MEASUREMENT OF VAPOR PRESSURE OF PALM OIL CONSTITUENTS UNDER VACUUM.

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Abstract

Vapor pressure is one of the most important properties in chemical process design for unit operations like distillation, extraction and absorption processes. Eventhough, vapor pressure data for most of the commonly used chemical compounds are available in the literature and the databank is continuously being updated, reliable vapor pressure data for vegetable oils are scarce. Vapor pressure of vegetable oils are not easily determined due to its complex nature (chemical composition) and temperature sensitivity. The vapor pressure measurements of all phlegmatic liquids including oils and its main constituent triglycerides, require a method which impose a minimum of thermal hazard to the substance under examination. It is also suggested that the vapor pressure of vegetable oils may be determined from the data on its constituent triglycerides by suitable interpolation/extrapolation. This paper discusses methods of determining vapor pressure of some of the major components found in palm oil. Some intricate problems related to temperature measurement and instrumentation under very low pressures are also indicated. Preliminary results of this investigation on the vapor pressure of the triglycerides are presented.

Introduction

Vapor pressure is one of the highest-impact physical properties of a substance in chemical process design. Most of the separation processes are based on differences in vapor pressure of components of the mixture and on the knowledge of vapor-liquid

equilibrium. Vapor pressure data are necessary in the design of all such unit operations where vapor are involved such as distillation, absorption etc. or where vapors may form during the operation such as extraction. Vapor pressure of liquid is strongly dependent on temperature and this thermodynamic relationship is commonly described by the Clausius Clapeyron equation;

$$\ln p = \frac{\Delta H_v}{RT} + B \qquad (1)$$

where B is a constant that depends on the characteristics of the material and ΔH_v is the enthalpy of vaporisation and R is the universal gas constant. However, a plot of ln p versus 1/T does not always give a linear relationship except in a narrow range. Therefore, vapor pressure data have frequently been correlated by a modified form of the above relationship known as the Antoine equation;

$$\log p = - \frac{A}{t + C} + B \qquad (2)$$

The reliable values of the constants A, B, C are obtained by regressing experimental data, these are published in textbooks such as *(Reid, Prausnitz and Poling, 1988)*. The vapor pressure data of common liquids are usually cited in generalised handbooks such as *Lange's, 1979* and *Perry's, 1985*. For organic liquids such as hydrocarbons, ethers, esters, aldehydes, ketones, acids and alcohols, vapor pressure data are available in a more specialised handbooks *(Timmermanns, 1950)*. Vapor pressure of polymer solutions are also easily available in related handbooks and journals. However, the vapor pressure data for the class of organic materials known as lipids which includes oils, fats and waxes are surprisingly lacking. The vapor pressure of vegetable oils such as soybean has been reported. The vapor pressure data for triglycerides, substances which constitute the major component of oils and fats are scarce. Vapor pressure data are available only for

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some synthesised long chain fatty acid triglycerides as reported by *Bailey's 1979*. So far, there is no known estimation methods that can be used to estimate the vapor pressure of triglycerides or vegetable oils. However, the vapor pressure data for fatty acids are available in handbooks such as *Timmermanns's, 1950, Bailey's, 1979* and *Perry's, 1985* and are relatively adequate for design purposes. The vapor pressure of fatty acids can be estimated by an equation similar to Antoine equation *(Bailey's, 1979)*.

In the deodorisation process of palm oil, all undesirable volatile impurities such as fatty acids, mono- and diglycerides are removed by steam stripping. The operating conditions are often approximated by the available vapor pressure of fatty acids and the constituent triglycerides. In view of the inadequate vapor pressure data for the pure triglycerides which form the major constituent of palm oil, it is highly desirable to generate the vapor pressure data of these components by experimental measurement. As a preliminary investigation, the vapor pressure of pure triglycerides are measured over a range of temperature in order to compare the results and verify the reliability of the experimental setup. Measurements for other pure triglycerides and mixtures of triglycerides over a wider range of temperature is planned subsequent to this.

