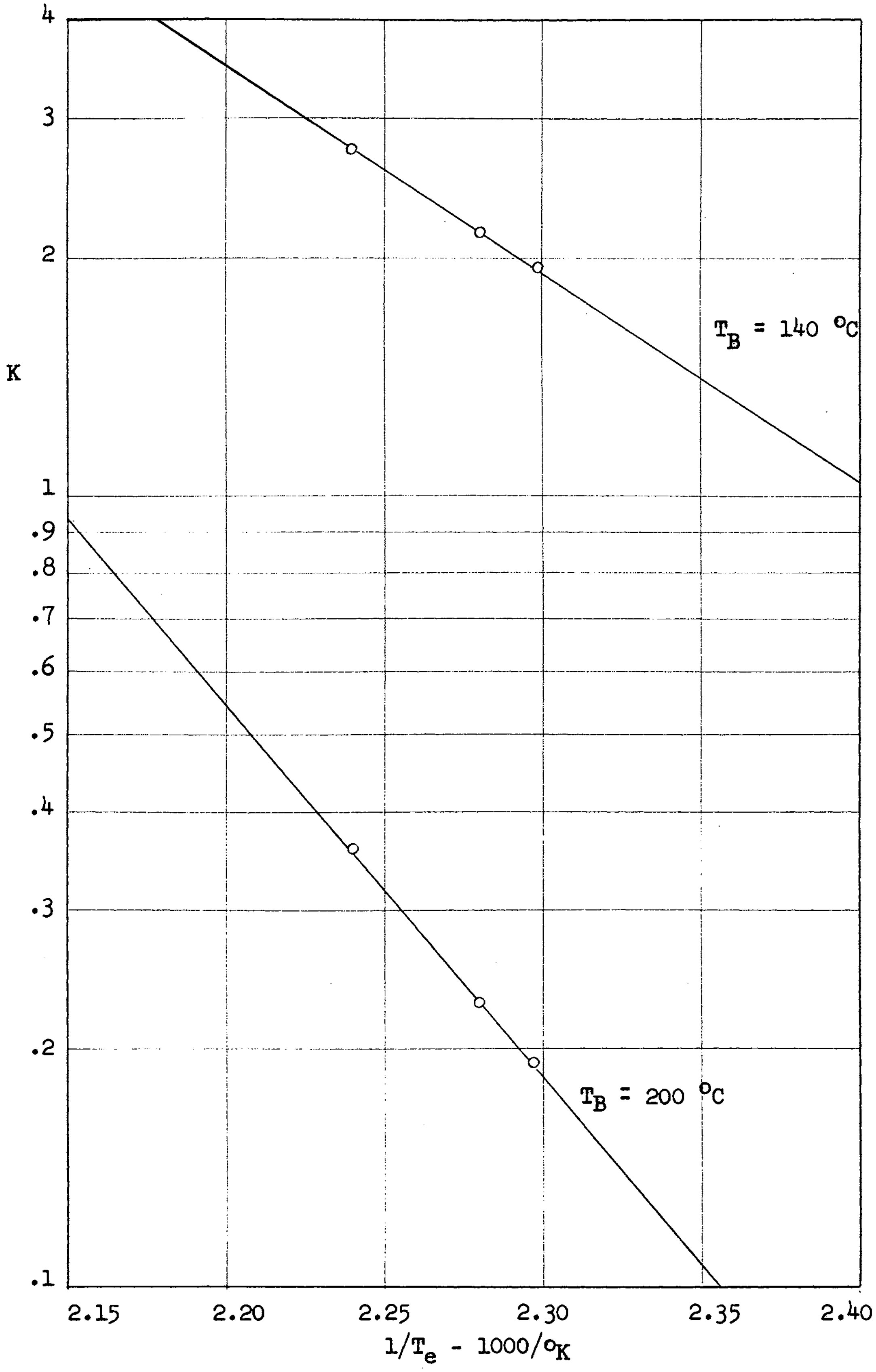


Figure 59 - Log K as the Function of $1/T_e$ - Oil B

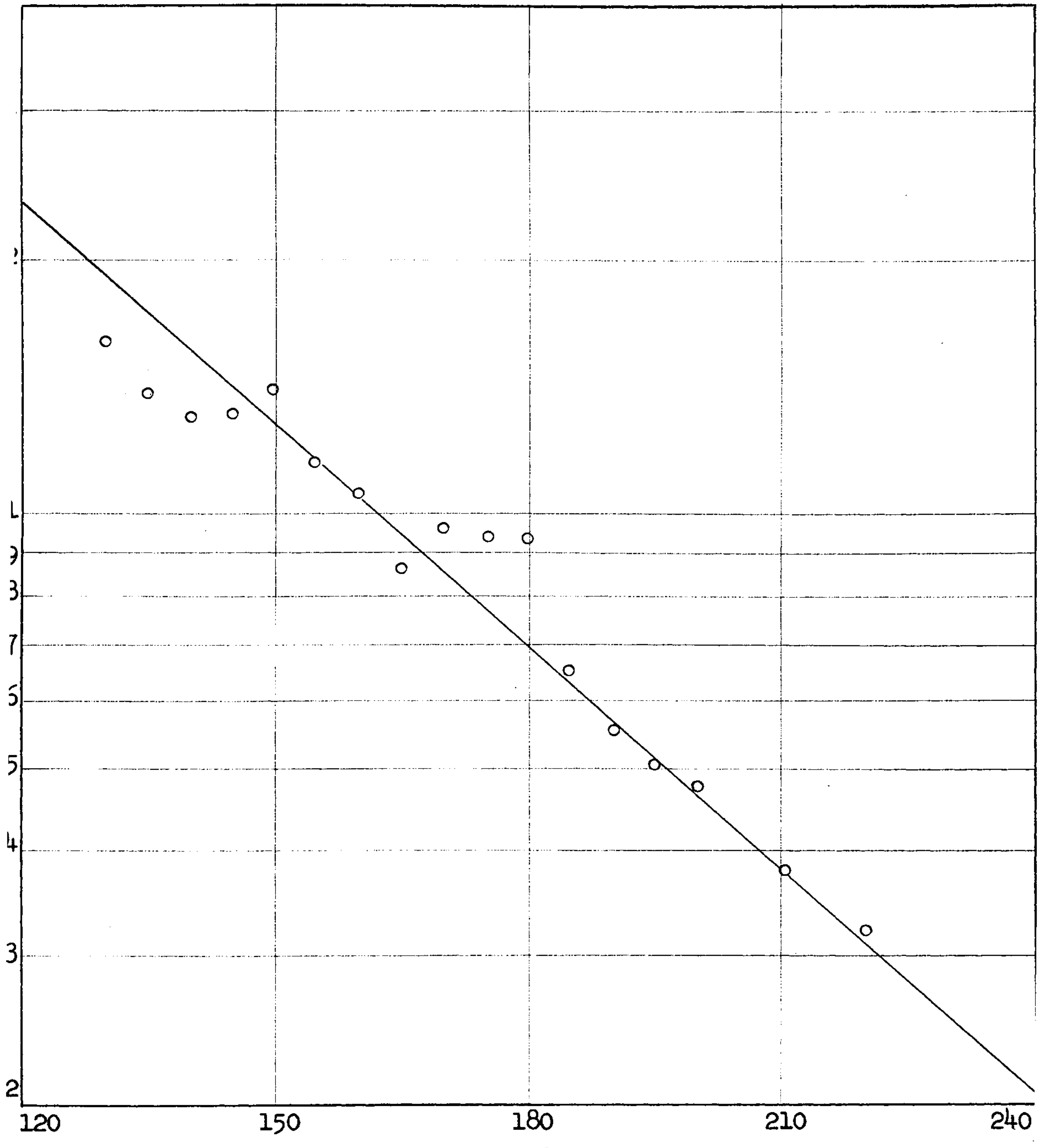


Figure 60 - Log K as the Function of T_B at T_e = 169.5 °C - Oil B'

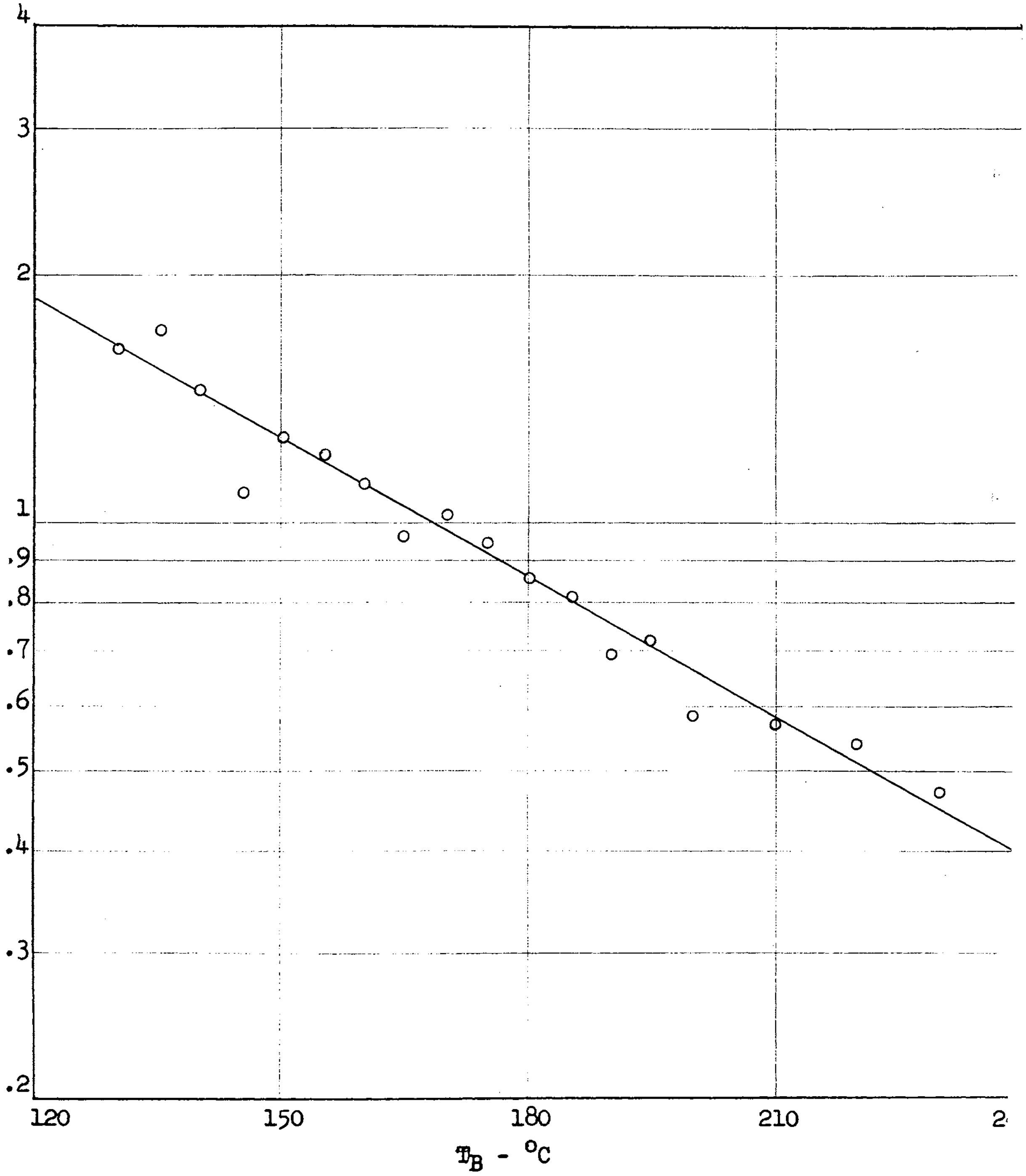


Figure 61 - Log K as the Function of T_B at T_e = 176 °C - Oil B'

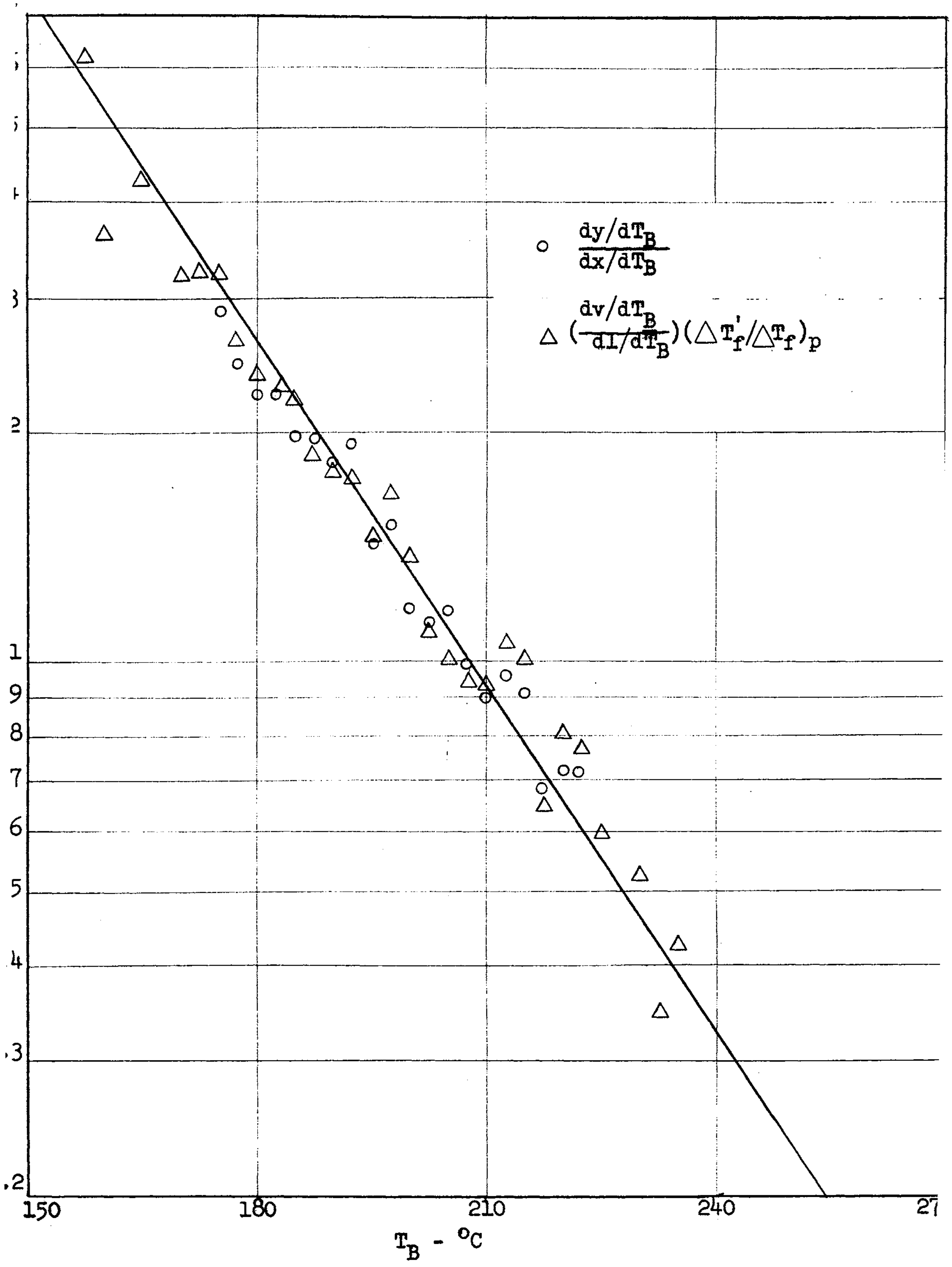


Figure 62 - Log K as the Function of T_B at T_e = 218 °C - Oil G

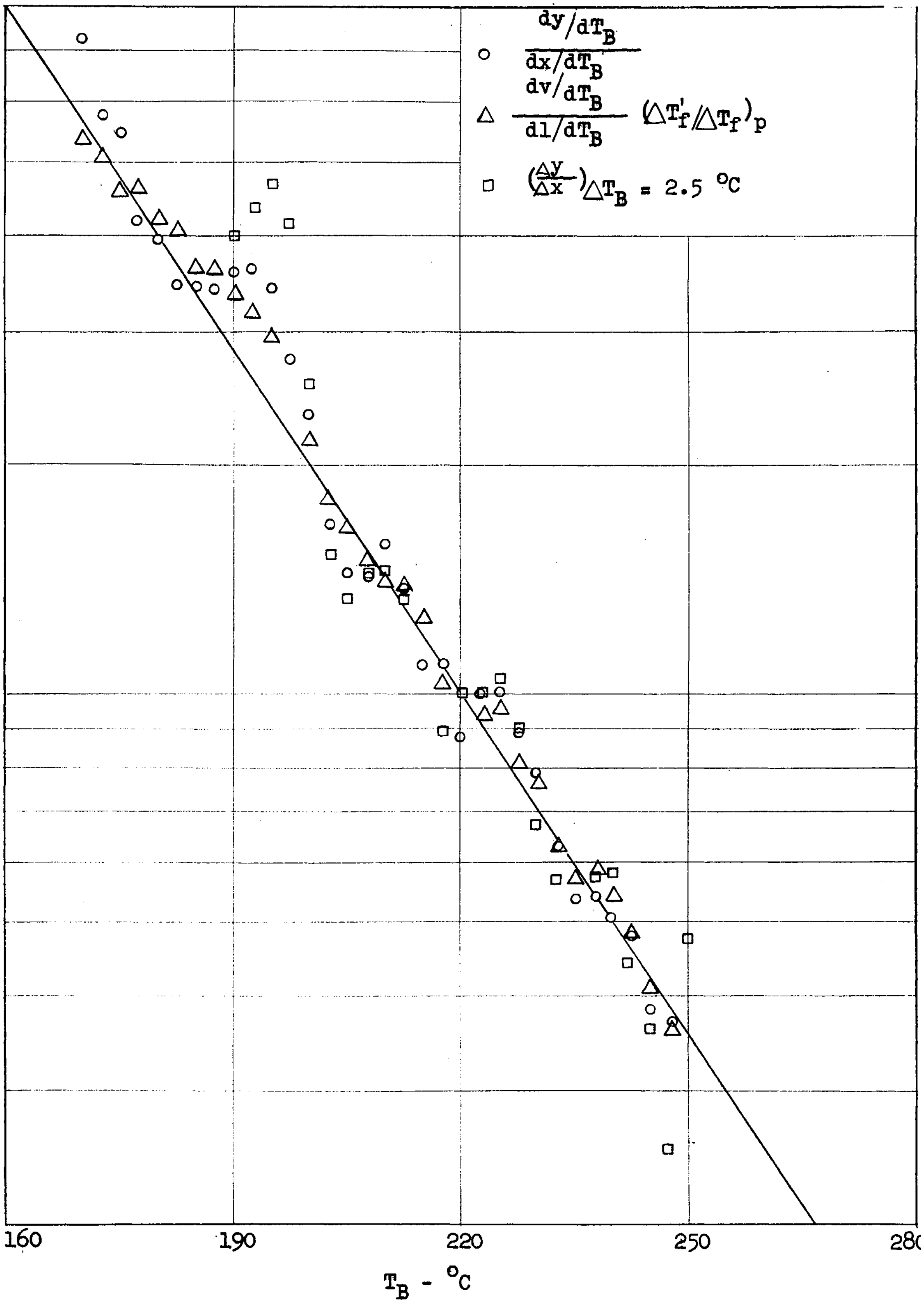


Figure 63 - Log K as the Function of T_B at T_e = 234 °C - Oil G

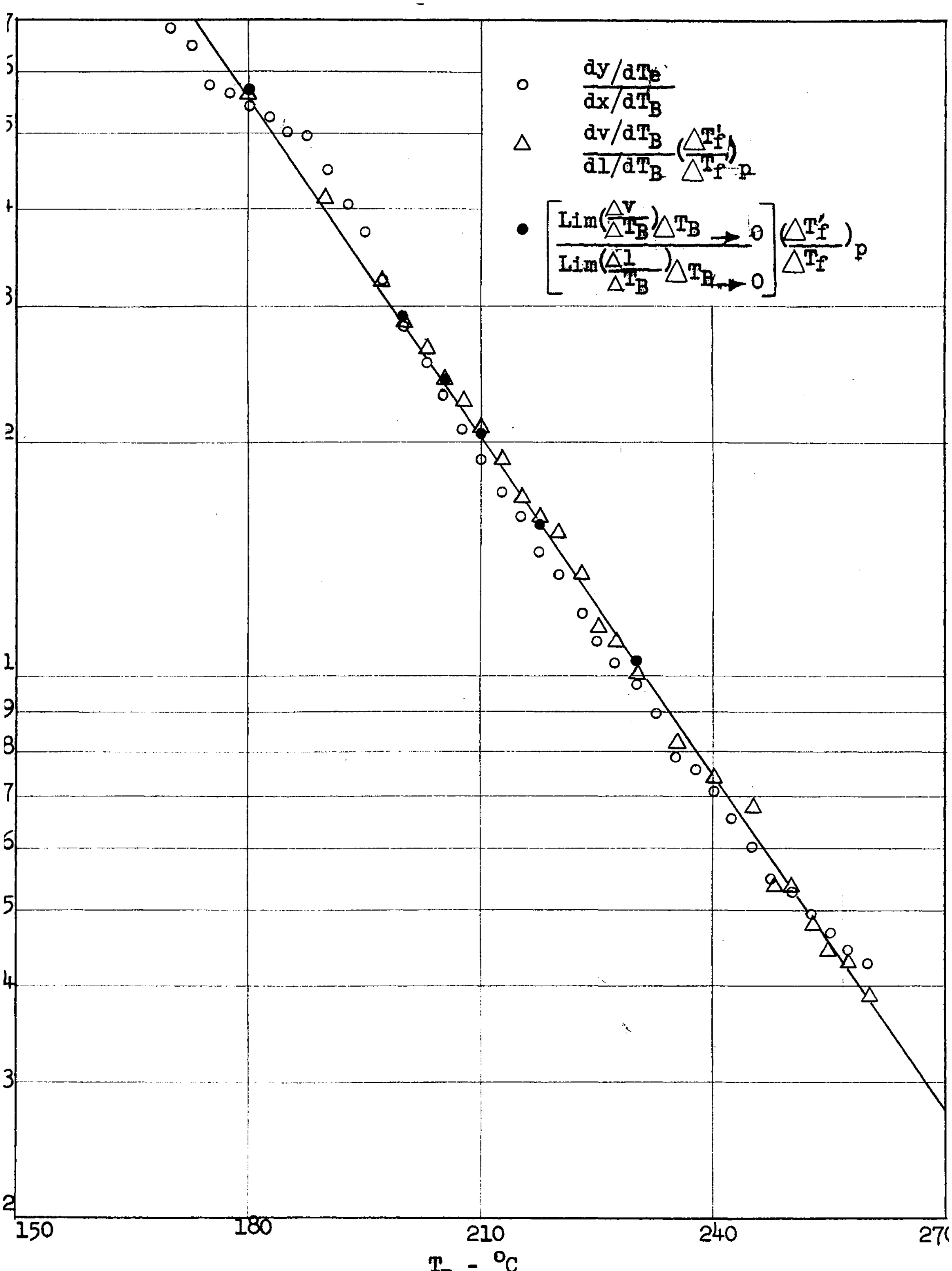


Figure 64 - Log K as the Function of T_B at T_e = 244 °C - Oil G

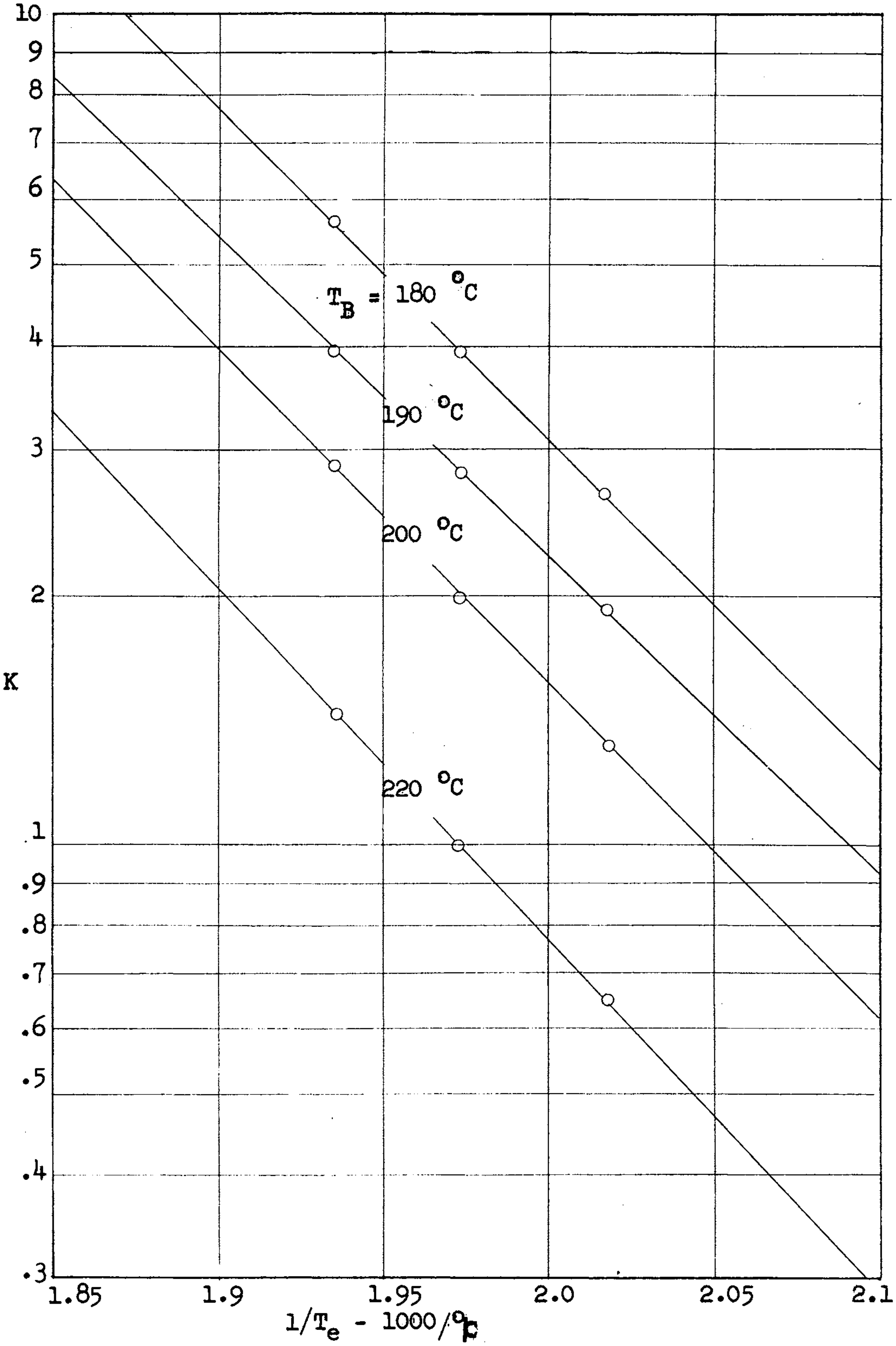


Figure 65 - Log K as the Function of $1/T_e$ - Oil G

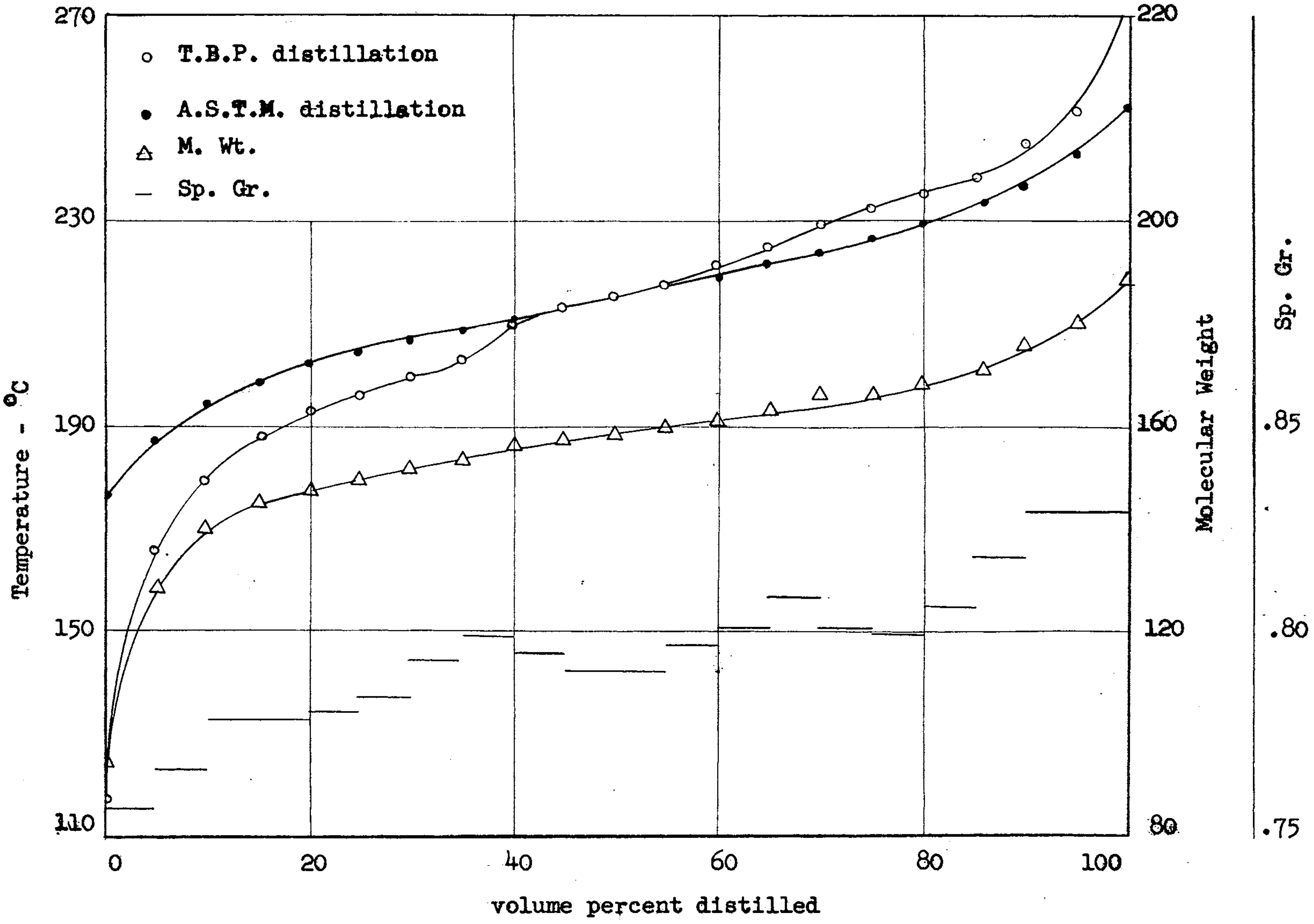


Figure 66 - Physical Properties of Oil F

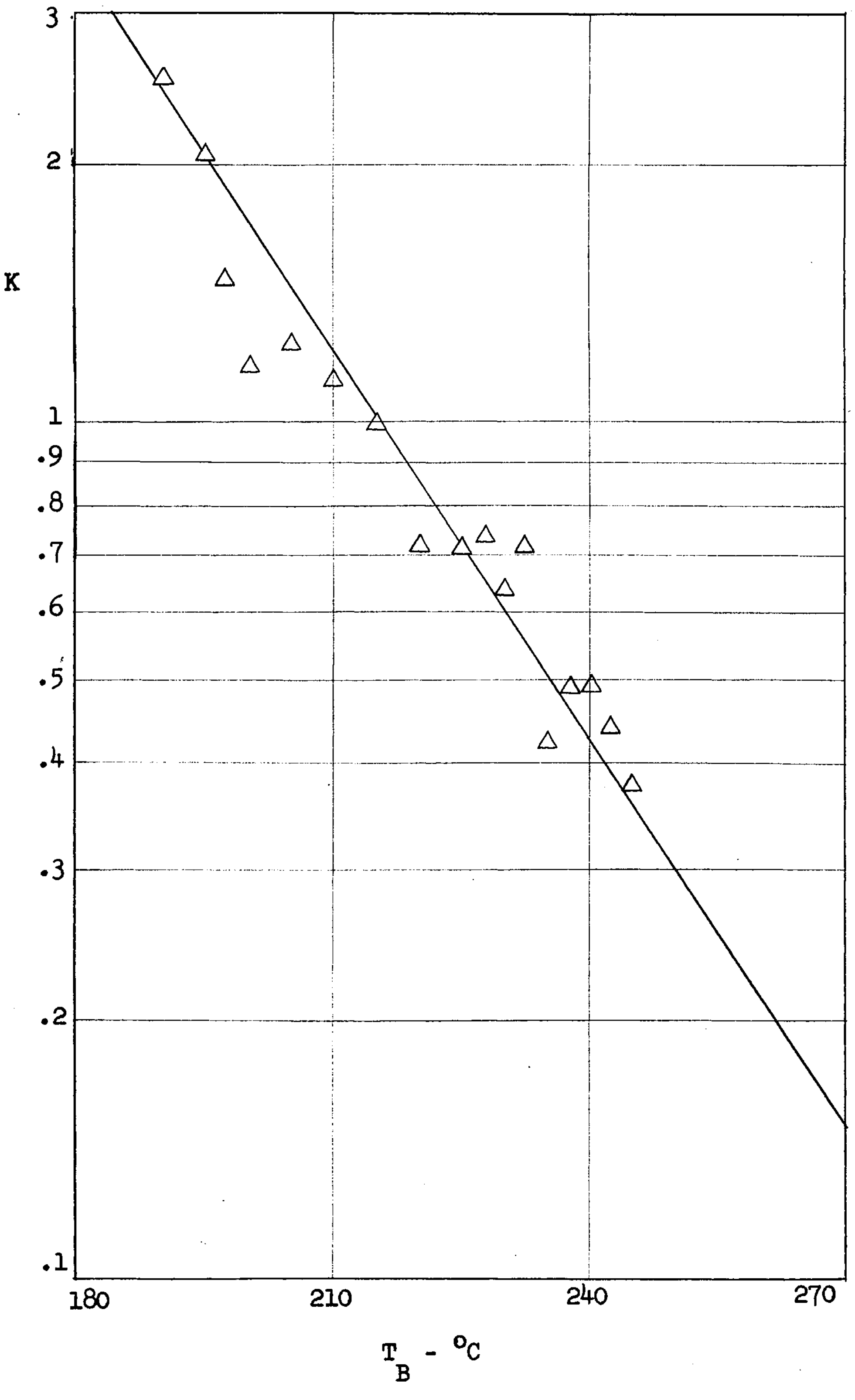


Figure 67 - Log K as the Function of T_B at T_e = 214.5 °C - Oil F

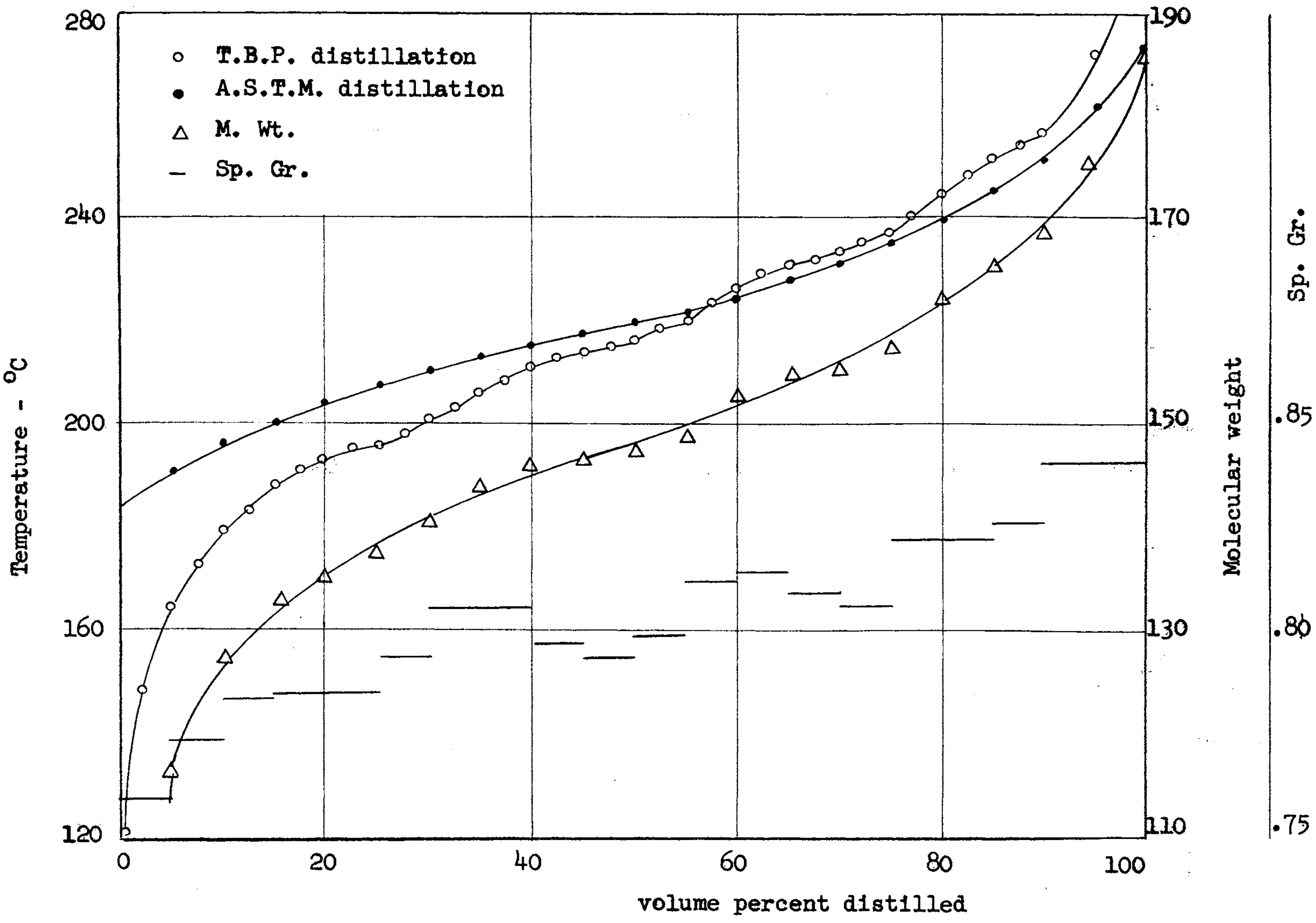


Figure 68 - Physical Properties of Oil F-G

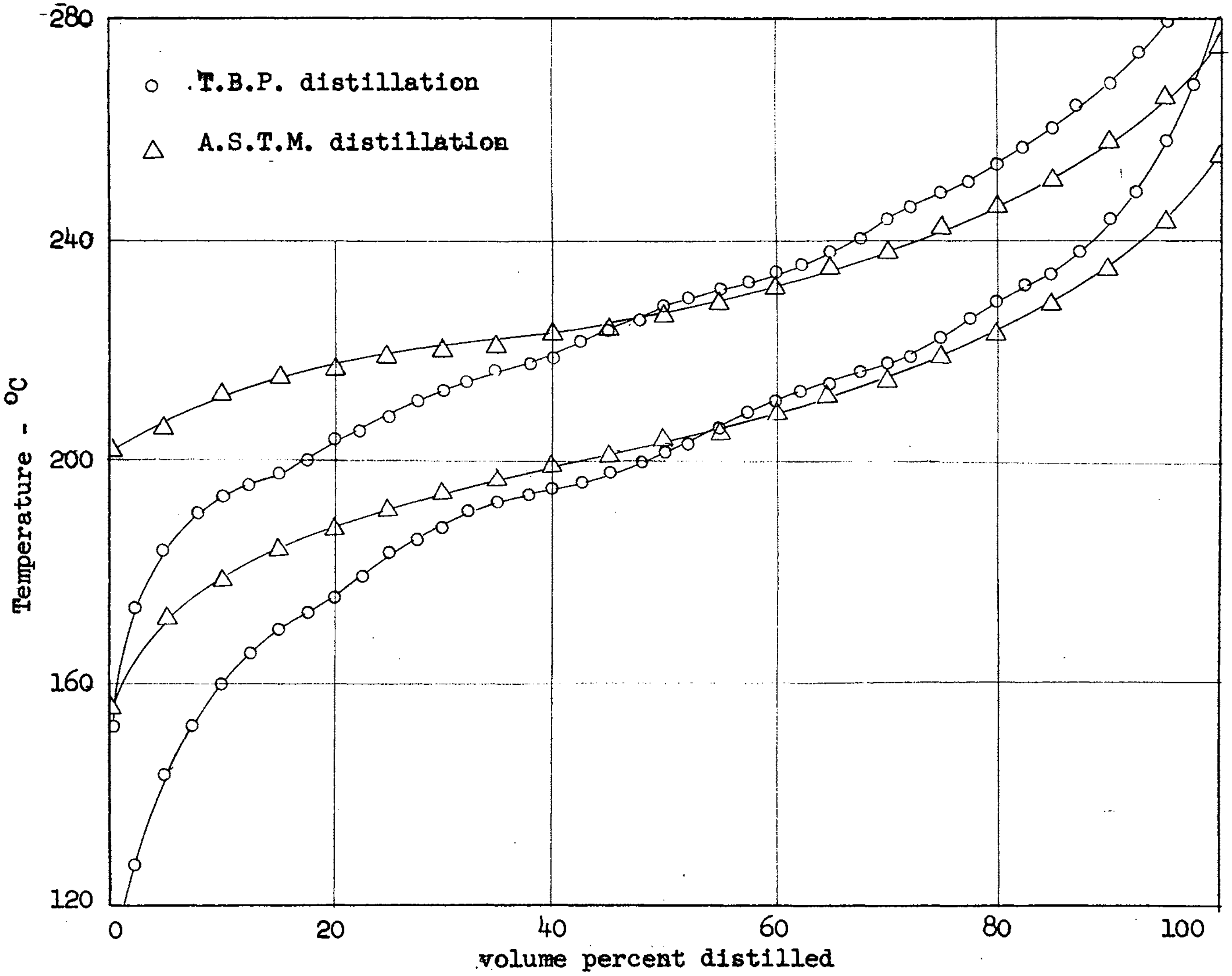


Figure 69 - Distillation Assays of Equilibrium Phases - Oil F-G at

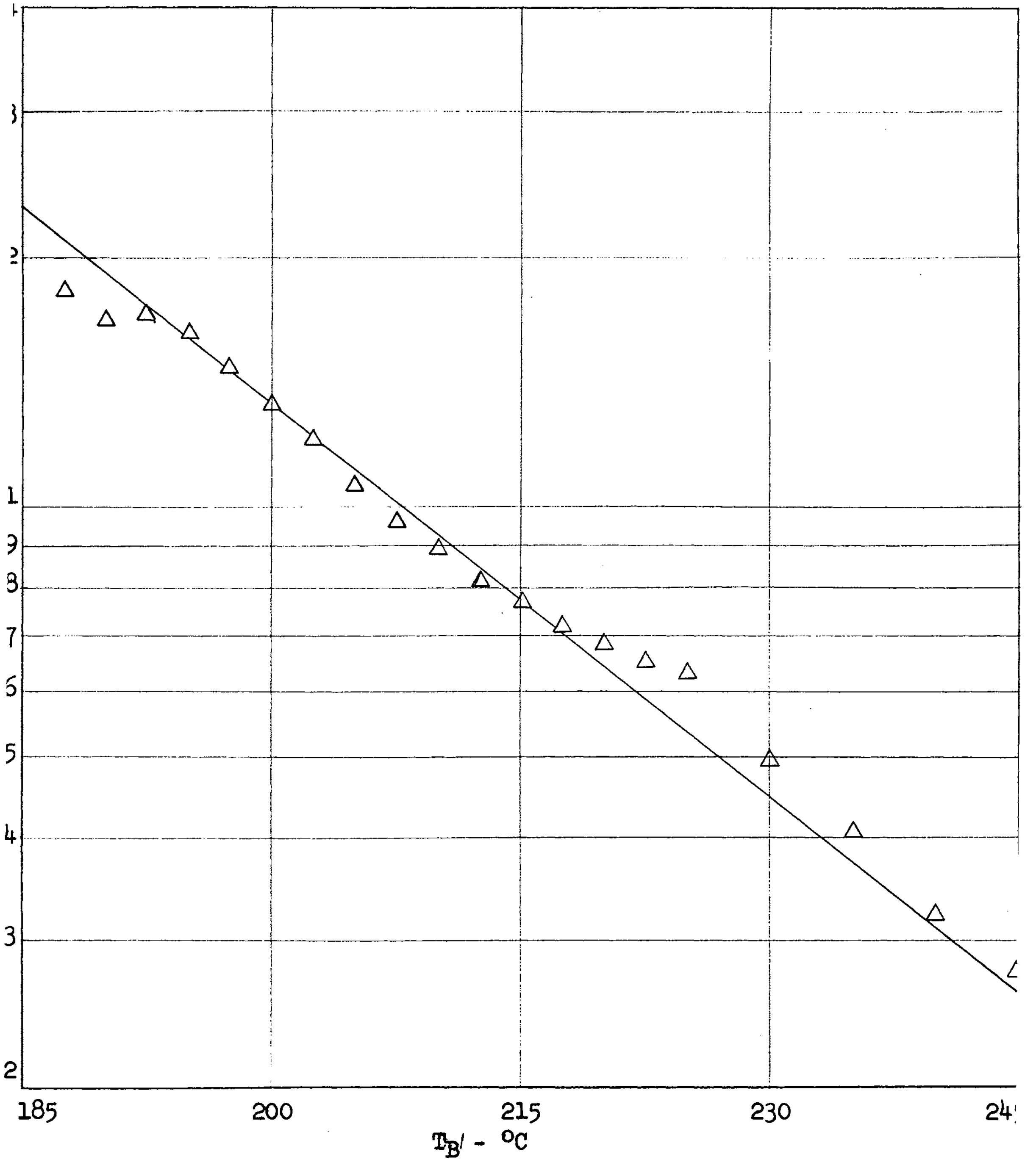


Figure 70 - Log K as the Function of $T_{B'}$ at T_e = 218 °C - Oil F-G

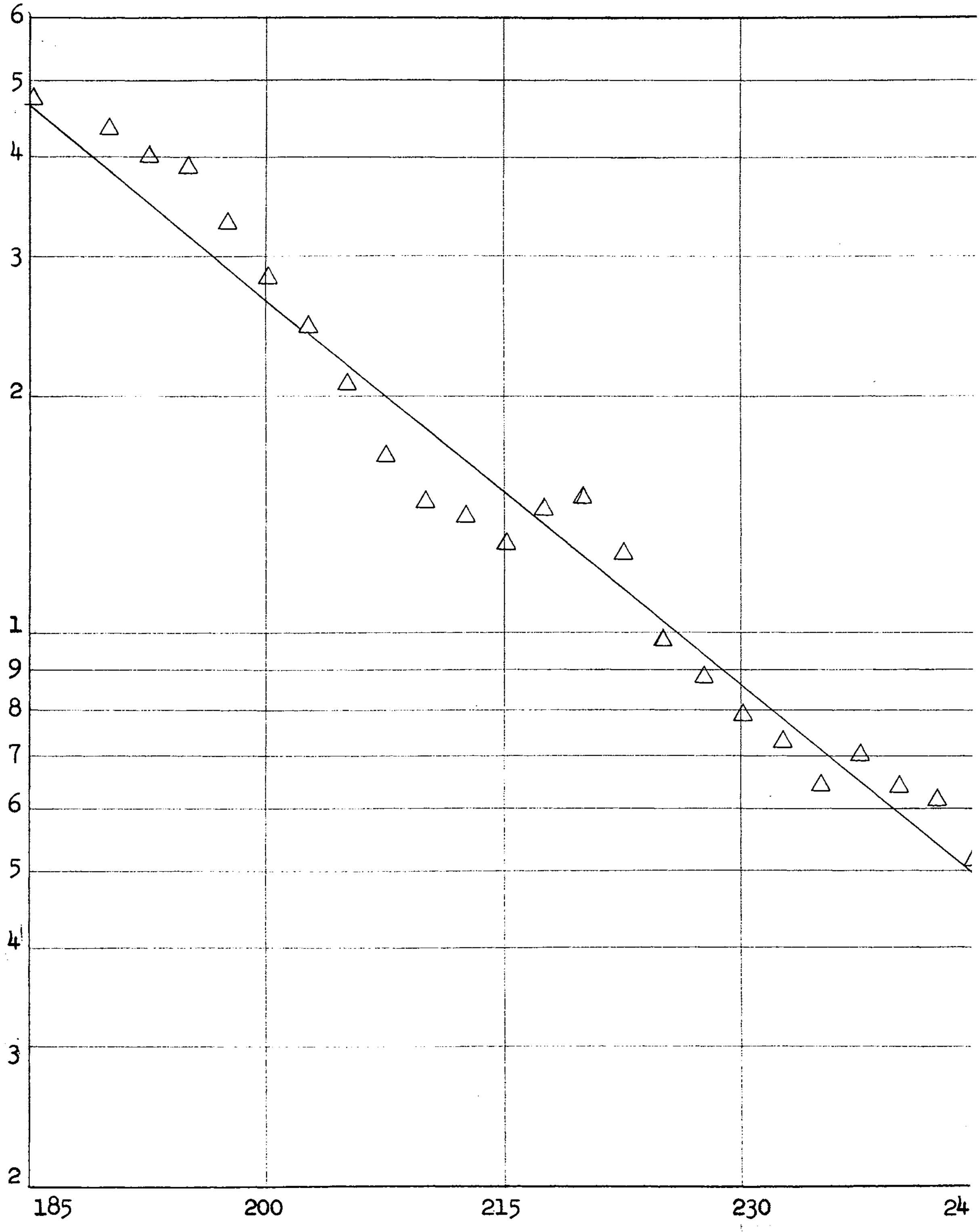


Figure 71 - Log K as the Function of T_B at T_e = 234 °C - Oil F-G

For most engineering calculations, the temperature ranges involved are not greater than those which are shown here; however for higher temperature ranges, equations such as (77a) instead of (77) may become useful.

The validity of these experimental K-values can be best examined by the methods of Chapter VIII, however they are compared with some of the values given in literature (88,89,138). As it is shown in the next chapter, the measured K-values are consistant.

Figure (72) shows the good agreement between the experimental K-values of oil A, and those of Smith and Smith (138), and Maxwell and Bonnell (88,89). The characterization factor of oil A is 12, and the literature values are also for the oils of that nature.

The Smith and Smith's K-values are taken from their K-value plot for paraffines. Maxwell and Bonnell present charts of vapor pressure (for characterization factor of 12), and correction charts for various characterization factors. Here the K-values were calculated as the ratios of vapor to system pressures.

Figures (73,74) compare the experimental K-values of non-paraffinic oils and the values calculated from the vapor pressure charts. The disagreement is evidently caused by insufficient characterization factor corrections, and also by taking the K-value as the ratio of partial to the system pressures.

The disagreements between the evaluated and the literature K-values for some oils indicate the existance of a great need for experimentation. These experimental K-values can subsequently be generalized into charts and equations.

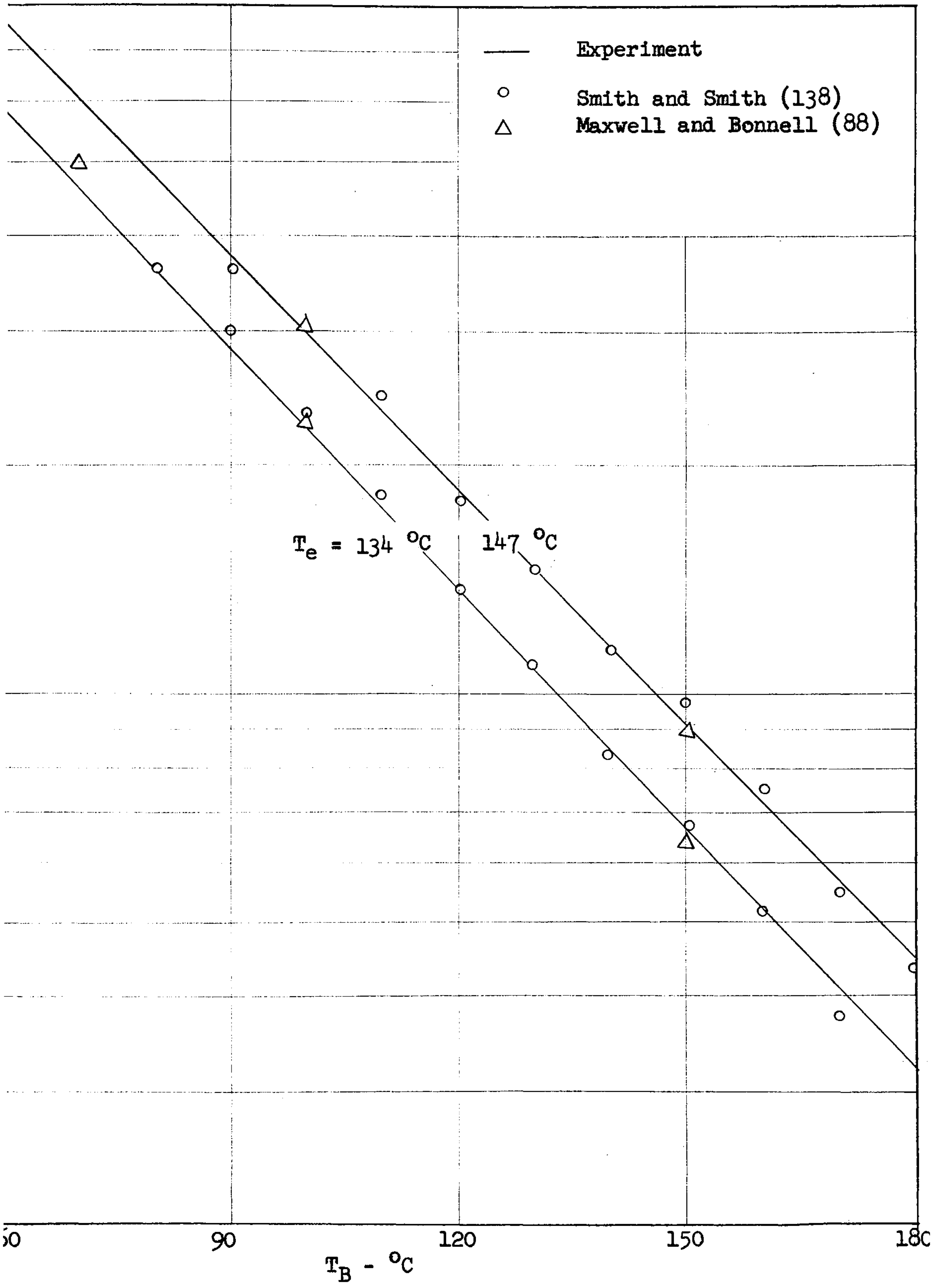


Figure 72 - Comparison of the Experimental and Literature K-Values - Oil A

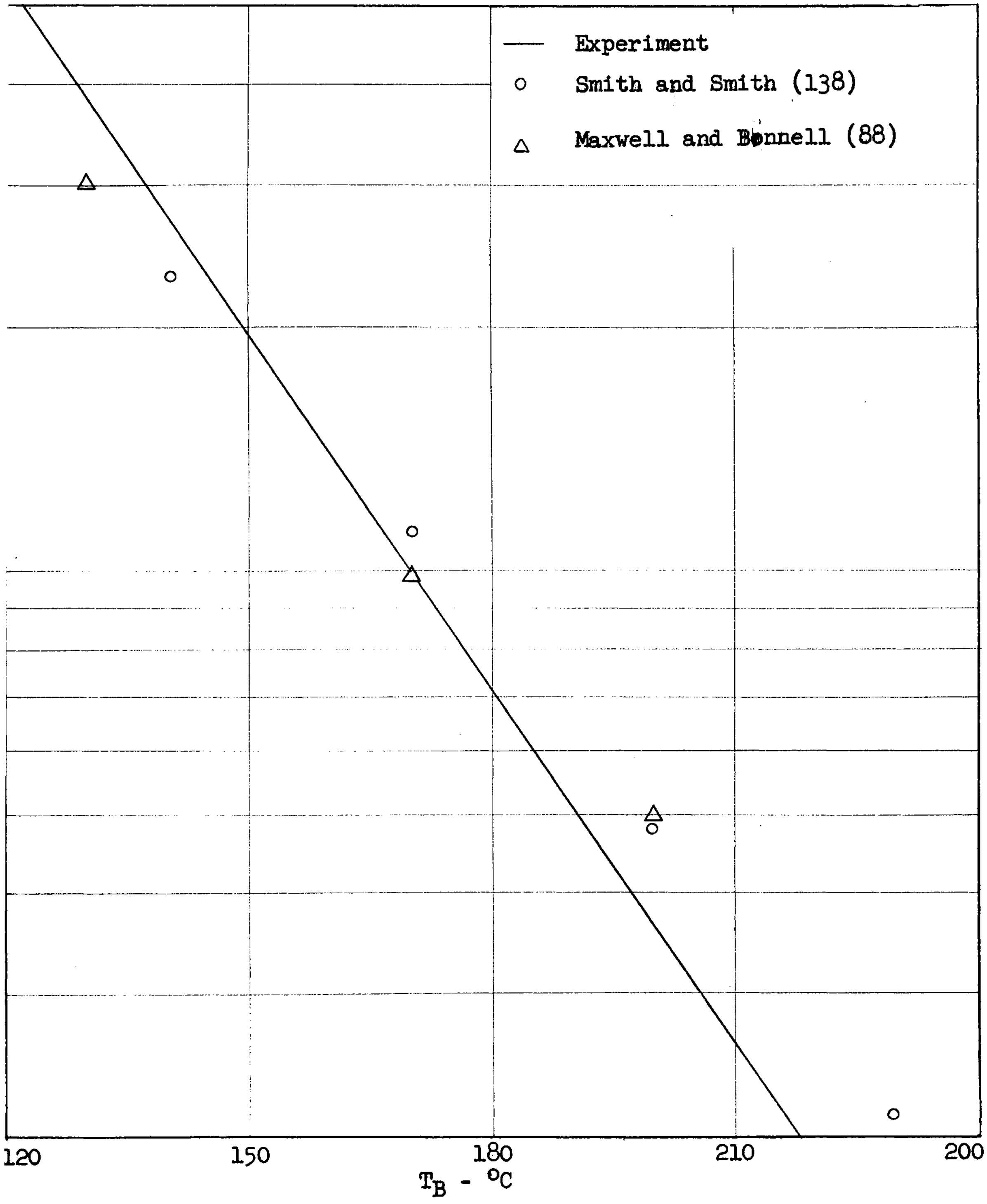


Figure 73 - Comparison of the Experimental and Literature K-Values - Oil at T_e = 174.5 °C

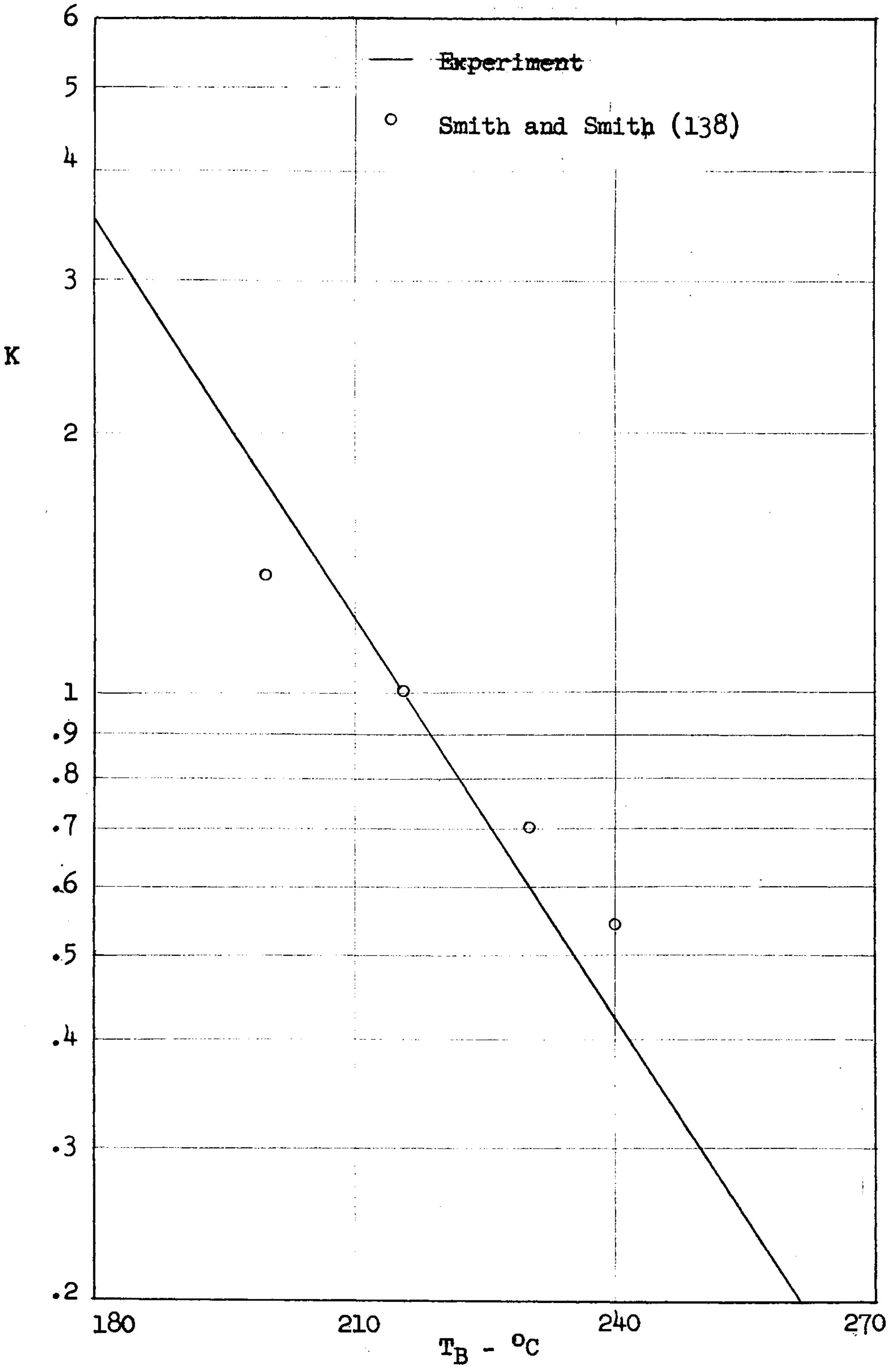


Figure 74 - Comparison of the Experimental and Literature K-Values - Oil F at T_e = 214.5 °C

Suggested Empirical Equations for Slopes of T.B.P. Curves:

From equation (77), it becomes quite evident, that the slope of the T.B.P. curve must be a continuous function of normal boiling temperature. Therefore,

$$\log \frac{dy/dT_B}{dx/dT_B} = C_1 - C_2T_B \qquad (77b)$$

Thus

$$dy/dT_B = e^{C_9(C_{10} - T_B)}\,\psi(T_B) \qquad (79)$$

and

$$dx/dT_B = e^{C_{11}(C_{12} - T_B)}\,\psi(T_B) \qquad (80)$$

Similar equations can also be written for $\frac{dv}{dT_B}$, and $\frac{dl}{dT_B}$. If $\psi(T_B)$ can be determined, then appropriate empirical equations can be deduced for T.B.P. curves, by simply integrating the above equations. With the exception of hydroformer product, the other petroleum fractions examined produced a continuous T.B.P. and slope curves. Evidences indicate that for these petroleum fractions the slopes of T.B.P. curves as functions of boiling temperature are Gaussian distributions. Therefore in such cases,

$$\frac{dy}{dT_B} = e^{C_9(C_{10} - T_B)}\,\psi(T_B) = \frac{1}{\alpha\sqrt{2\pi}}\,e^{\left[-(T_B-\mu)^2/2\alpha^2\right]} \qquad (81)$$

and

$$\frac{dx}{dT_B} = e^{C_{11}(C_{12} - T_B)}\,\psi(T_B) = \frac{1}{\alpha'\sqrt{2\pi}}\,e^{\left[-(T-\mu')^2/2\alpha'^2\right]} \qquad (82)$$

Where α 's and μ's are parameters.

In order to prove the validity of conditions of equations (81) and

(82), they must be examined with the available experimental data. Therefore,

$$\ln \left(\frac{dy}{dT_B}\right) = \ln \left(\frac{1}{\alpha\sqrt{2\pi}}\right) - (T_B - \mu)^2/2\alpha^2 \qquad (83)$$

By assuming the continuity of equation (83) and differentiating it with respect to T.B.P. temperature, then

$$\frac{d(\ln \frac{dy}{dT_B})}{dT_B} = \frac{\mu - T_B}{\alpha^2} \qquad (84)$$

Similarly

$$\frac{d(\ln \frac{dx}{dT_B})}{dT_B} = \frac{\mu' - T_B}{\alpha'^2} \qquad (85)$$

Equations (84) and (85) suggest, that plots of $\frac{d(\ln \frac{dy}{dT_B})}{dT_B}$ and $\frac{d(\ln \frac{dx}{T_B})}{dT_B}$ as functions of T_B, should be straight lines. In the cases where the above condition is true, then the limitations of equations (81) and (82) are satisfied.

The measured values of log $\frac{dy}{dT_B}$ were plotted versus the corresponding T.B.P. temperature, and then differentiated to obtain $\frac{d(\log \frac{dy}{dT_B})}{dT_B}$. Figures (77 and 78) show representative plots of $\frac{d(\log \frac{dy}{dT_B})}{dT_B}$ and $\frac{d(\log \frac{dx}{dT_B})}{dT_B}$ as straight line functions of T.B.P. temperature. Because of the repeated differentiation and plotting, the points are rather scattered, but however they satisfy the condition of equations (84) and (85).

The lines for each equilibrium vapor and liquid are parallel r nearly so. This means that the values of α and α' are equal. By ntegrating equation (84), the following equation would result.

$$\ln \frac{dy}{dT_B} = \frac{\mu T_B}{\alpha^2} - \frac{T_B^2}{2\alpha^2} + \gamma \qquad (86)$$

or

$$\frac{dy}{dT_B} = e^{\left(\frac{\mu T_B}{\alpha^2} - \frac{T_B^2}{2\alpha^2} + \gamma\right)} \qquad (86a)$$

Thus

$$K = \frac{dy}{dx} = e^{\left[\left(\frac{\mu T_B}{\alpha^2} - \frac{T_B^2}{2\alpha^2} + \gamma\right) - \left(\frac{\mu' T_B}{\alpha'^2} - \frac{T_B^2}{2\alpha'^2} + \gamma'\right)\right]} \qquad (87)$$

In order to compare equations (87) and (77), α^2 must be equal to α'^2, which has already been proved to be so. This may not be the case when larger T.B.P. temperature ranges are involved (equation 75). Also, the value of $\frac{\mu - \mu'}{\alpha^2}$ is equivalent to C_1 of equation (77).

It is evident that equations similar to (81) and (82) can be used to express the slopes of most T.B.P. curves, and can be utilized to improve the measured values.

Since equations (84) and (85) for most petroleum oils are parallel lines, therefore it is expected that the slopes of these lines and their average boiling points constitute useful parameters for generalized charts. However, because of insufficient experimental data, the above objective is not included in this work.

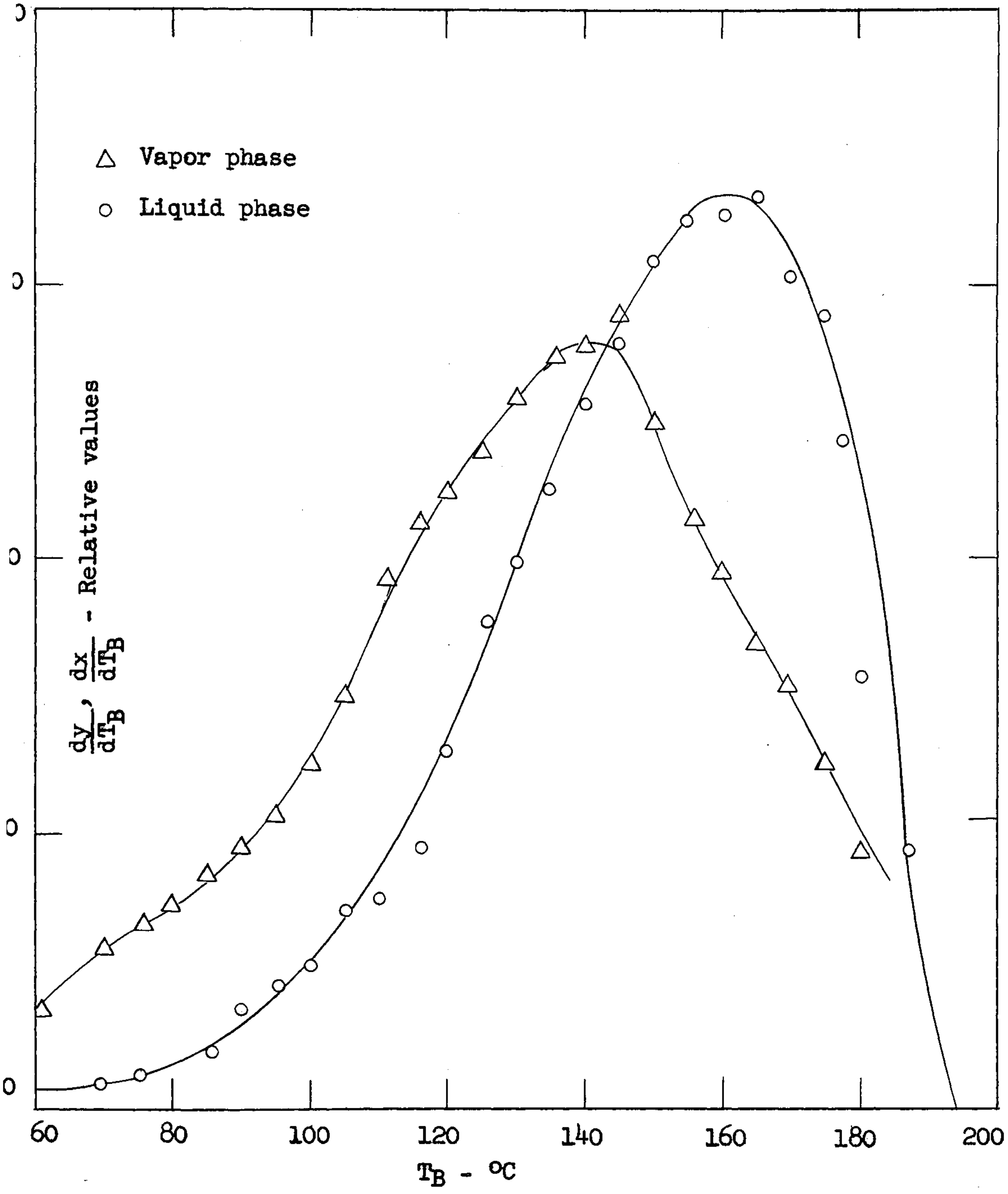
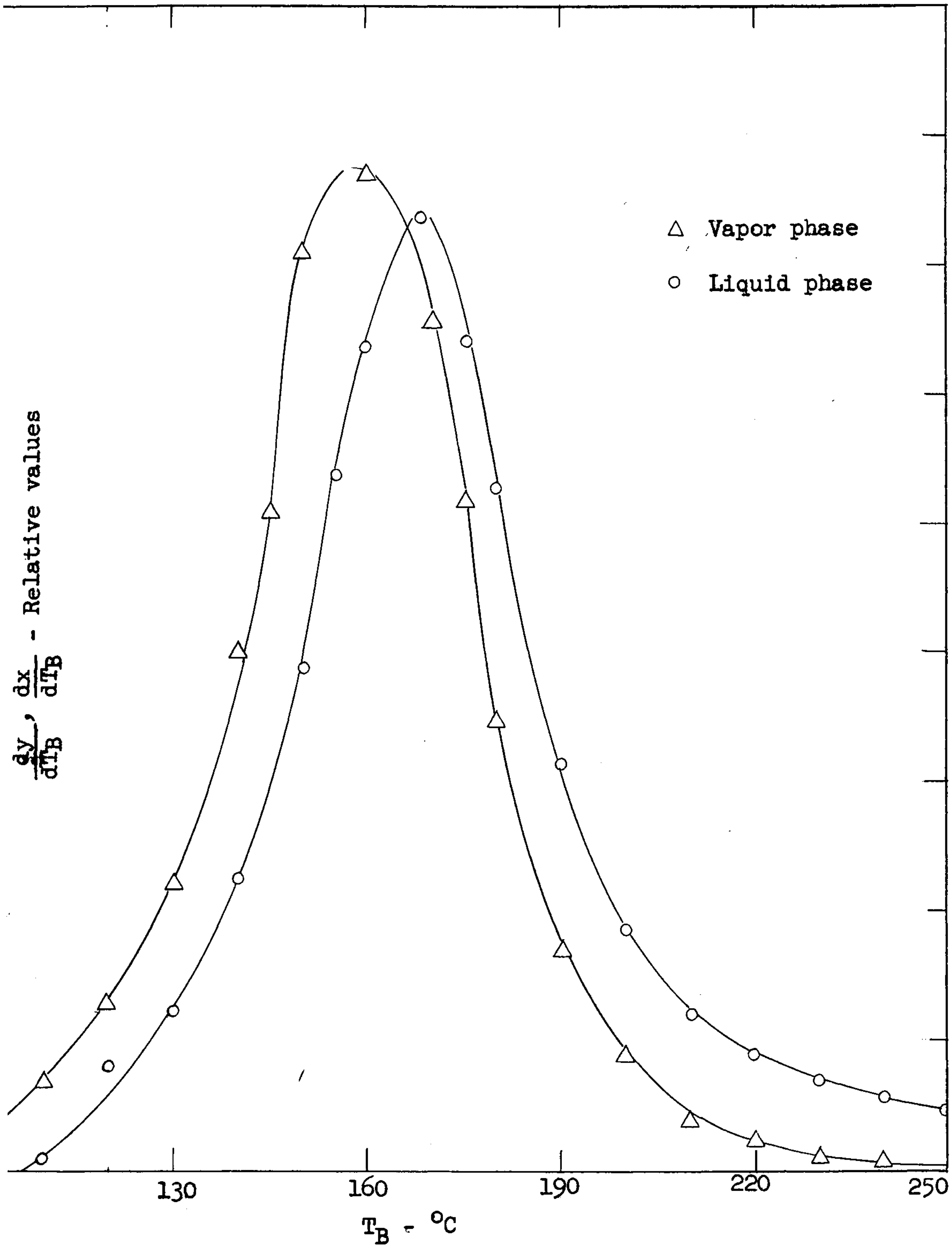


Figure 75 - Typical Plot of $\frac{dy}{dT_B}$, $\frac{dx}{dT_B}$ as the Function of T_B - Oil A at T_e = 141°C



gure 76 - Typical Plot of $\frac{dy}{dT_B}$, $\frac{dx}{dT_B}$ as the Function of T_B - Oil B at T_e = 174.5 °C

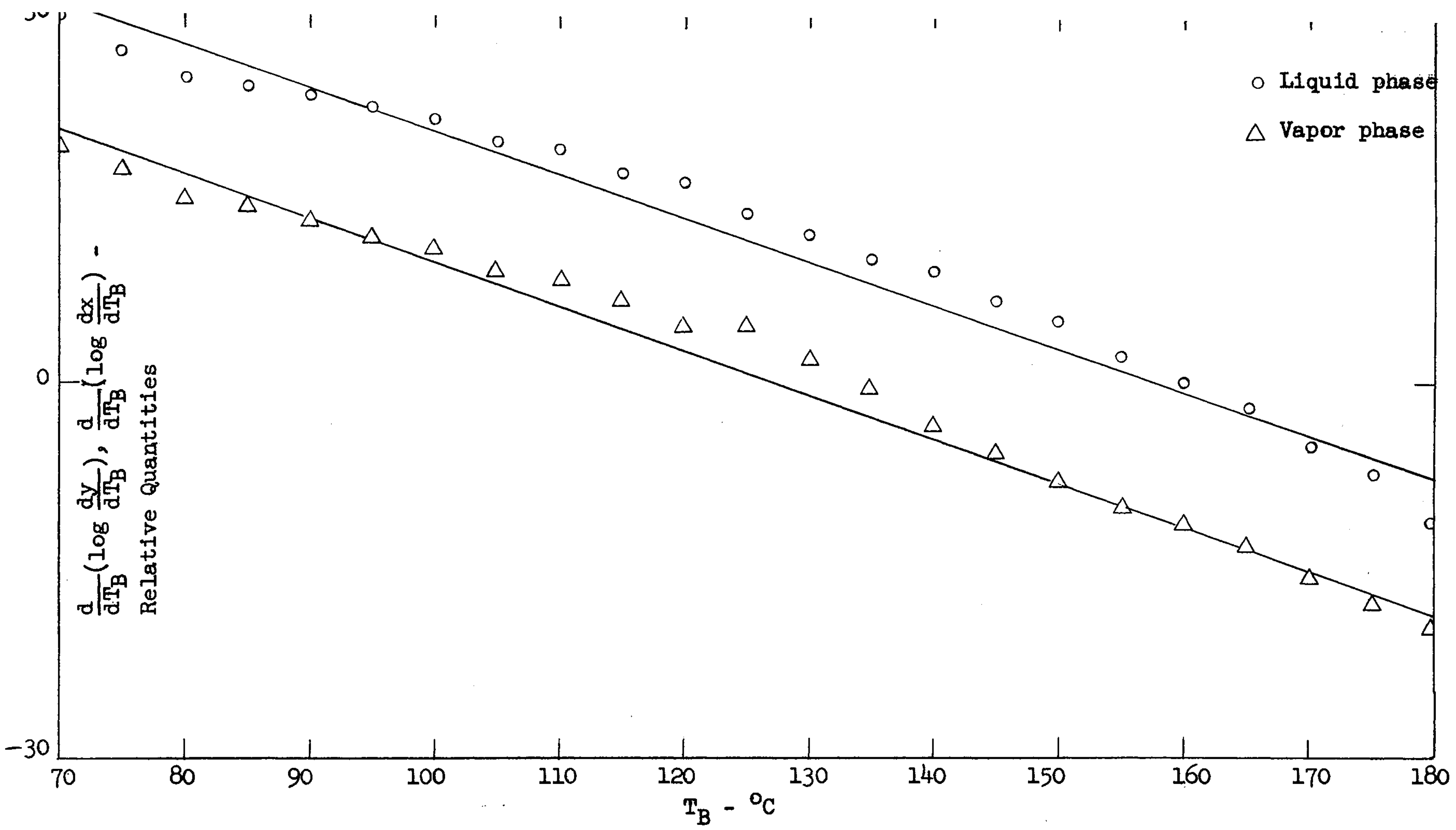


Figure 77 - Typical Plot of Equations (84, 85) - Oil A at T_e = 141°C

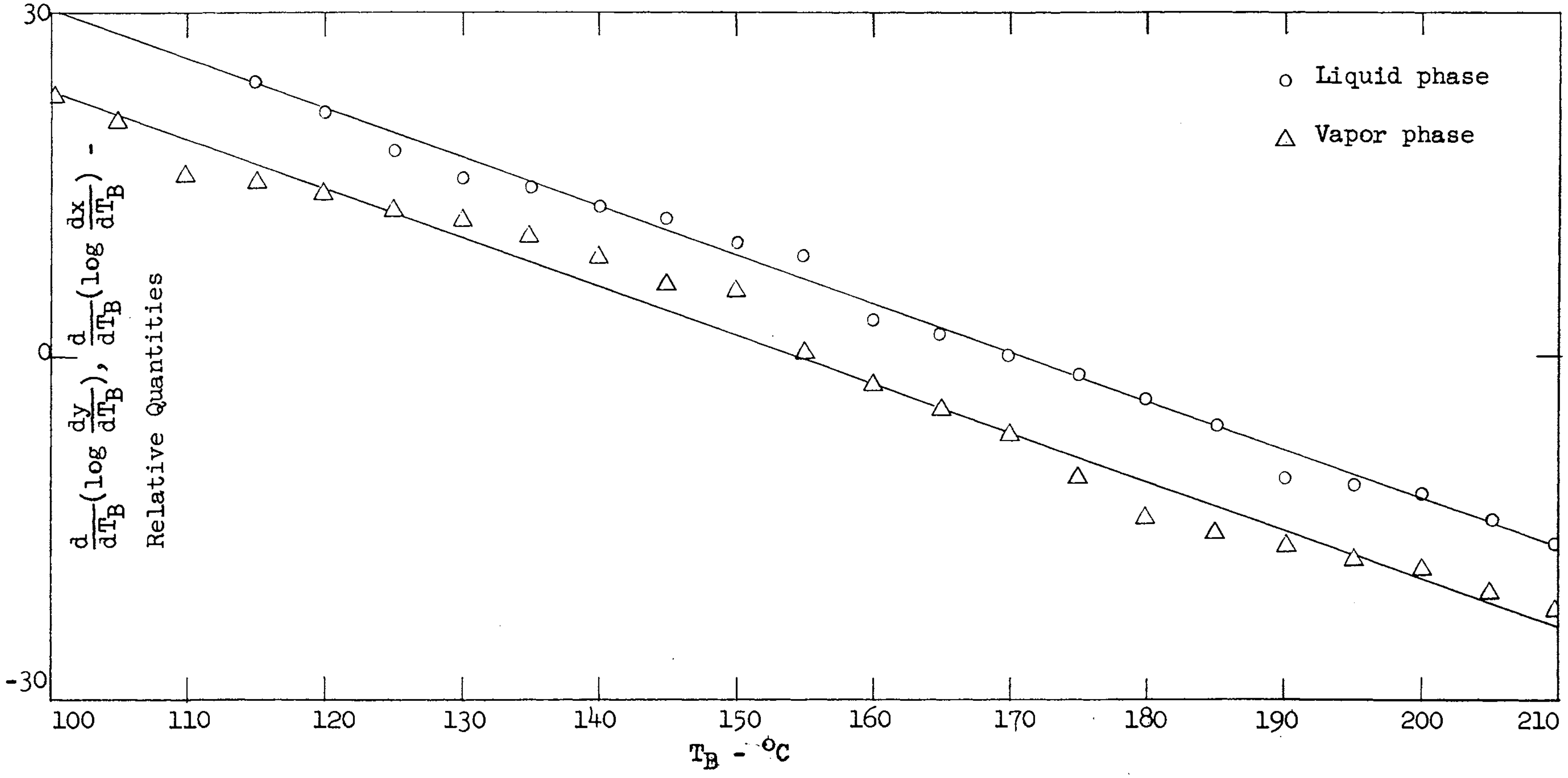


Figure 78 - Typical Plot of Equations (84, 85) - Oil B at T_e = 174.5 °C

CHAPTER VIII

APPLICATIONS OF INTEGRAL TECHNIQUE

The validity of the experimental vapor-liquid phase distribution coefficients presented in the previous part are ascertained in this chapter. Techniques for some of the more common vaporization calculations are also given. These computations indicate that the K-values so obtained for the continuums are suitable for integral vaporization calculations, which otherwise can not be satisfactorily performed by some conventional methods. Integral calculations for more complicated processes, such as fractionation, can be performed with the same relative degrees of ease and accuracy. The latter were not included in this work.

Calculation of Equilibrium Composition: As before, for any component of a mixture boiling at T_{Bi}

$$Ki = \frac{y_i}{x_i}$$

By differentiating the above equation

$$dy_i = K_i \, dx_i + x_i \, dK_i \tag{88}$$

But, as it has been stated before, $K_i = K_i(P_e, T_e, x)$ which is more conveniently given by $K_i = K_i(P_e, T_e, K_o)$. Thus

$$dK_i = \left(\frac{\delta K_i}{\delta P_e}\right) dPe + \left(\frac{\delta K_i}{\delta T_e}\right) dTe + \left(\frac{\delta K_i}{\delta K_o}\right) dK_o \tag{89}$$

At low pressures and at any constant equilibrium condition, equations (88) and (89) may be replaced by equation (90)

$$dy_i = K_i \, dx_i \qquad (90)$$

For continuum

$$x = \int_0^y \frac{dy}{K} \qquad (91)$$

Since both K and y are functions of normal boiling temperature, then plot of $1/K(T_B)$ versus $y(T_B)$ can be used to obtain T.B.P. curve for equilibrium liquid. Equation similar to (91) can be written for equilibrium vapor. A representative figure (79) shows the close comparison between the T.B.P. curve calculated by the use of equation (91) and the experimental curve

T.B.P. curves of equilibrium phases on the convenient volumetric basis, and the phase ratio, can be calculated at any equilibrium condition as follows:

$$K_i = \frac{\frac{\triangle V_i}{V}}{\frac{\triangle L_i}{L}} \left(\frac{\triangle T_f'}{\triangle T_f}\right)_P = \frac{v_i L}{f_i F - v_i V} \left(\frac{\triangle T_f'}{\triangle T_f}\right)_P \qquad (92)$$

where f_i is the volume fraction of the ith component in the feed.

So
$$v_i = \frac{f_i}{1 + (1/K_i)(\triangle T_f'/\triangle T_f)_P L/V} \qquad (92a)$$

For continuum

$$V = \int_0^1 \frac{df}{1 + (1/K)(\triangle T_f'/\triangle T_f)_P L/V} \qquad (93)$$

Similarly

$$L = \int_0^1 \frac{df}{1 + K(\triangle T_f/\triangle T_f')_P V/L} \qquad (94)$$

The above equations should be integrated between the limits of zero and 100 instead of zero and one, if the T.B.P. curve of feed is expressed in volume percent rather than volume fraction.

For each condition of equilibrium, f and K are continuous functions of T.B.P. temperature, and $(\triangle T_f'/\triangle T_f)_P$ is a constant. In order to solve equation (93) for V, the volume fraction of vapor phase, f should be plotted as the function of $1/\left[1+1/K(\triangle T_f'/\triangle T_f)_P \frac{L}{V}\right]$. The total area under the curve is obviously equal to V, and the area above it is the result of equation (94).

The volumetric T.B.P. curves of equilibrium phases can be calculated from the following equations,

$$v = \int_0^f \frac{df}{1 + (1/K)(\triangle T_f'/\triangle T_f)_P L/V} \Bigg/ \int_0^1 \frac{df}{1 + (1/K)(\triangle T_f'/\triangle T_f)_P L/V} \qquad (95)$$

Similarly

$$l = \int_0^f \frac{df}{1 + K(\triangle T_f/\triangle T_f')_P V/L} \Bigg/ \int_0^1 \frac{df}{1 + K(\triangle T_f/\triangle T_f')_P V/L} \qquad (96)$$

The plot of equation (93) is also used here, and v and l functions (T.B.P. plots of equilibrium phases) are calculated by addition of the successive increments. Figure (80) is a representative application of the technique, and it shows the close agreement between the experimental value of L/V and T.B.P. curves, and those calculated from equations (93,94,95,96).

Evidently a minimum of calculational effort and experimental data (T.B.P. curve of feed and K-values) are required to solve the equilibrium vaporization problem. Since $(\triangle T_f'/\triangle T_f)_P$ changes but very little with equilibrium temperature T_e, therefore the need for trial and error solution of the above equations has basically been eliminated. The upper limit of $(\triangle T_f'/\triangle T_f)_P$ is one and its lower limit for most petroleum oils is about 0.8, and it can be conveniently expressed as a function of T_e.

Edmister (31) has proposed methods whereby equilibrium flash vaporization, fractional distillation, bubble and dew point calculations can be performed graphically and with a minimum of labor. Some of these techniques are presented in the following pages.

The integral flash vaporization calculation for a continuum is essentially the same as that for a finite mixture. It involves the finding of the mole ratio of equilibrium phases $\frac{Y}{X}$ by trial and error. The following vaporization equations can be used for this purpose.

$$\int_0^y dy = \int_0^z \frac{dz}{1 + \frac{X}{KY}} \quad * \qquad (97)$$

or

$$\int_0^y dx = \int_0^z \frac{dz}{1 + \frac{KY}{X}} \qquad (98)$$

The procedure simply consists of assuming a $\frac{Y}{X}$ ratio, then plotting $\frac{1}{1 + \frac{X}{KY}}$ versus the mole fraction of feed (equation 97). The area under the curve is obviously equivalent to the moles of vapor Y, while the area above the curve is equal to the moles of equilibrium liquid X. The calculated $\frac{X}{Y}$ should then be compared with the assumed value, and the calculation must be repeated until a satisfactory check is obtained.

Assuming that the error caused from the measurement of the

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* Equations (97) and (98) appear in the original paper (31) by the following nomenclature (This nomenclature is not the same as that of this thesis),

$$v/f = \frac{1}{1 + \frac{L}{KV}} \quad (97*), \quad \frac{l}{f} = \frac{1}{1 + \frac{KV}{L}} \quad (98*)$$

where: L and V are moles of liquid and vapor mixtures; also v, l, and f are moles of infinitesimal increments of vapor, liquid, and feed respectively.

area under the curve and plotting is $\triangle Y$, then the calculated $\frac{Y}{X}$ would be equal to $\frac{Y + \triangle Y}{X - \triangle Y}$. Therefore if X is very small relative to Y or vice-versa, then the calculational error would be highly magnified. The accuracy of this method is obviously highest when X and Y are very close, and it decreases when the ratio is either very low or very high. Evidently only a few points are needed to draw a smooth curve, although greater accuracies can be obtained with more points.

T.B.P. distillation curves on mole percent basis for both equilibrium phases can easily be obtained by solving the above equation for successive increments. Figure (81) gives a comparison between the calculated and the experimental T.B.P. distillation curves. The comparison as it should be expected is within the limits of the expectancy, and the usual uncertainty in the first and the last few percent are also indicated there.

Bubble and dew point calculations for continuums are principally the same as for finite mixtures, and the above discussion applies to these cases as well. The integral relationship for bubble point calculation of continuum is

$$\int_0^1 K \, dz = 1 \qquad (99)$$

Values of $K(T_B)$ at an assumed T_e for a few T.B.P. points are plotted as a function of $z(T_B)$, and a smooth curve is then drawn through these points. In order to satisfy the condition of equation (99), the assumed T_e must be such as to produce an area under the curve equal to unity.

The integral relationship for dew point calculation is

$$\int_0^1 \frac{dz}{K} = 1 \qquad (100)$$

Values of $\frac{1}{K(T_B)}$ at an assumed T_e for several points on the molar T.B.P. distillation curve are plotted versus $z\,(T_B)$, and the area under the curve as before must be equal to unity.

T.B.P. curves for bubble-point vapor and dew-point liquid can be determined by solving equations (99) and (100) at their respective equilibrium temperatures by successive increments.

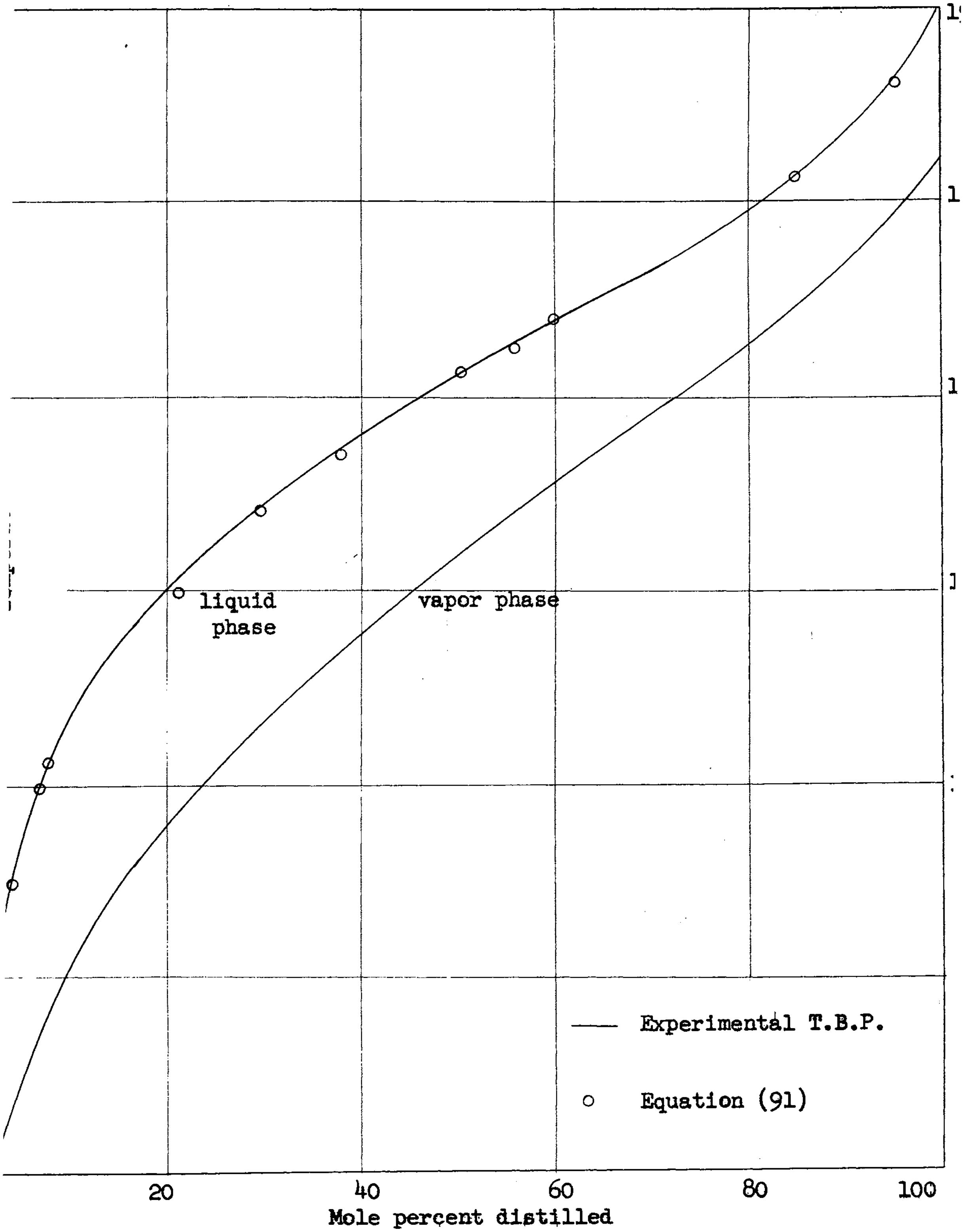

Figure 79 - Typical Application of Equation (91) - Oil A, T_e = 141.2 °C

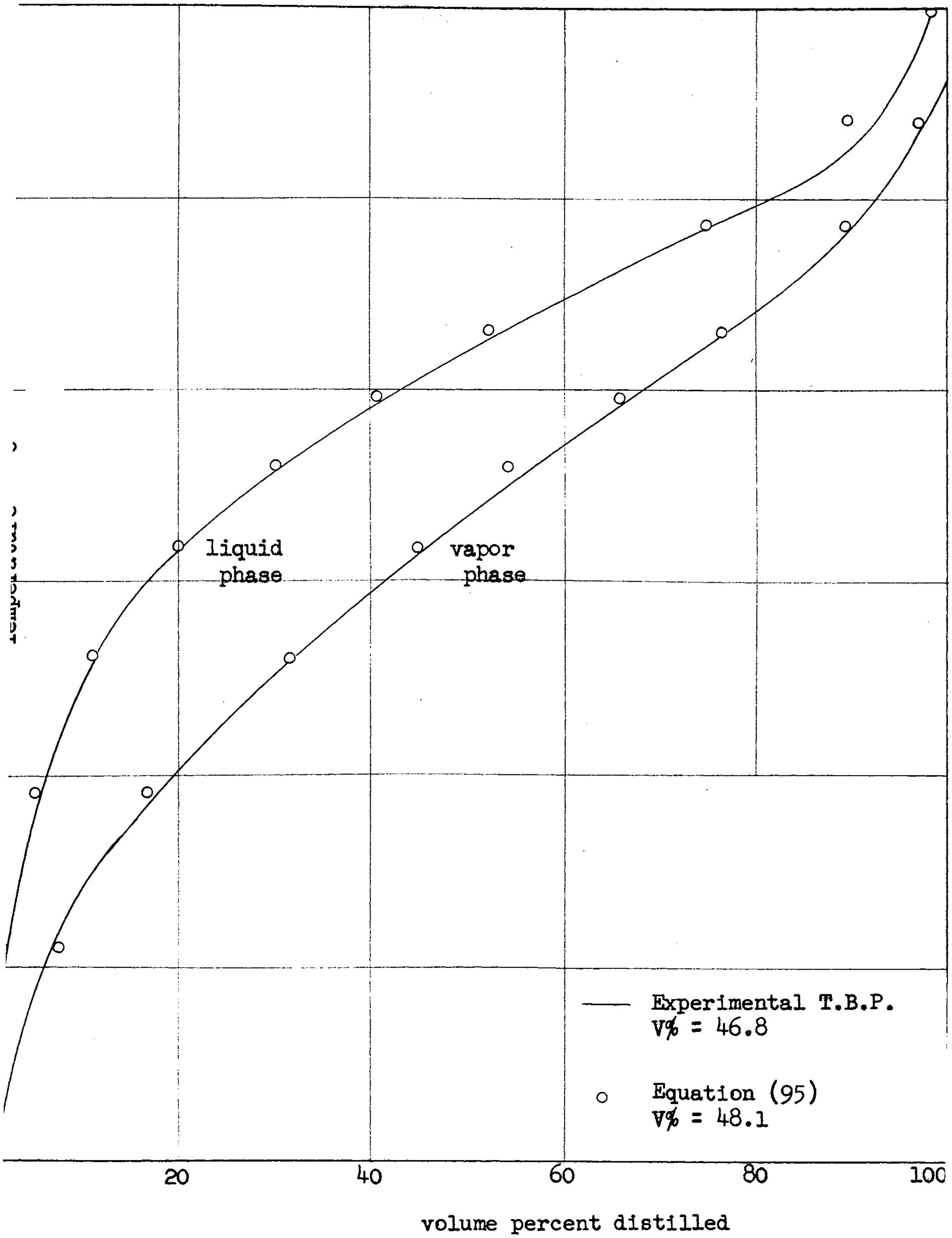

Figure 80 - Typical Application of Equation (95) - Oil A, T_e = 141.2 °C

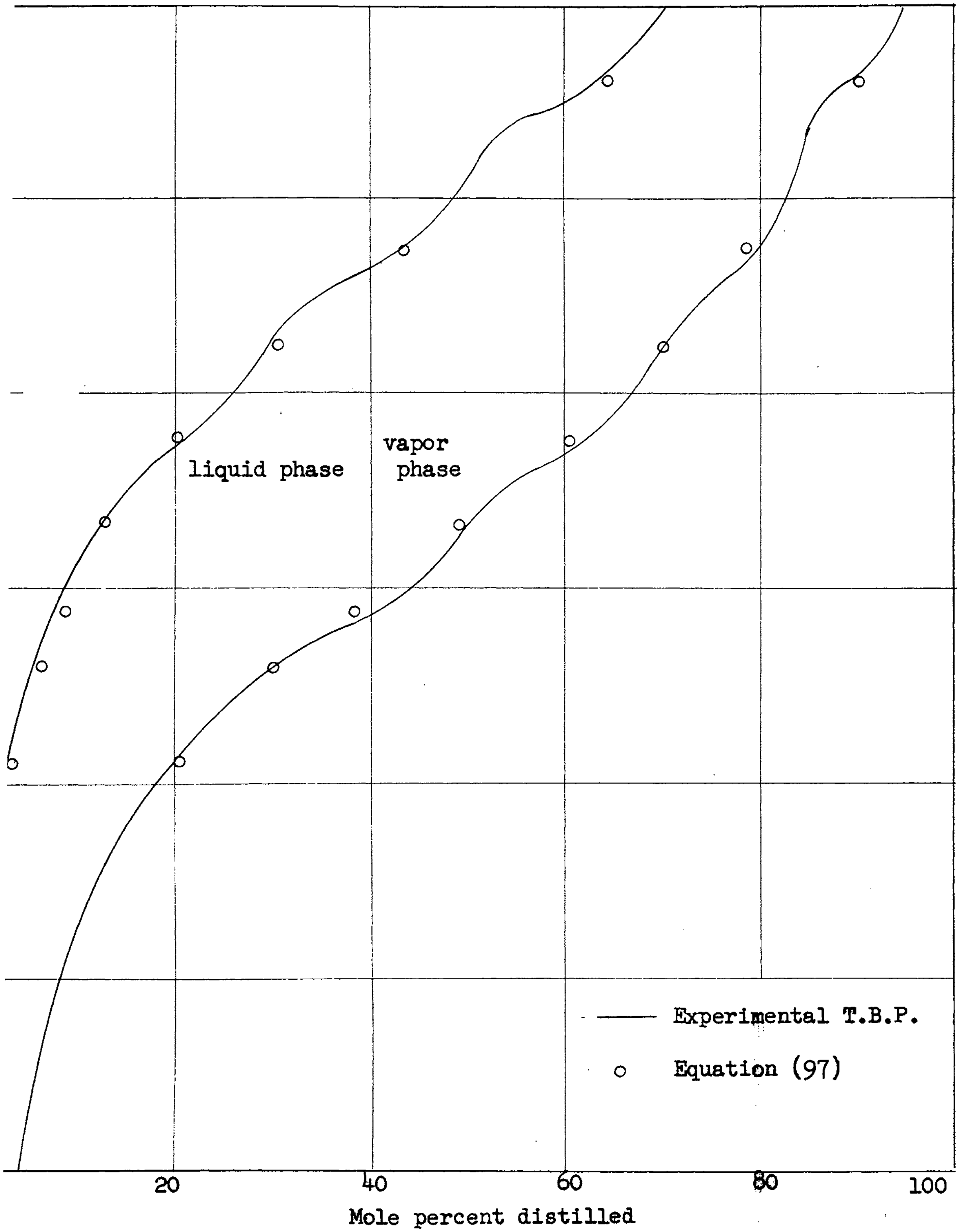

Figure 81 - Typical Application of Equation (97) - Oil G - $T_e = 234$ °C

CHAPTER IX

SUMMARY AND SUGGESTIONS FOR FUTURE STUDIES

The main objective of this investigation was the development of apparatus and techniques for evaluation of vapor-liquid equilibrium phase distribution coefficients (K-values) of petroleum fractions. These coefficients were to be presented in a useful and reliable form, and to be used in calculation of equilibrium vaporization process by some integral techniques. In order to achieve the goal, many related branches were studied independently, and they were finally consolidated in Chapters VII and VIII. To avoid duplications, the extensive discussions which are incorporated in Chapters III through VIII, are not reproduced here. The following are the summary of the main contributions of this investigation.

1. Survey of previous works in the fields of theory of equilibrium, vapor-liquid equilibrium apparatus, T.B.P. distillation, chromatography, molecular weight measurement of petroleum, and integral technique.
2. Modification and complete evaluation of the Othmer still, and a thermostatic flow equilibrium equipment.
3. Design and evaluation of a new flow equilibrium apparatus.
4. Suggestion of reliable techniques, used for ascertaining the condition of equilibrium in connection with the operation

of the apparatus.

5. Evaluation of the Oldershaw column, introduction of intermittent and transient distillation, and formulation of a sound technique for T.B.P. distillation.

6. Use of chromatography for analysis of simple petroleum fractions, and its application in conjunction with molecular weight measurement and equilibrium apparatus operation.

7. Introduction of some improved techniques for measurement and presentation of molecular weight of petroleum fraction.

8. Suggestion and comparison of various techniques for K-value derivation from experimental flash data and analytical assays.

9. Development of equations for K-values of petroleum oils, and T.B.P. curves.

10. Presentation of an integral formula (based on volumetric T.B.P. data), and application of the existing one for testing the experimental K-values, and equilibrium vaporization process.

Suggestions for Future Investigations

There are many problems encountered in any investigation. The researcher must set an over all objective and not deviate too far from it. However this is often difficult, because many of these relevant problems are both important and interesting. Since the objective must be achieved under some limited conditions, therefore these problems must be merely noted and be intrusted to the researchers to come. This section serves to point out the fields where further investigations should be desired.

1. Equilibrium Equipment: Although great efforts have been directed toward vapor-liquid equilibrium equipment design and operation, further systematic studies along the following lines investigated are needed:

    a) Study of theory of equipment design, leading to a more objective approach in design, evaluation and operation of apparatus.

    b) Further investigation of the techniques for ascertaining the condition of true equilibrium

2. Improvement of T.B.P. Equipment: It has already been mentioned that the consistency of results depend greatly on the accuracy and the reproducibility of T.B.P. distillation curves. Although Oldershaw distillation column, and the presented operating method have proved to be quite satisfactory, nevertheless the following suggestions are constructive.

    a) Use of automatic recorder, where the turning of the chart would be proportional to the volume distilled, and the top temperature be continuously recorded on it. This should noticeably improve the accuracy of T.B.P. plot, and practically eliminate the personal attention required during the entire operation.

    b) When the column is used for analysis of high boiling oils, then it should be operated at a constant reduced pressure. Also the column must be insulated with proper heating mantle.

c) Use of efficient spinning band and wetted wall columns in connection with smaller sample quantities.

3. Chromatography: Extensive use of chromatography for direct analysis of some simple petroleum fractions, and its application for indicating the true equilibrium condition of vaporization of petroleum oils should receive some additional attention.

4. Empirical Relationships: The techniques and the apparatus which are presented in this work, have made the experimental determination of K-values of petroleum oils an easy task. The K-values taken from the generalized charts are evidently less accurate than the experimental values. Therefore it is recommended that the K-values be evaluated experimentally, whenever possible. However, the empirical relations are useful for interpolation, extrapolation, and improvement of data. The following are a few important aspects of this phase of work, where further investigations are helpful.

a) Further study in the direction of characterizing petroleum oils by their molal volume-boiling temperature curves.

b) Study of the trend of variation of slopes and intercepts of K-value equations (77,78) as functions of equilibrium temperature, over some much wider temperature ranges.

Also application of equation (74) to represent data with wider boiling ranges.

c) Continuation of this study at other pressures.

d) Further study of the effect of blending of petroleum fractions on K-values.

e) Computer application of the suggested equations.

5. Integral Technique: The engineering importance of integral technique has already been discussed. Therefore, additional extension of this method would have a great industrial utility.

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APPENDIX A

DEFINITION OF TERMS

A = Helmholtz function, Total heat transfer area

a = Activity

B = Virial coefficient of state

b = Vaporization rate in the recirculation still

C = Constant

D = Distillate

dl/dT_B - Reciprocal of slope of T.B.P. curve of liquid phase on volume basis

dv/dT_B - Reciprocal of slope of T.B.P. curve for vapor phase on volume basis

dx/dT_B - Reciprocal of slope of molal T.B.P. curve for liquid phase

dy/dT_B - Reciprocal of slope of molal T.B.P. curve for vapor phase - (the numerical values of these slopes are relative quantities)

F = Total volume of feed

f = Fugacity, Mole percent (T.B.P. analysis) of feed

G = Gibbs function

H = Enthalpy

K = Vapor-liquid equilibrium phase distribution coefficient

k_f = Cryscopic constant

L = Total volume of liquid phase

l = Volume percent (T.B.P. analysis) of equilibrium liquid phase

M = Molecular weight of solvent (Chap. VI), molecular weight of each fraction

m = Molecular weight of solute (Chap. VI)

N = Mole fraction in solution

n = A component of system, Number of distillation plates

P = System pressure

P_e = Equilibrium pressure

p = Partial pressure

Q = Total heat loss

q = Heat loss per actual plate

R = Universal gas constant

S = Entropy

T = Temperature

T_B = T.B.P. temperature, the normal boiling point - °C

T_e = Equilibrium temperature - °C or 1/°K

ΔT_f = Freezing point depression (for 1 to 100 volumetric solvent-benzene to solute ratio) - °C

$(\Delta T'_f/\Delta T_f)_p$ = Ratio of ΔT_f of liquid and vapor phases in equilibrium with each other

U = Internal energy, Over-all heat transfer coefficient

V = Total volume of vapor phase

v = Volume percent (T.B.P. analysis) of equilibrium vapor phase

W = Watt, Weight of solvent

w = Weight of solute

X = Total moles of liquid phase

x = Mole percent (T.B.P. analysis) of equilibrium liquid phase

Y = Total moles of vapor phase

y = Mole percent (T.B.P. analysis) of equilibrium vapor phase

Z = Total moles of feed

z = Mole percent (T.B.P. analysis) of feed, Gas compressibility facto

α = Relative volatility, A constant
ρ = Density
ν = Fugacity coefficient
θ = A function, Time
ψ = A function
μ = A constant
γ = Activity coefficient, A constant

Subscripts

a = Ambient condition
f = Freezing point
l = Liquid
m = Mean value
s = Solid
v = Vapor
1, 2, · · · i, j, k = Number of component

Superscripts

' = Liquid phase
'', ''' = A phase
o = Standard state
* = In equilibrium
f = Final condition

Specifications

A.S.T.M. = American Society for Testing of Materials
B.P. = Boiling point
Cal. = Calorie
cc. = Cubic centimeter

m. = Centimeter

.C. = Extra coarse

.P. = Final boiling point

t. = Foot

.L.C. = Gas-liquid chromatography

.S.C. = Gas-solid chromatography

r. = Gram

Hr., hr = Hour

I.B.P. = Initial boiling point

liter = Liter

L.S.C. = Liquid solid chromatography

min. = Minute

mm. = Millimeter

T.B.P. = True boiling point

§ = Ball joint

₸ = Tapered joint

APPENDIX B

EXPERIMENTAL AND CALCULATED DATA

TABLE I

EVALUATION OF VAPOR-LIQUID EQUILIBRIUM APPARATUS WITH BINARY MIXTURES

Othmer still
Toluene and acetic acid mixture at 1 Atm.
total charge = 1 Lit.
(Literature - D. F. Othmer, Ind. Engr. Chem., 35, 614, 1943)

Equilibrium Temperature in °C	Mole percent toluene	
	Liquid	Vapor
105.0	38.90	22.20
105.5	38.09	22.20
107.5	30.06	14.61
107.5	30.00	13.75
106.5	92.80	95.25
106.7	89.05	95.05

Othmer still
Benzene and Toluene mixture at 1 Atm.
Total charge 1 to 2 Lit.
(Literature - E. Kirschbaum, "Distillation and Fractionation", Chem. Pub. Co., N. Y. 1948)

Over flow manifold

Equilibrium Temperature in °C	Mole percent benzene	
	Liquid	Vapor
99.0	28.20	48.30
97.5	34.55	55.50
105.5	11.50	25.50
90.0	56.80	77.20
85.5	75.00	88.40
100.5	24.70	43.60
84.5	90.80	96.00
98.5	28.30	47.80
106.0	9.15	21.65

Teflon needle valve

Equilibrium Temperature in °C	Mole percent benzene	
	Liquid	Vapor
81.0	95.00	97.50
84.5	79.20	90.80
82.0	90.75	96.00
88.5	73.55	84.50
97.0	35.20	56.80
93.0	47.60	70.20
105.0	12.60	27.45

Thermostatic flow equipment
Benzene and toluene mixture at 1 Atm.
With various feed compositions

Equilibrium Temperature in °C	Mole percent benzen	
	Liquid	Vapor
100	26.05	45.10
100	26.15	45.00
100	25.85	45.00
100	26.10	45.20

Cont.

Thermostatic flow equipment
Toluene and n-C_8 mixture at 1 Atm.
(Literature - Bromiley, E. C., and D. Quiggle, Ind. Eng. Chem., 25, 1136, 1933)
Constant feed composition
Equilibrium temperature = B.P. of 2, 3, 4 trimethyl-C_5

Feed Rate in ml/min.	Mole percent toluene	
	Liquid	Vapor
11.0	83.70	87.25
14.0	83.70	87.25
16.5	84.40	87.25
20.5	84.40	87.25
22.5	84.40	87.25
28.0	84.40	86.70
31.0	84.15	86.75
39.5	83.70	86.60
47.0	83.70	87.10
55.0	84.00	87.10
65.0	83.75	87.10
70.0	84.00	87.10
90.0	84.10	87.10
110.0	84.10	87.10

The new equilibrium flow equipment
Benzene and toluene mixture at 1 Atm.
(with max. hold-up in the contacting section)

Equilibrium temperature in °C	Mole percent benzene	
	Liquid	Vapor
108	4.3	12.5
107	5.6	16.0
107	6.4	17.5
106	10.5	23.8
106	10.3	23.5
103	15.5	31.6
103	15.4	31.6
102	19.6	37.0
-	21.3	38.7
100	28.0	47.5
96	37.2	59.6
96	38.3	59.8
-	38.5	60.5
96	41.2	63.5
93	48.8	71.2
92	52.2	74.0
90	60.5	79.3
90	61.2	80.0
96	72.5	86.4
86	73.6	87.8
84	84.2	93.0
-	85.2	93.2
-	87.0	94.5

Cont.

The new equilibrium flow equipment
Toluene and n-C_8 mixture at 745 mm. Hg.
(with min. hold-up in the contacting section)

Mole percent toluene Liquid	 Vapor
25.5	37.5
31.3	48.3
31.0	49.3
31.3	51.2
28.7	41.3
27.1	37.7
26.3	36.3
43.9	53.7
44.3	56.5
46.0	61.5
57.1	69.2

The new equilibrium flow equipment
Toluene and n-C_8 mixture at 745 mm. Hg.
(with max. hold-up in the contacting section)

Mole percent toluene Liquid	 Vapor
41.5	52.6
38.7	49.7
38.7	50.2
41.2	52.5
41.1	54.3
50.2	61.5
48.3	59.1
58.3	68.4
65.0	73.2
70.4	77.8
69.1	76.0
33.7	45.2
33.3	43.7
17.2	25.2
21.0	30.0
74.5	80.1
80.3	84.8
81.2	85.1
81.0	85.0
92.1	93.7
93.9	95.0
93.4	91.0
27.3	39.2
91.0	92.5
29.2	40.8
27.6	38.9

TABLE II

COMPARISON OF THE EQUILIBRIUM APPARATUS BY MEANS OF A PETROLEUM FRACTION

Oil C
Sp. Gr. = 0.811

Vol. %	Sp.Gr.	T.B.P. °C	A.S.T.M. °C
I.B.P.		126.0	190.5
2.5		162.0	-
5	.770	172.5	-
10	.781	185.0	202.5
15	.786	192.5	-
20	.787	197.5	213.0
25	.799	207.0	-
30	.799	212.5	221.5
35	.795	217.5	-
40	.805	224.0	230.0
45	.812	230.0	-
50	.808	234.0	239.0
55	.814	242.5	-
60	.819	249.0	248.0
		A.S.T.M.	
60		250.0	
65		266.0	
70		269.0	256.0
75		270.0	-
80		273.5	261.0
85		276.0	-
90		280.0	271.0
95		287.0	288.0
E.P.	.834	300.0	300.0

Othmer still		Thermostatic flow equipment		The new equilibrium equipment	
T_e in °C	V%	T_e in °C	V%	T_e in °C	V%
230.5	14.3	234.0	18.2	236.0	19.5
238.5	25.9	244.0	50.8	234.0	16.8
243.0	43.5			236.0	21.6
245.0	59.4			239.0	29.8
				240.0	32.5
				242.0	42.1
				245.0	54.4
				247.0	64.8

TABLE III

VACUUM OPERATION OF THE NEW EQUILIBRIUM EQUIPMENT

Oil E
Sp. Gr. = .805

A.S.T.M.	
Vol.%	°C
I.B.P.	160.0
10	180.5
20	196.0
30	205.5
40	214.0
50	220.5
60	229.5
70	239.0
80	251.0
90	272.0
E.P.	323.0

Equilibrium Flash					
250 mm.Hg.		450 mm.Hg.		745 mm.Hg.	
V%	T_e in °C	V%	T_e in °C	V%	T_e in °C
0	145	0	166	0	186
9.1	154	11.1	176	13.5	198
15.9	160	35.0	189	47.5	213
21.0	162	45.9	193	48.4	214
36.4	171	74.2	205	67.3	220
64.8	182	94.3	218	100	238
86.2	193	100	224		
100	209				

TABLE IV

HEAT LOSS AND PRESSURE DROP OF OLDERSHAW DISTILLATION COLUMN

40-plate Oldershaw, as it was used for T.B.P. distillation

Boiling Material	Pressure Loss in inches of Liquid	Heat Loss in ml. of boiling liquid/Hr.	Heat Loss in K Cal./Hr.	Over Head Rate in ml./Hr.	Boil-up Rate in ml./Hr.	Tower Temp. °C	Ambient Temp. in °C
Benzene	15.0	122.5	9.32	1000	1111	80	35
"	20.0	104.0	7.95	2000	2096	80	35
"	23.0	111.0	8.47	3000	3102	80	35
Toluene	15.5	270.0	18.35	1000	1244	110	32
"	20.0	270.0	18.35	2000	2244	110	32
"	23.0	266.0	18.20	3000	3240	110	32
O-xylene	14.5	440.0	28.23	1000	1388	144	35
"	17.5	460.0	29.55	2000	2405	144	34.5
"	22.5	452.0	29.00	3000	3398	144	34
O-Ethyl-	14.0	645.0	39.50	1000	1582	165	36
Toluene	15.7	636.0	39.00	2000	2575	165	36
"	17.5	634.0	38.80	3000	3572	165	36
2,2,4 Tri	15.0	373.0	14.80	1000	1338	99.8	33
methyl-C_5	15.5	370.0	14.68	2000	2335	99.8	33
"	17.0	357.0	14.13	3000	3230	99.8	34
n-C_{10}	14.0	960.0	38.20	1000	1802	174	35
"	14.5	1015.0	40.60	2000	1848	174	35
"	15.0	1000.0	40.10	3000	3835	174	34.5

TABLE V

START-UP CHARACTERISTICS OF OLDERSHAW COLUMN

Testing mixture = benzene and toluene
Boil-Up rate = 2.25 Lit./Hr.

Time in Min.	Condition of Operation						
	30-plate Total Reflux	30-plate Total take off	15-plate Total Reflux	15-plate Total take off	15-plate 1/1 Reflux (4 Sec.cycle)	15-plate 1/1 Reflux (10 Sec.cycle)	15-plate 1/1 Reflux (20 Sec.cycle)
	Pot.Comp=10.48	10.48	9.50	8.50	7.50	7.50	9.14
	Over-head concentration in mole percent benzene						
0	97	97	95	94	88	88	95
1/3	93	91	74	--	69	70	73
2/3	89	88	61	--	59	59	62
1	83	60	50	21	50	50	50
1 1/3	73	--	46	18	--	--	--
1 2/3	71	--	47	17	--	--	43
2	69	30	48	18	32	34	41
2 1/3	69	--	--	--	--	--	40
2 2/3	68	22	50	--	--	--	39
3	69	--	52	19	27	28	38
3 1/3	70	22	53	--	--	--	--
3 2/3	71	--	54	--	--	--	--
4	73	23	56	20	27	--	--
5	79	--	60	21	26	--	33
6	83	--	63	--	--	--	--
7	87	--	66	--	--	--	32
8	90	--	70	--	--	--	32
10	97	--	77	21	25	--	32
12	98	--	83	--	--	--	32
15	98	--	90	21	--	--	32
20	99	23	--	21	--	--	--
60	99.8	--	95	--	--	--	--

TABLE VI

EFFECT OF BOIL-UP RATE AND REFLUX RATIO UPON OPERATING (DYNAMIC) HOLD-UP

0-plate Oldershaw column, as it was used for T.B.P. distillation.

esting material - iso-octane

oil-Up Rate in ml/Hr	Operating Condition	Total Hold-Up in ml.	Hold-Up/Plate in ml.
650	Total Reflux	58.0	1.450
1500	Total Reflux	64.5	1.612
2220	Total Reflux	66.2	1.652
2820	Total Reflux	67.0	1.675
485	Total Take off	25.5	.637
1500	Total Take off	32.0	.800
2220	Total Take off	33.0	.825
2820	Total Take off	34.2	.855

Testing material - n-heptane

1500	Total Reflux	63.5	1.588
1810	Total Reflux	64.2	1.604
2000	Total Reflux	65.0	1.625
2240	Total Reflux	65.8	1.645
2550	Total Reflux	66.7	1.665
3140	Total Reflux	68.5	1.712

Static Hold-Up

Total static hold-up (average value)= 0.86 ml.
Static hold-up/plate (average value)= 2.15 x 10^{-2} ml.

TABLE VII

EFFECT OF CYCLE OF INTERMITTENT PRODUCT TAKE-OFF ON EFFICIENCY

0-plate Oldershaw column
oil-Up Rate = 2.25 Lit/Hr.
esting mixture = benzene and toluene

roduct ake-off ycle in econds	D/L=4/1	D/L=2/1	D/L=1/4	D/L=1/1		
				at the beginning of take off cycle	at the end of take off cycle	Product Concentration
			mole percent benzene in over-head			
5	41.5	25.0	16.0	25.0	25.0	25.0
10	42.0	--	--	27.0	27.0	27.0
15	--	27.0	--	--	--	--
20	--	--	--	30.0	27.5	28.5
25	49.0	--	16.0	--	--	--
30	--	30.0	--	33.0	27.5	29.5
40	50.0	33.0	16.0	35.0	27.0	30.5
50	50.5	--	16.0	39.0	26.0	31.0
60	51.5	35.5	--	42.0	23.5	31.5
80	54.0	--	16.0	--	--	--
90	55.0	35.0	--	--	--	--
100	55.0	--	--	49.0	20.0	32.5
120	55.0	35.0	16.0	50.0	20.0	33.0
140	55.0	--	--	--	--	33.0

ote: The pot composition of each run is different.
= Product Rate, L = Reflux Rate

0-plate Oldershaw column
esting mixture = toluene and nC_8

roduct ake-off ycle in econds	D/L=1/4	1/2	2/1	1/2	2/1
	Rate=3.0 Lit./Hr.	3.0	3.0	2.9	2.9
	Pot.Comp.=14.2	15.5	15.5	17.0	17.0
		mole percent toluene in over-head			
3	--	35.2	26.7	37.2	27.6
5	49.5	--	--	--	--
9	--	--	--	41.0	--
10	52.7	--	--	--	--
15	--	40.2	27.8	--	28.8
25	56.1	--	--	--	--
60	--	--	27.6	--	28.5
100	62.2	--	--	--	--

ont.

Product	D/L = 1/2	2/1	1/1	4/1
take-off	Rate = 1.08 Lit./Hr.	1.08	1.08	1.08
cycle in	Pot.Comp. = 22.5	22.5	21.5	22.5
seconds	mole percent toluene in over-head			
2	--	33.8	--	--
3	--	35.8	--	--
5	48.7	--	--	33.3
6	--	36.5	41.3	--
9	--	37.3	--	--
10	--	--	42.7	33.9
15	51.5	--	--	34.0
16	--	--	44.1	--
20	--	--	44.5	34.0
25	--	--	--	34.0
30	--	37.5	--	35.0
40	--	--	--	34.3
45	--	37.5	--	--
75	--	--	--	34.3
90	--	37.5	--	--
100	--	--	--	34.3
125	--	--	--	34.3

TABLE VIII

EFFECT OF BOIL-UP RATE UPON EFFICIENCY

10-plate Oldershaw column
Test mixture = toluene and nC_8
Condition of Operation = Total Reflux
Bottom composition = 28.8 percent toluene

Boil-Up rate in Lit./Hr.	Over-head composition in mole% of toluene	Plate efficiency
.42	75.8	61.0
.89	77.7	63.7
1.04	78.0	64.5
1.38	78.3	65.2
1.41	78.7	65.7
1.76	78.9	66.1
2.21	79.8	67.7
3.02	80.0	68.0
3.75	78.5	65.5
4.21	75.0	59.6
at flooding	61.2	40.4

TABLE IX

COMPARISON OF PERFORMANCES OF DISTILLATION APPARATUS

Oil D (hydroformer product) at 1 Atm.

Vol.% distilled	40-plate Oldershaw D/L = 12/1	Sarnia D/L = 12/1	Sarnia D/L = 5/1
	T.B.P. temperature in °C		
0	60.5	61.0	61.0
5	61.5	71.5	80.0
10	71.0	78.0	88.0
15	78.5	81.0	90.0
20	79.5	85.0	93.0
25	88.5	89.0	96.0
30	97.0	91.0	99.0
35	108.0	93.5	102.0
40	109.0	97.0	105.0
45	109.5	100.0	
50	109.5	108.0	
55	110.0	112.0	
60	110.0	116.0	
62.5	120.0	--	
65	134.0	119.0	
70	138.0	123.0	
75	138.0	126.5	
80	138.5	129.5	
85	139.0	131.5	
87.5	140.0	--	
90	141.0	132.0	
92.5	143.0	--	
95	156.0	--	
97.5	171.0	--	
100	196.0	--	

TABLE X

COMPARISON OF T.B.P. AND G.L.C. ANALYSES

Oil D (hydroformer product)
40-plate Oldershaw - at 1 Atm.

Analysis of Charge	Mole%
light	trace
n-C_5	0.133
i-C_6	1.823
i-C_6(60°C)	1.657
n-C_6	2.154
hexene-1	.928
i-C_7	2.552
3m-C_6	3.248
n-C_7	2.088
3-Cyclo-C_6	.895
n-C_8	.265
Benzene	11.468
Toluene	31.058
(p,m)xylene	34.471
o-xylene	6.463
Heavy	trace

T.B.P. Vol.%	T.B.P. °C	G.L.C. mole percent
0	60.5	benzene 4.42; i-C_6 11.60; i-C_6(60°C) 17.30; n-C_6 66.30; hexene-1 .28; C_5 1.0
10	71.0	benzene 28.3; i-C_6 7.42; i-C_6(60°C) 15.12; n-C_6 34.36; hexene-1 6.87; m-C_6 7.97
20	79.5	benzene 78.09; m-C_6 10.46; 3m-C_6 10.46; hexene-1 .57;
30	97.0	n-C_7 2.0; m-C_6 9.20; 3m-C_6 1.25; benzene; toluene
40	109.0	benzene .41; toluene 95.36; n-C_7 .12; m-Cyclo-C_6 .3
50	109.5	toluene 97.31; m-Cyclo-C_6 2.68; n-C_7
60	110.0	toluene 97.96; m-Cyclo-C_6 1.32; n-C_7 .7; xylene
70	138.0	(p, m) xylene 95.2; O-xylene 4.7; toluene
80	138.5	(p, m) xylene 89.20; o-xylene 10.80
90	141.0	(p, m) xylene 43.04; o-xylene 56.96
100	196.0	heavy; o-xylene - trace

TABLE XI

EQUILIBRIUM FLASH VAPORIZATION OF OIL D (HYDROFORMER PRODUCT) AND CALCULATION OF K-VALUES BY G.L.C. ANALYSIS

ressure = 740 mm. Hg.

	T_e=110.6°C		T_e=99.8°C		T_e=125.7°C	T_e= 105.2°C		T_e=119.8°C	
	y/x	p/P	y/x	p/P	y/x	y/x	p/P	y/x	p/P
ight	--	--	--	--	--	--	--	--	--
-C_5	16.796	--	10.400	--	27.100	--	--	--	--
-C_6	11.310	--	7.334	--	18.352	8.233	--	5.274	--
-C_6(60°C)	8.006	--	5.322	--	17.944	6.248	--	4.817	--
-C_6	5.255	--	3.905	--	16.000	4.297	--	4.945	--
exene-1	4.083	3.785	2.411	2.840	14.308	3.547	--	3.620	4.45
-C_7	2.972	1.930	2.772	--	8.739	2.604	--	2.872	2.350
3m-C_6	2.860	1.770	1.344	1.310	6.414	2.084	--	2.449	2.220
-C_7	1.577	1.468	.862	1.090	4.615	1.540	1.260	2.165	1.890
-cyclo-C_6	1.165	1.720	.910	.985	1.858	1.106	1.140	1.318	1.690
-C_8	1.431	--	.537	.487	1.552	.891	.582	1.264	1.031
enzene	2.477	2.462	2.181	1.840	--	2.449	2.110	3.043	3.081
toluene	1.056	1.053	.896	.764	1.554	1.047	.906	1.429	1.350
(p,m)xylene	.497	.457	.287	.314	.397	.387	.379	.599	.601
o-xylene	.389	.385	.249	.265	.361	.281	.218	.491	.507
heavy	--	--	--	--	--	--	--	--	--

	T_e=116°C		T_e=91.5°C	T_e=111.2°C		T_e=105.5°C		T_e=116.5°C	
	y/x	p/P	y/x	y/x	p/P	y/x	p/P	y/x	p/P
light	--	--	--	--	--	--	--	--	--
n-C_5	16.523	--	7.879	11.583	--	6.077	--	--	--
i-C_6	5.718	--	6.765	5.713	--	4.394	--	4.088	--
i-C_6(60°C)	4.936	--	4.105	8.979	--	4.659	--	3.773	--
n-C_6	5.174	--	5.250	5.666	--	3.916	--	3.119	--
hexene-1	4.053	4.090	3.470	4.256	3.68	4.313	--	3.346	4.0
i-C_7	2.916	2.120	2.412	2.329	1.90	2.830	--	1.934	2.1
3m-C_6	2.554	4.020	1.988	2.427	1.75	2.486	--	2.246	2.0
n-C_7	2.138	1.700	1.590	2.062	1.46	2.182	--	2.068	1.7
m-cyclo-C_6	1.453	1.521	.804	1.202	1.35	1.881	1.140	1.155	1.5
b-C_8	1.267	.810	.837	.824	.68	1.813	--	.848	.8
benzene	2.833	2.780	2.300	2.858	2.46	2.555	2.110	2.460	2.7
toluene	1.243	1.210	.768	1.347	1.06	1.166	.906	1.417	1.2
(p,m)xylene	.606	.535	.159	.467	.45	.383	.379	.600	.5
o-xylene	.412	.413	.124	.376	.38	.325	.318	.427	.4
heavy	--	--	--	--	--	--	--	--	--

The new equilibrium equipment T_e=125.7, 105.2, 119.8, 116, 91.5, 111.2, 1
116.5°C.

The thermostatic flow equipment T_e=99.8, 110.6°C.

TABLE XII

K-VALUES CALCULATED FROM EXPERIMENTAL WORK OF WHITE AND BROWN (152)

Material - light naphtha
Conditions - 700 °F, 650 psia [Exp. No. 8, (152)]

T.B.P. Temp. Range - °F	Moles of vapor	Moles of liquid	K (Brown)	This method	
				T_B - °F	K
86-95	43.78	31.49	1.39	350	.91
135-156	10.72	13.74	1.22	375	.85
175-209	10.25	8.30	1.24	400	.80
209-300	2.13	1.85	1.15	425	.78
300-350	1.95	2.15	.91	450	.72
350-400	3.95	5.06	.78	475	.71
400-450	4.00	4.35	.92	500	.67
450-500	3.30	5.35	.62	525	.59
500-550	3.16	4.93	.64	550	.58
550-600	4.14	8.18	.51	575	.52
600-650	3.72	7.13	.52	600	.51
650-700	1.88	4.50	.42	625	.50
700-750	1.02	2.98	.34	675	.42

TABLE XIII

PHYSICAL PROPERTIES OF OIL A

Vol.% Distilled	T.B.P. Temp. °C	ΔT_f °C	$(\Delta T_f)_{ave.}$ °C	$(Sp.\ Gr.)_{ave.}$	M.Wt.
I.B.P.	64.0	.531			87.0
			.495		
5	95.5	.462		.725	94.4
			.453		
10	105.5	.440			99.8
			.432		
15	117.5	.419		.735	104.0
			.413		
20	122.0	.410			108.0
			.406		
25	125.5	.402		.742	109.2
			.397		
30	133.5	.390			111.5
			.387		
35	137.5	.382		.766	114.2
			.380		
40	142.0	.376			116.7
			.370		
45	146.5	.368		.750	118.3
			.365		
50	149.0	.363			121.0
			.360		
55	151.5	.359		.766	122.8
			.358		
60	155.0	.353			123.2
			.352		
65	159.0	.347		.771	125.0
			.345		
70	162.0	.342			127.2
			.340		
75	165.5	.338		.776	132.5
			.335		
80	169.0	.332			132.0
			.330		
85	171.5	.329		.767	134.0
			.323		
90	178.0	.320			136.3
	A.S.T.M.		.317		
95	182.5	.314		.775	142.0
			.306		
E.P.	190.5	.302			--

TABLE XIV

EQUILIBRIUM PROPERTIES AND K-VALUES OF OIL A

quipment - Othmer still
onditions - P_e = 1 Atm.; T_e=141.2°C; percent vapor = 46.8

	Vapor				Liquid			
ol.% istilled	T.B.P. °C	Sp.Gr.	$(\Delta T_f)_{ave.}$	Mole%	T.B.P. °C	Sp.Gr.	$(\Delta T_f)_{ave.}$	Mole%
I.B.P.	95.5			0	69.0			0
5	87.0	.716	.470		104.0	.742	.420	
10	96.0			12.1	120.0			11.6
15	100.5	.741	.441		125.5	.747	.400	
20	111.0			23.4	132.0			22.7
25	118.0	.734	.420		137.5	.756	.382	
30	121.0			34.2	142.0			33.3
35	124.0	.739	.408		146.0	.759	.370	
40	127.0			44.7	148.0			43.5
45	132.5	.764	.390		150.0	.772	.363	
50	137.0			54.8	153.0			53.6
55	141.0	.760	.377		156.0	.773	.353	
60	145.0			64.5	159.0			63.3
65	148.0	.751	.367		162.0	.779	.342	
70	150.5			73.9	166.0			72.8
75	153.5	.765	.353		168.0	.779	.337	
80	158.5			83.0	170.5			82.1
85	163.0	.780	.340		172.0	.780	.330	
90	168.0			91.8	175.0			91.2
95	173.0	.772	.322		182.0	.780	.320	
E.P.	182.0			100.0	193.0			100.0
Conditions - P_e = 1 Atm; T_e = 134°C; percent vapor = 31.9								
I.B.P.	65.0			0				0
5	87.0	.716	.482		100.0	.738	.452	
10	95.0			12.1	118.5			12.2
15	99.0	.734	.455		123.5	.737	.408	
20	105.0			23.3	129.0			23.4
25	115.0	.735	.431		133.0	.764	.391	
30	119.0			33.6	140.0			34.4
35	122.5	.730	.410		145.0	.752	.368	
40	125.0			43.6	147.0			44.5
45	129.0	.752	.397		149.0	.753	.363	
50	134.0			52.5	151.0			54.2
55	137.5	.763	.382		155.0	.755	.353	
60	143.0			62.7	157.5			63.9
65	146.5	.751	.370		161.0	.772	.348	
70	149.5			72.2	164.0			73.4
75	162.0	.758	.361		168.0	.776	.328	
80	157.0			81.7	170.0			82.4
85	162.0	.773	.343		172.0	.765	.323	
90	167.0			90.9	174.0			91.2
95	172.5	.774	.328		180.0	.777	.318	
E.P.	180.0			100.0	192.0			100.0

Cont.

Equipment - Othmer still
Conditions - P_e = 1 Atm.; T_e = 144.5°C; percent vapor = 53.9

	Vapor				Liquid			
Vol.% Distilled	T.B.P. °C	Sp.Gr.	$(\Delta T_f)_{ave.}$	Mole%	T.B.P. °C	Sp.Gr.	$(\Delta T_f')_{ave.}$	Mole%
I.B.P.	66.0			0	84.0			0
5	90.0	.720	.470		112.0	.731	.450	
10	97.0			12.3	121.0			11.8
15	108.0	.742	.440		127.0	.742	.425	
20	114.0			23.7	133.0			22.9
25	119.0	.733	.410		135.0	.756	.408	
30	122.5			34.4	143.5			33.6
35	125.0	.738	.400		147.0	.747	.390	
40	131.5			44.8	150.0			43.6
45	136.0	.769	.380		151.0	.750	.380	
50	140.0			54.7	155.0			53.5
55	142.0	.757	.370		158.5	.767	.370	
60	148.0			64.4	161.0			63.2
65	150.5	.752	.355		164.0	.771	.360	
70	153.0			73.6	166.0			72.6
75	156.5	.769	.350		169.0	.770	.355	
80	161.0			82.8	171.0			81.8
85	165.0	.776	.335		173.0	.760	.350	
90	169.0			91.5	175.0			91.0
95	177.0	.772	.320		184.0	.779	.335	
E.P.	185.0			100.0	203.0			100.0

Conditions - P_e = 1 Atm.; T_e = 147.0°C; percent vapor = 59.5

I.B.P.	82.0			0	86.0			0
5	92.0	.717	.460		109.5	.730	.430	
10	99.0			12.2	121.5			12.1
15	108.0	.741	.430		128.0	.745	.393	
20	112.0			23.7	130.0			23.2
25	121.0	.731	.405		139.5	.751	.373	
30	124.0			34.4	145.5			33.8
35	128.5	.748	.392		148.0	.747	.360	
40	133.0			44.8	150.5			43.9
45	137.0	.766	.378		153.0	.753	.350	
50	142.0			54.4	156.0			53.8
55	146.0	.752	.362		158.5	.769	.346	
60	149.0			63.8	162.5			63.5
65	151.0	.755	.355		165.0	.770	.335	
70	154.0			73.3	167.5			73.0
75	158.5	.772	.345		170.0	.769	.327	
80	163.0			82.4	172.0			82.2
85	167.0	.777	.330		174.0	.759	.320	
90	171.0			91.1	175.0			91.2
95	178.0	.769	.318		184.0	.778	.308	
E.P.	184.0			100.0	193.0			100.0

Cont.

	T_e = 134.0 °C					T_e = 141.2 °C		
T_B °C	dy/dT_B	dx/dT_B	K	K-Values of Lit. (138)	(88)	dy/dT_B	dx/dT_B	K
60	--	--	--	--	--	7.0	1.0	7.1
75	16.0	3.7	4.30	--	4.40	13.0	2.2	5.90
80	18.5	5.3	3.49	3.70	--	15.0	3.0	5.00
85	22.5	7.5	3.00	--	--	17.0	4.2	4.04
90	25.0	8.3	2.94	3.05	--	19.0	6.0	3.17
95	28.5	11.5	2.48	--	--	22.0	8.0	2.75
100	31.2	14.2	2.20	2.40	2.30	25.0	10.5	2.38
105	34.2	17.2	2.01	--	--	30.0	14.9	2.16
110	36.0	20.5	1.75	1.75	--	36.0	17.3	2.08
115	37.0	25.2	1.51	--	--	41.0	22.0	1.86
120	43.0	29.3	1.47	1.35	--	45.0	26.5	1.69
125	45.5	35.0	1.30	--	--	48.2	33.0	1.82
130	47.2	43.0	1.09	1.10	--	51.0	40.0	1.27
135	47.5	51.5	.92	--	--	55.0	47.0	1.17
140	49.2	59.5	.83	.83	--	56.0	52.0	1.08
145	49.1	65.2	.75	--	--	55.0	57.0	.96
150	47.5	78.0	.61	.68	.64	50.0	61.5	.81
155	45.2	78.0	.58	--	--	43.0	65.0	.66
160	41.7	76.2	.55	.52	--	39.0	66.6	.59
165						34.0	65.7	.52
170						30.0	62.0	.48
175						25.0	55.0	.45
180						18.2	45.0	.40

	T_e = 147.0 °C					T_e = 144.5 °C		
70				6.0	6.3			
85	22.0	5.0	4.40	--	--	17.0	4.0	4.25
90	24.0	7.0	3.43	3.6	--	18.5	5.0	3.70
95	27.0	8.0	3.38	--	--	20.5	6.5	3.17
100	29.0	11.0	2.64	3.0	3.1	23.5	8.0	2.95
105	32.0	13.0	2.46	--	--	27.0	11.0	2.46
110	36.0	14.5	2.48	2.5	--	33.0	14.5	2.28
115	37.5	20.0	1.88	--	--	87.0	20.0	1.86
120	44.0	23.5	1.87	1.8	--	42.0	25.0	1.68
125	44.5	26.0	1.71	--	--	44.0	33.0	1.33
130	45.0	30.5	1.48	1.4	--	49.0	35.0	1.40
135	46.0	41.0	1.12	--	--	52.5	42.0	1.25
140	52.0	43.0	1.21	1.15	--	54.5	46.0	1.16
145	56.0	48.2	1.15	--	--	55.5	52.0	1.06
150	54.0	55.0	.98	.97	.90	55.0	62.0	.89
155	50.5	62.5	.81	--	--	50.0	68.5	.73
160	46.0	71.0	.65	.75	--	45.0	70.0	.64
165	44.5	72.0	.62	--	--	39.0	73.0	.53
170	39.5	72.5	.54	.55	--	36.0	64.0	.56
175	32.0	62.5	.51	--	--	26.0	50.0	.52
180	17.0	36.3	.47	.43	--	16.5	37.0	.45
185	10.0	22.0	.45	--	--			

TABLE XV

PHYSICAL PROPERTIES OF OIL B

Condition - 1 Atm.

Vol.% Distilled	T.B.P. Temp. °C	Sp. Gr.	ΔT_f	M.Wt.
I.B.P.	60.0	--	.640	69.2
5	127.5	.750	.427	102.5
10	137.0	--	.400	108.9
15	142.5	.755	.380	112.5
20	146.8	--	.379	115.3
25	149.0	.760	.375	118.5
30	151.5	--	.370	120.7
35	155.0	.766	.360	123.5
40	158.0	--	.354	125.3
45	161.0	.776	.350	129.0
50	163.2	--	.346	132.0
55	166.0	.780	.340	133.2
60	168.5	--	.334	135.2
65	170.5	.772	.330	136.5
70	172.3	--	.327	137.9
75	175.0	.768	.320	139.5
80	179.0	--	.312	142.5
85	185.0	.787	.302	151.2
90	200.0	--	.276	161.0
95	213.0	.800	.253	186.0
E.P.	275.0	--	.230	212.0

E.F.V.	
T_e-°C	V%
161.5	12.1
162.0	15.6
165.0	50.9
174.5	70.5
196.0	86.2
212.0	89.1

TABLE XVI

EQUILIBRIUM PROPERTIES AND K-VALUES - OIL B

Equipment - Othmer Still at 1 Atm.
Condition - 162.0 °C

	Vapor				Liquid			
Vol.% Distilled	T.B.P. °C	Sp.Gr.	$(\Delta T_f)_{ave.}$	Mole%	T.B.P. °C	Sp.Gr.	$(\Delta T_f')_{ave.}$	Mole%
I.B.P.	62.0	--	--	0	116.0	--	--	0
5	115.0	.718	.532	6.96	136.3	.756	.425	6.42
10	124.0	.730	.450	12.87	143.2	.767	.398	12.35
15	129.0	.732	.440	18.64	147.3	.757	.380	18.10
20	134.0	.756	.418	24.13	149.7	.755	.345	23.75
25	136.3	.774	.405	29.44	152.0	.757	.360	29.28
30	139.5	.770	.400	34.69	155.0	.767	.355	34.71
35	142.7	.760	.395	39.87	158.2	.773	.355	40.04
40	145.5	.753	.387	44.95	161.0	.777	.350	45.30
45	147.8	.748	.380	49.93	164.0	.780	.345	50.43
50	149.5	.749	.376	54.87	166.5	.783	.330	55.51
55	151.0	.749	.371	59.73	171.0	.779	.335	60.50
60	153.7	.754	.368	64.56	172.7	.774	.330	65.35
65	156.7	.765	.360	69.28	174.6	.769	.325	70.18
70	159.5	.773	.355	73.93	178.3	.773	.320	74.97
75	162.5	.776	.350	78.52	183.0	.786	.315	79.72
80	166.0	.777	.342	83.00	189.5	.791	.315	84.20
85	169.5	.778	.335	87.49	196.0	.787	.327	88.50
90	173.0	.774	.330	91.91	203.0	.787	.397	92.68
95	183.0	.770	.318	96.28	222.0	.805	.270	96.53
E.P.	202.0	.770	.287	100.00	283.0	.805	.270	100.00

T_e = 165.0 °C

I.B.P.	83.0	--	--	0	124.0	--	--	0
5	123.3	.732	.500	6.90	141.0	.764	.413	6.32
10	131.7	.750	.427	12.79	146.6	.758	.385	12.23
15	136.7	.774	.411	18.46	152.8	.756	.372	17.91
20	140.5	.772	.397	23.94	155.8	.764	.363	23.47
25	143.5	.764	.390	29.33	159.0	.774	.356	28.92
30	148.2	.753	.382	34.59	162.0	.777	.350	34.28
35	150.0	.752	.375	39.77	164.8	.780	.343	39.53
40	151.5	.753	.371	44.93	167.0	.781	.340	44.74
45	153.2	.760	.368	49.97	169.2	,782	.335	49.87
50	156.0	.770	.362	54.97	171.0	.777	.330	64.92
55	158.8	.774	.355	59.87	172.8	.771	.327	59.93
60	161.5	.778	.350	64.69	174.0	.765	.323	64.88
65	164.0	.779	.346	69.71	177.0	.769	.320	69.77
70	166.8	.783	.340	74.16	181.5	.779	.314	74.68
75	169.0	.783	.335	78.78	185.0	.789	.305	79.25
80	171.5	.777	.330	83.34	191.0	.789	.298	83.82
85	174.0	.770	.324	87.81	195.2	.790	.287	88.21
90	179.0	.771	.316	92.17	204.3	.793	.275	92.42
95	192.0	.790	.300	96.31	240.0	.816	.260	96.40

Cont.

Condition - T_e = 174.5 °C

	Vapor				Liquid			
Vol.% Distilled	T.B.P. °C	Sp.Gr.	$(\Delta T_f)_{ave.}$	Mole%	T.B.P. °C	Sp.Gr.	$(\Delta T'_f)_{ave.}$	Mole%
I.B.P.	90.0	--	--	0	120.0	--	--	0
5	126.0		.480	6.81	140.0		.420	6.56
10	135.3	.745	.416	12.72	149.0	.760	.385	12.57
15	140.0		.400	18.40	152.5		.370	18.35
20	145.0	.755	.389	23.92	156.5	.762	.363	24.03
25	147.5		.380	29.31	160.0		.355	29.57
30	150.0	.756	.375	34.64	163.0	.775	.347	34.99
35	152.0		.370	39.89	165.5		.340	40.30
40	155.0	.757	.364	45.05	169.0	.782	.335	45.53
45	158.3		.357	50.12	170.0		.330	50.68
50	160.5	.776	.352	55.12	173.0	.772	.328	55.80
55	164.0		.347	60.05	175.0		.321	60.81
60	166.0	.780	.340	64.88	178.0	.768	.318	65.77
65	169.0		.335	69.64	182.0		.311	70.62
70	171.0	.780	.330	74.32	186.5	.785	.304	75.38
75	173.0		.327	78.96	191.6		.295	79.99
80	176.3	.765	.323	83.54	198.0	.785	.285	84.44
85	182.2		.315	88.01	211.0		.270	88.66
90	185.0	.780	.305	92.34	218.0	.797	.255	92.64
95	200.0		.290	96.46	255.0		.242	96.42
E.P.	215.0	.792	.245	100.00	285.0	.818	.230	100.00

ont.

ondition - T_e = 162.0 °C

T_B °C	dy/dT_B	dx/dT_B	K	K-Values from Lit. (138)	(88)
120	24.8	6.2	4.02	2.5	
125	37.0	11.0	3.36		
130	48.0	15.5	3.10		2.3
135	55.0	18.0	3.05		
140	59.0	27.0	2.18		
145	70.2	49.0	1.43		
150	90.3	69.5	1.30		
155	66.0	64.0	1.03		
160	54.8	63.2	.87	1.0	
165	57.0	64.0	.73		
170	41.0	59.3	.69		.78
175	27.1	56.3	.48		
180	16.5	40.0	.41		
185	11.1	32.0	.23		
190	7.5	28.0	.27		
195	5.0	22.4	.22		
200	4.2	17.5	.23	.38	.29

T_e = 165.0 °C

T_B °C	dy/dT_B	dx/dT_B	K
125	20.0	5.7	3.52
130	30.2	9.5	3.1
135	44.0	16.0	2.7
140	54.0	21.0	2.5
145	56.0	26.0	2.1
150	84.5	55.8	1.5
155	72.1	60.0	1.2
160	67.2	66.0	1.0
165	62.2	78.8	.7
170	64.0	91.7	.7
175	45.0	81.5	.5
180	20.0	50.0	.4
185	15.2	40.1	.3
190	10.5	31.0	.3
195	7.0	25.0	.2
200	5.2	22.2	.2

T_e = 174.5 °C

130	22.0	5.8	3.98		3.0
135	30.2	8.7	3.49		
140	46.5	18.6	2.56	2.3	
145	56.0	22.4	2.51		
150	75.0	37.2	1.98		
155	75.0	44.2	1.70		
160	77.0	55.8	1.38		
165	71.0	61.2	1.16		
170	69.5	66.8	1.04	1.2	1.0
175	52.4	64.0	1.82		
180	35.0	53.0	.66	.98	
185	26.1	44.3	.59		
190	17.0	31.0	.55		
195	11.0	26.2	.42		
200	6.5	18.6	.35	.48	.50
210	3.6	13.9	.26		
220	2.0	9.5	.21		
230	1.0	7.0	.14	.22	

TABLE XVII

VAPOR-LIQUID EQUILIBRIUM PROPERTIES OF OIL B'

Equipment - Othmer Still
Condition - P_e = 1 Atm.; T_e = 176.0 °C

	Vapor			Liquid				
Vol.% Distilled	T.B.P. °C	Sp.Gr.	Mole%	T.B.P. °C	Sp.Gr.	Mole%	T_B °C	K
I.B.P.	98.0	--	0	105.0	--	0	130	1.62
5	130.0	.743	6.66	135.0	.750	6.73	135	1.71
10	137.5	.768	12.58	143.0	.767	12.73	140	1.46
15	143.0	.765	18.27	148.0	.757	18.53	145	1.09
20	147.0	.757	23.77	150.8	.755	24.18	150	1.28
25	149.5	.753	29.19	154.2	.761	29.75	155	1.21
30	151.5	.756	34.56	158.0	.772	35.18	160	1.11
35	155.0	.764	39.85	161.0	.777	40.50	165	.97
40	157.0	.771	45.04	164.0	.777	45.72	170	1.03
45	160.0	.776	50.15	167.0	.779	50.87	175	.94
50	162.8	.779	65.18	169.0	.782	65.93	180	.86
55	166.0	.782	60.10	171.8	.778	60.92	185	.81
60	168.0	.783	64.94	173.5	.771	65.82	190	.69
65	170.5	.781	69.72	176.0	.768	70.66	195	.72
70	172.3	.775	74.46	180.0	.778	75.44	200	.59
75	175.0	.769	79.12	185.0	.789	80.09	210	.57
80	178.0	.771	83.71	191.5	.792	84.57	220	.54
85	182.5	.783	88.21	197.0	.785	88.89	230	.47
90	192.5	.791	92.53	211.5	.801	92.98		
95	208.0	.794	96.53	251.0	.813	96.23		
E.P.	260.0	.804	100.00	295.0	.826	100.00		

Condition - T_e = 1 Atm.; T_e = 169.5 °C

Vol.% Distilled	Vapor T.B.P. °C	Vapor Sp.Gr.	Vapor Mole%	Liquid T.B.P. °C	Liquid Sp.Gr.	Liquid Mole%	T_B °C	K
I.B.P.	94.0	--	0	115.0	--	0	130	1.61
5	127.0	.740	6.76	134.0	.759	6.61	135	1.39
10	131.0	.769	12.81	145.0	.767	12.65	140	1.30
15	142.0	.769	18.56	149.5	.757	18.46	145	1.32
20	146.3	.758	24.10	162.0	.762	24.12	150	1.40
25	148.5	.755	29.57	154.5	.767	29.69	155	1.15
30	152.0	.754	34.91	160.0	.778	35.14	160	1.07
35	154.8	.764	40.16	163.0	.782	40.46	165	.86
40	157.8	.774	43.33	165.8	.785	45.71	170	.96
45	160.0	.777	50.41	168.0	.785	50.83	175	.94
50	162.5	.780	55.42	170.2	.781	55.93	180	.93
55	165.0	.783	60.35	172.0	.776	60.94	185	.65
60	168.0	.784	65.12	174.0	.771	65.90	190	.55
65	170.0	.784	69.97	177.2	.773	70.79	195	.50
70	172.0	.780	74.69	181.8	.785	75.57	200	.48
75	174.0	.774	79.36	187.0	.794	80.20	210	..38
80	178.0	.768	83.94	193.0	.790	84.70	220	.32
85	182.2	.772	88.41	199.5	.787	89.01		
90	190.0	.782	92.72	215.0	.805	93.05		
95	211.0	.791	96.56	254.5	.817	96.74		
E.P.	240.0	.795	100.00	298.0	.828	100.00		

TABLE XVIII

PHYSICAL PROPERTIES OF OIL F

Pressure = 1 Atm.

Vol.% Distilled	T.B.P. °C	A.S.T.M. °C	Sp. Gr.	ΔT_f	M.Wt.
I.B.P.	170.0	175.0	--	.463	94.7
5	166.0	188.0	.753	.341	128.5
10	180.0	195.0	.767	.319	140.5
15	188.5	199.0	.779	.311	146.0
20	193.0	202.0	.779	.307	147.9
25	196.0	204.5	.781	.305	149.2
30	200.0	207.0	.784	.302	151.0
35	203.0	209.5	.792	.300	154.0
40	210.0	311.0	.799	.295	157.8
45	213.0	213.0	.794	.293	158.2
50	215.0	215.0	.790	.290	159.0
55	217.2	217.0	.790	.289	159.5
60	221.0	219.5	.796	.287	161.5
65	225.0	222.0	.801	.285	163.9
70	229.0	224.0	.808	.281	167.2
75	232.5	227.0	.800	.280	166.7
80	235.0	230.0	.798	.278	167.4
85	239.5	234.0	.806	.275	171.0
90	246.5	237.5	.818	.272	175.5
95	251.0	243.5	.829	.269	179.5
E.P.	276.0	252.0	.829	.257	188.0

(Oil F is a sweet kerosene, from Texas)

TABLE XIX

EQUILIBRIUM PROPERTIES AND K-VALUES - OIL F

Equipment - Thermostatic flow
Condition - P_e = 1 Atm.; T_e = 214.5 °C; %V = 47.4

	Vapor					Liquid				
Vol.% Distilled	T.B.P. °C	A.S.T.M. °C	Sp.Gr.	$(\Delta T_f)_{ave.}$	Mole%	T.B.P. °C	A.S.T.M. °C	Sp.Gr.	$(\Delta T_f')_{ave.}$	Mole%
I.B.P.	109.0	162.0	--	--	0	154.0	208.0	--	--	0
2.5	134.0			.460	3.76	177.0			.338	2.95
5	150.0	175.0	.746	.392	6.96	187.2	210.0	.774	.318	5.73
7.5	159.0			.361	9.90	192.0			.310	8.44
10	166.3	187.0	.762	.345	12.72	194.0	212.0	.783	.307	11.12
12.5	170.0			.336	12.46	196.2			.305	13.78
15	174.0	191.0	.766	.330	18.16	199.0	214.0	.786	.303	16.43
17.5	177.5			.325	20.81	201.5			.301	19.06
20	181.0	194.0	.771	.321	23.43	204.0	215.0	.796	.299	21.67
22.5	184.0			.317	26.02	206.5			.297	24.26
25	187.0	196.0	.782	.314	28.59	209.0	217.0	.800	.295	26.84
27.5	189.5			.312	31.13	211.0			.294	29.40
30	191.5	198.0	.783	.310	33.66	213.0	218.0	.799	.292	31.95
32.5	193.0			.308	36.18	214.0			.291	34.50
35	194.0	200.0	.781	.307	38.69	215.5	219.5	.794	.290	37.03
37.5	195.0			.306	41.14	216.5			.290	39.56
40	196.5	201.0	.781	.305	43.67	218.0	221.0	.793	.289	42.09
42.5	198.0			.303	46.15	219.0			.288	44.60
45	200.0	204.0	.789	.302	48.61	221.0	222.5	.799	.287	47.12
47.5	202.5			.300	51.06	222.5			.287	49.61
50	204.5	206.0	.798	.299	53.50	225.0	224.0	.806	.285	52.10
52.5	206.2			.297	55.93	226.5			.284	54.58
55	208.5	208.0	.802	.296	58.35	228.0	225.5	.808	.283	57.05
57.5	210.5			.294	60.75	230.2			.282	59.51

Cont.

	Vapor					Liquid				
Vol.% Distilled	T.B.P. °C	A.S.T.M. °C	Sp.Gr.	$(\Delta T_f)_{ave.}$	Mole%	T.B.P. °C	A.S.T.M. °C	Sp.Gr.	$(\Delta T_f')_{Ave.}$	Mole%
60	212.5	210.5	.799	.293	63.14	231.0	227.5	.806	.281	61.96
62.5	213.5			.292	65.52	232.0			.280	64.41
65	215.0	213.0	.794	.291	67.90	233.0	229.5	.802	.280	66.86
67.5	216.0			.290	70.28	234.0			.279	69.29
70	217.5	216.0	.793	.289	72.63	235.0	231.5	.802	.279	71.73
72.5	219.5			.288	74.98	237.2			.278	74.16
75	220.0	218.5	.800	.287	77.32	239.0	234.0	.808	.277	76.58
77.5	224.0			.286	79.66	241.8			.275	78.98
80	227.5	221.5	.809	.284	81.97	245.0	236.5	.819	.274	81.37
82.5	230.0			.282	84.28	247.0			.272	83.75
85	232.0	225.0	.805	.281	86.57	249.0	240.0	.819	.271	86.11
87.5	234.0			.280	88.56	251.0			.270	88.47
90	237.0	229.0	.803	.278	91.13	253.0	245.0	.814	.269	90.82
92.5	241.0			.276	93.38	261.0			.266	93.14
95	249.0	234.0	.819	.273	95.61	263.0	248.5	.827	.264	95.45
97.5	252.0			.270	97.82	266.5			.263	97.75
E.P.	258.0	242.0	.819	.267	100.00	286.0	247.0	.827	.257	100.00

ont.

il F at P_e = 1 Atm.; T_e = 214.5 °C; $\left(\triangle T_f/\triangle T_f\right)_p$ = 0.940

T_B °C	dv/dT_B	dl/dT_B	K	K-Lit. (138)
170	11.5			
175	14.0			
180	15.5			
185	17.0			
190	20.0	8.0	2.50	
195	41.0	19.0	2.03	
197.5	30.0	19.5	1.45	
200	24.0	20.0	1.13	1.35
202.5	21.0	20.0	.99	
205	23.0	20.0	1.08	
207.5	25.0	20.0	1.17	
210	26.0	22.0	1.11	
212.5	32.0	26.0	1.15	
215	38.0	37.0	.97	1.00
217.5	30.0	38.5	.73	
220	23.5	31.5	.69	
222.5	19.5	28.0	.64	
225	21.0	27.5	.71	
227.5	21.5	27.0	.74	
230	21.0	32.0	.62	.77
232.5	21.0	25.0	.79	
235	16.5	37.5	.42	
237.5	13.0	24.5	.50	
240	11.0	21.0	.49	.54
242.5	8.8	19.0	.43	
245	7.5	19.0	.37	

cont.

Oil F at P_e = 1 Atm.; T_e = 218 °C; V% = 51.2

Vol.% Distilled	Vapor T.B.P. °C	Vapor A.S.T.M. °C	Vapor Sp.Gr.	Liquid T.B.P. °C	Liquid A.S.T.M. °C	Liquid Sp.Gr.
I.B.P.	109.5	168.0		160.0	195.0	
2.5	135.5			177.0		
5	153.5	176.0	.751	188.5	210.0	.777
7.5	159.0			192.5		
10	167.0	186.5	.760	196.0	214.5	.783
12.5	171.0			198.0		
15	174.5	191.0	.762	200.5	215.5	.788
17.5	178.0			201.0		
20	181.5	193.5	.764	205.5	217.0	.797
22.5	184.5			208.5		
25	187.7	195.0	.782	211.0	218.5	.800
27.5	190.0			212.5		
30	192.0	197.5	.783	213.5	219.5	.795
32.5	193.0			214.2		
35	194.5	200.0	.780	215.5	221.0	.791
37.5	195.5			216.5		
40	197.0	202.0	.781	218.0	222.5	.792
42.5	198.8			219.0		
45	201.0	203.5	.790	221.0	223.5	.799
47.5	203.0			223.0		
50	205.0	205.0	.799	225.0	225.0	.807
52.5	207.0			226.5		
55	209.2	207.5	.800	228.5	227.0	.807
57.5	210.5			230.0		
60	212.5	210.0	.798	231.0	228.5	.807
62.5	213.5			232.5		
65	215.2	212.5	.793	233.5	230.0	.790
67.5	216.0			234.0		
70	218.0	215.0	.793	235.0	232.0	.798
72.5	220.0			237.0		
75	223.0	217.0	.801	238.5	235.0	.806
77.5	225.5			241.2		
80	228.0	219.5	.809	244.0	237.5	.820
82.5	230.0			247.0		
85	232.2	223.0	.805	248.5	240.0	.819
87.5	234.0			250.5		
90	237.0	228.0	.802	252.5	244.0	.813
92.5	242.0			261.0		
95	248.0	229.0	.820	262.5	250.0	.828
97.5	250.5			265.0		
E.P.	260.0	240.5	.820	284.5	260.0	.828

TABLE XX

PHYSICAL PROPERTIES OF OIL G

Condition = 1 Atm.

Vol.% Distilled	T.B.P. °C	A.S.T.M. °C	Sp.Gr.	T_f	M. Wt.
I.B.P.	115.0	175.0		.473	93.5
5	166.5	190.5	.765	.374	120.8
10	180.0	197.0	.780	.352	129.1
15	189.0	204.0	.786	.337	136.0
20	194.0	206.0	.784	.330	139.5
25	198.0	210.0	.794	.324	142.2
30	203.5	212.0	.802	.317	147.1
35	210.0	215.5	.806	.309	151.5
40	214.0	218.0	.802	.305	152.9
45	218.0	222.5	.800	.301	154.5
50	222.0	224.0	.803	.297	158.5
55	229.0	227.5	.815	.297	163.8
60	232.5	231.0	.816	.287	166.0
65	238.0	235.0	.817	.283	168.5
70	245.5	240.0	.823	.277	177.0
75	252.0	244.5	.826	.271	178.0
80	265.0	249.0	.840	.262	183.0
85	267.5	265.0	.840	.260	188.5
90	269.0	260.0	.841	.252	190.0
95	274.0	268.0	.842	.255	192.5
E.P.	289.0	280.0	.842	—	—

(Oil G is a kerosene after hydroforming, from Texas)

TABLE XXI

EQUILIBRIUM PROPERTIES - AND K-VALUES - OIL G

Equilibrium Equipment - Thermostatic Flow
Condition - T_e = 218.0 °C; P_e = 1 Atm.; V% = 26.3

	Vapor					Liquid				
Vol.% Distilled	T.B.P. °C	A.S.T.M. °C	Sp.Gr.	$(\Delta T_f)_{ave.}$	Mole%	T.B.P. °C	A.S.T.M. °C	Sp.Gr.	$(\Delta T_f)_{ave.}$	Mole%
I.B.P.		162.0			0	143.0	200.0			0
2.5	120.5			.478	3.62	170.0			.394	3.37
5	127.0	169.0	.764	.456	7.07	180.0	207.0	.780	.360	6.48
7.5	141.0			.436	10.38	188.0			.345	9.44
10	147.5	175.0	.787	.416	13.53	192.5	210.0	.782	.335	12.31
12.5	156.0			.403	16.57	195.0			.330	15.13
15	163.0	180.0	.775	.388	19.51	197.0	215.0	.783	.327	17.90
17.5	168.0			.377	22.37	199.5			.323	20.70
20	172.5	184.0	.778	.369	25.17	203.0	218.0	.794	.320	23.44
22.5	176.0			.361	27.90	206.0			.316	26.15
25	179.0	187.5	.776	.356	30.60	208.5	220.5	.808	.309	28.83
27.5	182.0			.351	33.26	211.0			.309	31.47
30	185.5	191.0	.783	.346	35.88	214.0	224.0	.801	.306	34.09
32.5	188.0			.341	38.46	215.5			.303	36.70
35	191.0	195.0	.789	.336	41.01	217.5	226.0	.790	.301	39.29
37.5	192.5			.333	43.53	219.5			.298	41.87
40	194.0	198.0	.785	.330	46.03	222.0	228.0	.795	.295	44.42
42.5	195.0			.329	48.52	225.5			.292	46.95
45	197.0	201.0	.783	.327	51.00	229.0	231.0	.811	.289	49.45
47.5	198.5			.325	53.46	231.0			.288	51.94
50	200.0	204.0	.789	.323	55.91	233.0	234.5	.813	.286	54.40
52.5	202.0			.320	58.33	234.0			.285	56.85
55	205.0	207.5	.803	.317	60.74	236.0	237.0	.810	.283	59.29
57.5	207.0			.314	63.11	239.0			.280	61.71
60	210.0	212.0	.809	.311	65.47	243.0	240.5	.817	.277	64.11

Cont.

	Vapor					Liquid				
Vol.% Distilled	T.B.P. °C	A.S.T.M. °C	Sp.Gr.	$(T_f)_{ave.}$	Mole%	T.B.P. °C	A.S.T.M. °C	Sp.Gr.	$(T_f)_{ave.}$	Mole%
62.5	212.0			.308	67.80	246.0			.275	66.49
65	214.0	214.0	.800	.306	70.12	249.0	244.0	.821	.273	68.84
67.5	216.0			.304	72.32	251.5			.271	71.18
70	218.5	218.0	.792	.302	74.71	253.0	248.5	.820	.270	73.50
72.5	221.0			.299	76.98	254.0			.269	75.81
75	226.0	222.0	.803	.295	79.21	256.5	253.0	.838	.268	78.12
77.5	229.5			.292	81.42	260.0			.264	80.41
80	232.5	226.0	.816	.289	83.61	263.0	258.0	.840	.261	82.67
82.5	236.0			.286	85.78	268.0			.257	84.91
85	241.0	233.0	.817	.283	87.92	275.0	263.0	.840	.255	87.11
87.5	247.5			.278	90.03	276.5			.254	89.29
90	252.0	242.5	.826	.273	92.09	277.0	268.5	.840	.253	91.47
92.5	261.0			.268	94.12	278.5			.252	93.64
95	265.0	--	.840	.263	96.11	280.0	277.0	.840	.250	95.49
97.5	270.0			.260	98.08	284.0			.244	97.93
E.P.	286.0	272.0	.840	.253	100.00	300.0	--	.840	--	100.00

Condition = T_e = 23.0 °C; P_e = 1 Atm.; Vp = 61.2

Vol.% Distilled	Vapor T.B.P. °C	Vapor A.S.T.M. °C	Vapor Sp.Gr.	Vapor $(\Delta T_f)_{ave.}$	Vapor Mole%	Liquid T.B.P. °C	Liquid A.S.T.M.	Liquid Sp.Gr.	Liquid $(\Delta T_f')_{ave.}$	Liquid Mole%
I.B.P.	103.0	185.0			0	129.0	197.0			0
2.5	138.5			.463	3.68	188.5			.387	3.44
5	155.0	189.0	.763	.412	6.95	196.0	203.0	.791	.333	6.41
7.5	165.0			.387	10.03	201.0			.323	9.29
10	171.0	191.5	.778	.373	12.99	206.5	227.5	.803	.317	12.11
12.5	176.0			.363	15.88	210.0			.311	14.87
15	180.0	194.5	.779	.355	18.76	213.0	229.5	.806	.307	17.61
17.5	183.5			.349	21.54	215.0			.305	20.32
20	187.0	197.5	.787	.343	24.26	217.0	232.5	.799	.303	23.03
22.5	189.5			.338	26.96	220.0			.300	25.69
25	192.0	201.0	.788	.334	29.61	223.5	235.0	.807	.297	28.3
27.5	193.5			.332	32.25	227.0			.294	30.95
30	195.0	204.0	.787	.330	34.87	229.0	237.0	.817	.291	43.54
32.5	196.0			.328	37.48	231.0			.289	36.11
35	197.5	206.0	.787	.326	40.07	332.0	239.0	.817	.288	38.86
37.5	199.0			.324	42.65	334.0			.287	41.23
40	201.0	209.0	.798	.321	45.20	235.5	241.0	.815	.285	43.77
42.5	204.0			.318	47.73	238.0			.284	46.29
45	206.5	211.5	.811	.315	50.24	241.0	242.5	.821	.281	48.80
47.5	208.5			.312	52.72	244.0			.279	51.28
50	211.5	213.5	.810	.310	55.18	247.0	244.5	.826	.276	53.74
52.5	213.0			.307	57.62	249.0			.275	56.18
55	214.5	216.5	.800	.305	60.04	249.5	248.0	.825	.274	58.62
57.5	216.0			.304	62.46	251.5			.273	61.05
60	217.5	220.0	.794	.302	64.87	253.0	250.5	.828	.271	63.46
62.5	220.5			.300	67.25	255.0			.270	65.86
65	244.0	223.0	.803	.296	69.61	257.0	253.5	.836	.268	68.25
67.5	226.5			.294	71.95	268.0			.265	70.65
70	229.5	226.0	.818	.291	74.26	271.5	260.0	.844	.260	72.92

Cont.

	Vapor					Liquid				
Vol.% Distilled	T.B.P. °C	A.S.T.M. °C	Sp.Gr.	$(\Delta T_f)_{ave.}$	Mole%	T.B.P. °C	A.S.T.M. °C	Sp.Gr.	$(\Delta T_f')_{ave.}$	Mole%
72.5	232.0			.289	76.56	272.0			.257	75.21
75	234.0	232.0	.817	.287	78.84	272.5	259.5	.844	.257	77.49
77.5	237.5			.284	81.10	273.0			.256	79.78
80	242.5	237.0	.820	.281	83.23	273.5	266.0	.844	.256	82.06
82.5	249.0			.279	85.55	274.0			.256	48.34
85	251.5	242.0	.828	.273	87.72	275.0	267.0	.844	.255	86.60
87.5	253.5			.271	89.87	275.5			.255	88.87
90	259.0	250.0	.836	.267	91.99	276.5	271.8	.844	.254	91.13
92.5	271.0			.262	94.08	278.0			.253	93.38
95	273.5	267.0	.846	.257	91.12	281.0	276.0	.844	.251	95.62
97.5	289.5			.251	98.11	293.0			.248	97.82
E.P.	297.0	273.0	.846	.244	100.00	298.0	287.0	.844	.243	100.00

Condition - Te = 244 °C; P_e = 1 Atm.; V% = 77.6

Vol.% Distilled	Vapor T.B.P. °C	 A.S.T.M. °C	 Sp.Gr.	 $(\Delta T_f)_{ave.}$	 Mole%	Liquid T.B.P. °C	 A.S.T.M. °C	 Sp.Gr.	 $(\Delta T'_f)_{ave.}$	 Mole%
I.B.P.	100.0	159.0			0	108.0	200.0			0
5	159.5	183.0	.763	.443	7.13	200.0	227.0	.797	.343	6.24
10	157.0	189.5	.779	.375	13.16	212.5	232.0	.803	.314	11.59
15	184.0	195.5	.782	.352	18.83	220.0	235.0	.804	.303	17.46
20	190.0	200.0	.784	.340	24.30	227.0	238.0	.811	.295	22.83
25	194.0	203.0	.786	.333	29.66	231.5	241.0	.812	.290	28.10
30	197.0	206.0	.789	.328	34.94	236.0	243.0	.816	.286	33.30
35	201.5	208.5	.796	.323	40.13	242.0	245.5	.820	.282	38.43
40	206.0	311.5	.804	.316	45.22	247.5	248.0	.823	.277	43.47
45	210.5	214.0	.805	.311	50.22	250.0	250.0	.825	.274	48.45
50	214.5	216.0	.799	.306	55.15	252.5	252.0	.827	.272	53.40
55	218.0	219.0	.793	.302	60.01	257.0	254.5	.833	.270	58.31
60	224.0	222.5	.803	.298	64.81	261.0	257.0	.837	.266	63.15
65	230.0	226.0	.814	.292	69.51	272.0	259.0	.841	.261	67.89
70	234.0	230.0	.815	.288	74.15	274.0	262.0	.841	.256	72.55
75	240.0	234.0	.817	.283	78.70	275.0	264.5	.841	.255	77.19
80	249.0	238.5	.825	.277	83.16	276.0	268.0	.841	.254	81.81
85	253.0	246.0	.828	.272	87.54	277.5	271.0	.841	.253	86.41
90	260.0	253.0	.836	.267	91.83	279.5	275.0	.841	.252	91.00
95	278.0	262.5	.846	.259	96.00	283.5	281.5	.841	.250	95.55
E.P.	291.5	271.0	.846	.249	100.00	294.5	--	.841	.245	100.00

ndition - T_e = 218.0 °C; P_e = 1 Atm.; $(\triangle T_f'/\triangle T_f')_p$ = .885

	dy/dT_B	dx/dT_B	K	dv/dT_B	dl/dT_B	K
55				7.70	1.10	6.18
60				8.70	2.00	3.62
65				10.1	2.10	4.26
70				11.5	3.25	3.13
72.5				12.9	3.51	3.26
75	15.4	5.35	2.88	13.4	3.20	3.71
77.5	16.1	6.50	2.48	14.2	4.83	3.61
80	17.0	6.51	2.62	14.8	6.00	2.19
82.5	17.5	7.80	2.24	16.6	6.75	2.16
85	18.1	9.10	1.98	17.7	7.45	2.10
87.5	20.0	10.2	1.96	19.6	9.17	1.89
90	22.2	12.2	1.83	22.5	11.2	1.77
92.5	29.0	14.9	1.94	27.5	14.0	1.74
95	33.0	23.0	1.43	31.5	19.0	1.46
97.5	32.2	21.2	1.51	44.0	18.0	1.67
200	24.5	21.0	1.17	29.0	18.4	1.39
202.5	21.0	18.5	1.13	21.0	18.3	1.01
205	19.6	16.5	1.18	19.0	18.3	.92
207.5	18.8	19.0	.99	19.5	18.2	.95
210	18.0	17.1	.90	19.0	18.2	.92
212.5	20.0	20.8	.96	22.0	18.0	1.07
215	22.0	24.0	.92	26.0	22.6	1.02
217.5	19.0	27.8	.68	24.0	33.0	.65
220	16.2	22.0	.73	19.5	21.5	.80
222.5	13.0	18.3	.72	16.5	18.5	.78
225				14.5	21.5	.60
230				13.2	22.0	.53
232.5				12.3	31.0	.34
235				11.5	23.5	.43

dition - $T_e = 234.0\ ^{o}C$; P_e = 1 Atm.; $(\triangle T_f'/\triangle T_f)_p = .894$

	dy/dT_B	dx/dT_B	K	dv/dT_B	dl/dT_B	K	K= $(\triangle y/\triangle x)_{\triangle T_B = 2.5}$
0	11.0	1.50	7.33	9.50	1.61	5.31	
2.5	11.5	2.00	5.75	10.7	1.90	5.03	
5	12.0	2.20	5.45	11.2	2.20	4.55	
7.5	12.6	3.02	4.20	12.0	2.30	4.66	
0	13.8	3.51	3.94	12.9	2.74	4.19	
2.5	15.5	4.50	3.45	14.1	3.10	4.03	
5	17.2	5.00	3.44	15.2	3.71	3.67	
7.5	20.1	5.82	3.43	18.0	4.30	3.73	
0	22.5	6.20	3.63	20.1	5.44	3.37	4.00
2.5	28.0	7.70	3.63	23.7	6.68	3.17	4.43
5	29.6	8.50	3.47	26.6	8.14	2.92	4.75
7.5	26.5	9.62	2.75				4.14
0	24.0	10.2	2.35	20.7	8.95	2.07	2.55
2.5	19.2	11.6	1.66	18.0	9.00	1.78	1.53
5	18.7	13.0	1.44	19.1	10.3	1.64	1.33
07.5	21.0	14.8	1.42	20.0	12.0	1.48	1.42
10	22.1	14.0	1.58	21.8	14.0	1.39	1.45
12.5	29.0	21.0	1.38	24.8	16.8	1.31	1.32
15	28.0	26.0	1.07	32.7	23.0	1.27	1.08
17.5	22.0	23.0	1.10	24.0	21.0	1.02	.88
20	16.5	19.0	.87	19.7	17.4	1.01	1.00
22.5	14.0	14.0	1.00	14.8	14.0	.94	1.00
25	14.5	14.2	1.02	14.5	13.5	.96	1.05
27.5	18.0	20.0	.90	18.0	20.0	.80	.90
30	19.0	24.0	.79	22.0	25.5	.77	.67
232.5	21.2	33.3	.64	22.0	31.0	.63	.57
235	15.5	29.0	.53	18.0	28.5	.56	.53
237.5	12.0	22.0	.55	14.2	21.2	.59	.57
240	9.5	16.8	.56	10.8	17.6	.54	.59
242.5	7.5	15.5	.48	9.50	17.0	.49	.44
245	6.2	16.2	.38	7.80	17.0	.41	.36
247.5	7.4	20.0	.37	8.00	20.0	.36	.25
250							.48

ndition - T_e = 244.0 °C; P_e = 1 Atm.; $(\Delta T_f/\Delta T_f)_p$ = .895

	dy/dT_B	dx/dT_B	K	dv/dT_B	dl/dT_B	K	Lim $\left(\Delta v/dT_B\right)_{\Delta T_B \to 0}$	Lim $\left(\Delta l/dT_B\right)_{\Delta T_B \to 0}$	K
0	8.51	1.23	6.88						
2.5	9.60	1.48	6.50						
5	10.1	1.75	5.77						
7.5	11.3	2.00	5.65						
0	12.7	2.35	5.42	11.6	1.85	5.61	11.68	1.845	5.62
2.5	14.5	2.75	5.28						
5	16.5	3.25	5.07						
7.5	19.0	3.75	5.06						
0	20.0	4.40	4.55	20.2	4.38	4.12			
2.5	20.7	5.10	4.06						
5	21.5	5.80	3.72						
7.5	21.7	6.71	3.24	25.5	7.00	3.26			
0	21.8	7.50	2.91	25.5	8.00	2.85	24.42	7.92	2.88
2.5	22.0	8.50	2.59	24.0	8.20	2.62			
5	22.0	9.51	2.30	22.5	8.40	2.39	22.50	8.365	2.41
7.5	22.0	10.5	2.09	22.5	9.02	2.24			
10	22.1	11.6	1.90	22.5	9.60	2.10	22.35	9.71	2.06
12.5	22.2	12.7	1.73	22.2	10.4	1.92			
15	22.1	13.7	1.60	22.0	11.0	1.79			
17.5	21.7	15.0	1.45	21.3	12.0	1.59			
20	21.5	16.0	1.35	21.8	12.7	1.54	21.73	12.66	1.53
22.5	20.7	17.2	1.20	21.0	14.0	1.34			
25	20.2	18.2	1.11	21.0	16.3	1.15			
27.5	19.5	19.0	1.03	21.8	17.5	1.12			
30	18.8	20.0	.94	22.5	20.4	.90	22.67	19.50	1.04
32.5	18.5	20.5	.90						
35	17.8	22.5	.79	21.5	21.8	.88			
37.5	16.0	21.0	.76						
240	14.8	20.8	.71	16.0	17.0	.84			
242.5	14.2	21.6	.66						
245	12.8	21.2	.60	15.5	22.5	.68			
247.5	12.7	23.3	.55	15.0	25.0	.54			
250	12.0	22.7	.53	14.2	24.0	.53			
252.5	11.2	22.8	.49	13.0	24.5	.48			
255	10.5	22.5	.46	12.1	24.3	.44			
257.5	9.7	22.0	.44	11.2	23.0	.43			
260	9.2	21.5	.43	9.6	22.0	.39			

TABLE XXII

PHYSICAL PROPERTIES OF OIL F-G

ssure = 1 Atm.

.% tilled	T.B.P. °C	A.S.T.M. °C	Sp. Gr.	ΔT_f	M.Wt.
.P.	120.0				
5	149.5				
	165.0	191.0	.759	.375	116.2
.5	173.0				
	179.0	197.0	.773	.354	127.5
.5	184.5				
	188.5	201.0	.783	.343	133.4
.5	191.0				
	193.5	206.0	.785	.338	135.5
.5	195.0				
	196.5	208.0	.785	.336	136.4
.5	198.5				
	201.0	210.0	.794	.330	140.5
.5	203.5				
	206.0	213.0	.806	.326	144.5
.5	208.5				
	211.0	215.0	.806	.322	146.2
.5	213.0				
	214.0	218.0	.797	.319	146.0
.5	215.5				
	216.5	220.0	.793	.317	146.2
.5	218.5				
	219.5	222.5	.798	.315	148.0
.5	223.0				
	226.5	225.0	.812	.309	153.4
2.5	228.5				
5	230.5	229.0	.814	.305	155.7
7.5	232.0				
0	233.5	232.0	.809	.304	155.3
2.5	235.0				
5	237.0	235.5	.807	.301	156.5
7.5	240.5				
0	244.0	240.5	.823	.296	162.3
2.5	248.0				
5	251.5	246.0	.822	.291	164.7
7.5	254.0				
0	257.5	251.5	.826	.287	168.2
2.5	269.5				
5	272.0	263.0	.841	.277	177.5
7.5	277.0				
E.P.	293.0	272.0	.841	.264	186.2

Oil F-G is a 50/50 by volume blend of oils F and G

TABLE XXIII

EQUILIBRIUM PROPERTIES AND K-VALUES OF OIL F-G

Equilibrium equipment = Thermostatic flow
Condition = P_e = 1 Atm.; T_e = 218.0 °C; V% = 35.6

	Vapor			Liquid		
Vol.% Distilled	T.B.P. °C	A.S.T.M. °C	Sp.Gr.	T.B.P. °C	A.S.T.M. °C	Sp.Gr.
I.B.P.	99.5	155.0		153.0	202.0	
2.5	128.0			147.5		
5	144.0	172.0	.752	185.0	205.0	.775
7.5	153.5			191.0		
10	162.5	179.0	.762	194.0	212.5	.785
12.5	166.0			196.0		
15	170.0	184.0	.773	198.5	215.0	.786
17.5	173.0			201.0		
20	176.0	187.5	.773	204.0	216.0	.798
22.5	179.5			206.5		
25	183.0	191.0	.779	209.0	218.0	.802
27.5	186.0			211.0		
30	188.0	194.0	.787	213.0	220.0	.798
32.5	191.0			214.5		
35	193.0	197.0	.787	216.0	221.5	.795
37.5	194.0			217.5		
40	195.5	199.0	.783	219.0	223.5	.792
42.5	196.5			221.0		
45	198.0	201.5	.784	223.5	225.0	.805
47.5	200.00			225.5		
50	202.0	204.0	.795	228.0	227.0	.814
52.5	204.0			229.5		
55	207.0	206.5	.806	231.0	229.5	.811
57.5	209.0			232.5		
60	211.0	209.0	.805	234.0	232.0	.805
62.5	213.0			235.5		
65	214.5	212.0	.796	238.0	235.5	.808
67.5	216.0			240.5		
70	217.5	216.0	.791	243.5	238.5	.820
72.5	219.5			246.5		
75	223.0	219.0	.800	249.0	243.0	.824
77.5	226.5			250.5		
80	229.5	223.0	.815	253.0	246.5	.821
82.5	232.0			256.0		
85	234.0	229.0	.810	260.0	251.5	.833
87.5	238.0			264.0		
90	244.0	235.0	.815	267.5	258.0	.837
92.5	249.0			277.0		
95	258.0	243.0	.833	279.0	266.0	.845
97.5	268.5			283.5		
E.P.	284.5	256.0	.833	301.0	275.5	.845

Equipment = Thermostatic flow
Condition = P_e = 1 Atm.; T_e = 234.0 °C; V% = 77.0

	Vapor					Liquid				
Vol.% Distilled	T.B.P. °C	A.S.T.M. °C	Sp.Gr.	$(\Delta T_f)_{ave.}$	Mole%	T.B.P. °C	A.S.T.M. °C	Sp.Gr.	$(\Delta T'_f)_{ave.}$	Mole%
I.B.P.	120.0	182.0			0	164.0	212.0			0
2.5	143.5			.520	3.97	190.5			.360	3.01
5	159.0	186.0	.759	.406	7.06	198.5	223.5	.786	.342	5.86
7.5	165.5			.380	9.96	204.0			.340	8.70
10	174.0	192.5	.774	.367	12.76	209.0	227.5	.801	.325	11.42
12.5	178.0			.358	15.49	211.5			.322	14.11
15	183.0	197.0	.778	.353	18.18	214.0	230.0	.800	.320	16.78
17.5	186.5			.348	20.83	216.5			.318	19.43
20	190.0	200.5	.787	.344	23.46	219.0	232.0	.797	.316	22.07
22.5	191.5			.340	26.05	221.5			.314	24.70
25	194.0	203.5	.786	.339	28.64	224.0	234.5	.805	.312	27.30
27.5	195.0			.337	31.61	226.5			.318	29.89
30	196.5	206.0	.782	.336	33.78	229.0	235.0	.812	.308	32.46
32.5	198.0			.334	36.31	230.0			.307	35.03
35	199.5	208.5	.789	.333	38.85	231.0	237.0	.810	.307	37.59
37.5	202.0			.331	41.38	233.0			.305	40.14
40	204.5	210.0	.803	.329	43.89	234.0	238.5	.805	.304	42.67
42.5	207.0			.326	46.37	235.5			.303	45.21
45	209.0	212.5	.809	.324	48.84	237.5	240.5	.807	.302	47.73
47.5	211.5			.323	51.30	239.0			.301	50.24
50	213.0	215.0	.801	.320	53.74	242.0	243.0	.818	.299	52.47
52.5	214.5			.320	56.18	245.0			.297	55.22
55	215.5	216.5	.794	.319	58.61	246.5	235.0	.823	.295	57.68
57.5	217.0			.317	61.03	238.0			.294	60.14
60	218.0	219.5	.793	.316	63.44	250.5	246.0	.820	.293	62.59
62.5	219.5			.316	65.85	251.5			.291	65.02
65	222.5	222.5	.801	.314	68.25	253.0	248.5	.822	.290	67.44
67.5	225.5			.312	70.63	254.0			.290	69.86
70	228.0	226.5	.814	.309	72.98	255.0	251.0	.827	.289	72.27

Cont.

	Vapor					Liquid				
Vol.% Distilled	T.B.P. °C	A.S.T.M. °C	Sp.Gr.	$(\Delta T_f)_{ave.}$	Mole%	T.B.P. °C	A.S.T.M. °C	Sp.Gr.	$(\Delta T'_f)_{ave.}$	Mole%
72.5	230.0			.308	75.33	267.0			.285	47.40
75	232.0	222.8	.811	.306	77.67	268.0	254.5	.839	.281	76.75
77.5	233.5			.304	79.98	269.5			.279	79.08
80	236.0	232.0	.804	.303	82.29	270.5	258.0	.829	.278	81.40
82.5	238.5			.301	84.59	271.0			.278	83.73
85	243.0	238.0	.814	.300	86.88	272.0	262.0	.839	.277	86.04
87.5	247.5			.296	89.14	273.0			.277	88.35
90	251.0	248.5	.821	.292	91.36	274.0	267.0	.839	.276	90.66
92.5	260.0			.288	93.56	276.0			.275	92.95
95	263.0	252.5	.836	.284	95.72	279.0	272.0	.839	.273	95.23
97.5	266.0			.282	97.88	282.5			.272	97.51
E. P.	276.0	254.0	.836	.278	100.00	302.0	284.0	.839	.268	100.00

	T_e = 218.0 °C $({}^eT_f/\ T_f)$ = .914			T_e = 234.0 °C $({}^eT_f/\ T_f)$ = .915		
	dv/dT_B	dl/dT_B	K	dv/dT_B	dl/dT_B	K
0	16.5			12.0	2.2	5.02
2.5	17.2					
5	18.0			16.0	3.1	4.76
7.5	19.5	9.8	1.82			
0	22.1	12.1	1.67	20.0	4.2	4.36
2.5	27.2	14.5	1.71	22.1	5.0	4.00
5	29.1	16.3	1.63	24.3	5.7	3.90
7.5	29.3	18.0	1.49	26.0	7.2	3.31
0	28.0	19.3	1.33	27.1	8.8	2.82
2.5	27.2	20.7	1.21	24.7	9.2	2.46
5	25.5	22.0	1.06	33.9	10.5	2.08
7.5	24.0	23.0	.95	23.7	13.0	1.67
10	23.5	24.0	.90	24.7	15.5	1.46
12.5	23.0	26.0	.81	28.4	18.4	1.41
15	22.8	27.0	.77	31.2	22.0	1.31
17.5	22.0	28.0	.72	30.5	19.0	1.46
20	21.5	28.3	.69	31.0	19.0	1.49
22.5	20.1	28.3	.66	26.0	19.0	1.28
25	19.1	27.2	.64	22.0	20.8	.98
27.5				24.0	25.0	.88
30	17.2	31.3	.50	26.01	30.0	.79
32.5				22.2	27.8	.73
35	14.5	32.5	.41	19.0	27.1	.64
37.5				17.5	22.8	.70
40	11.2	31.6	.32	16.5	23.4	.64
42.5				15.7	23.2	.62
45	7.2	21.8	.28	13.1	23.0	.52
47.5				13.2	24.5	.49
50	5.2	18.0	.26	10.0	27.0	.34
52.5						
55	3.5	16.0	.20			
60						

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