Theoretical Background and Preliminary Investigations

Since the vapor pressure of a pure substance at a specific temperature is the pressure exerted by the vapor on the liquid when the vapor and liquid phases are at equilibrium, it involves precise measurement of only two parameters: temperature and pressure. There are several methods of measuring vapor pressure of pure components at low pressures, and these can be classified into two categories - static and dynamic *(Shoemaker et.al., 1989)*. Most of the vapor pressure measurements at low pressure reported in the past are based on the dynamic principle. The apparatus used in this work for the measurement of the vapor pressure of pure triglycerides is a modified form of the

commonly used ebulliometer which is based on the principle of dynamic method. The modifications made in this work are necessary since triglycerides the main components of oils and fats are known to decompose on boiling even below atmospheric pressure. Furthermore, the pure triglycerides are rather expensive and the apparatus has to be setup in such a way that only small quantities of samples are required.

Description Of Apparatus And Experimental Condition

The apparatus, shown in *figure 1* consists of a simple set-up using the principle of common dynamic method. The apparatus consists of a round-bottomed flask with three 'necks'. One of the necks is connected to a diffusion pump which has a vacuum capacity of 10E-6 mbar. Two thermocouples are inserted into the other two necks; one measuring the liquid temperature and the other measuring the vapor temperature. The vapor pressure of trilaurin, trimyristin and tripalmitin were measured using the thermocouple setting shown in the figure, i.e. the thermocouple measuring the liquid temperature fully immersed below the liquid surface.

The exploratory experiment were conducted with glycerol to measure the effect of thermocouple positioning. Two different cases of thermocouple positioning have been studied, the first case where the thermocouple measuring the liquid temperature just touches the surface of the liquid (*figure 2a)* and the other, the thermocouple measuring the liquid temperature were immersed into the liquid by 2cm as illustrated in *figure 2b*. The vapor pressures inside the sampling bulb are measured using the Pirani and barocel for the case of glycerol and tripalmitin. For trilaurin and trimyristin the vapor pressures were measured using only the Pirani gauge.

The Pirani gauge used here is corrosion resistant, 'constant-voltage' and is capable of measuring pressure in the range of 50 - 1E-4 mbar. The barocel or capacitance manometer, contains a taut diaphragm, one side of which is exposed to the gas under test and the other side contains an electrode placed in a sealed-off vacuum

maintained at a pressure of less than 10E-6mbar with the aid of a getter. The thermocouples used are of K-type which is made of chromel-alumel junction. The effects of heat losses through heating has been studied using both heating mantle and a silicone oil bath as a heating method. The heating mantle consists of an insulated electrical-resistance heater and is electrically heated via a PID controller. Temperatures of up to 450°C can be obtained using heating mantle.

In all the vapor pressure measurements, the main objective is to measure the temperature at which boiling occurs; therefore, the two most important measurements are the respective temperature at a particular vapor pressure. It was expected that the vapor and liquid temperatures should be the same at a corresponding vapor pressure. Previous researchers have measured either the vapor or liquid temperature and assumed both to be the same or have not mentioned which temperature was being measured. For instance, during the vapor pressure measurement of phtalic esters using tensimeter-hypsometer, *Hickman, Hecker and Embree (1937)* measured only the vapor temperature. Vapor liquid equilibrium temperature based on temperature measurement in the vapor phase through thermocouple was also reported by *Daubert and Jones; (1990)* and *Rosen and Dickinson; (1969)*. However, *Perry, Weber and Daubert; (1949)* when measuring the vapor pressure of simple triglycerides, measured the temperature through a well-thermometer which protruded into the boiler and dipped below the surface of the liquid. In another measurement using small quantities of mixed triglycerides, the temperature well was above the liquid surface. *Osborn and Douslin; 1966* on the other hand did not mention which temperature was measured in their experiments with comparative ebulliometer. It can be concluded from the above review that the position of temperature measurement in the vapor-liquid equilibrium has been arbitrary: liquid phase, vapor phase or vapor phase touching the liquid presuming that all would be same (theoretically they ought to be the same). However, preliminary experiments with vapor pressure measurement of simple triglycerides in this work showed that the vapor and liquid

temperatures were different especially at very low pressures. These observations were rather curious and unexpected since it contradicts the basic principle of vapor-liquid equilibrium. Moreover, all the previous reported data on vapor pressure measurements become doubtful. Differences in vapor-liquid equilibrium temperatures were also observed when glycerol was used in the vapor-liquid equilibrium cell. Glycerol, has been used extensively in the exploratory experiment to investigate the liquid and vapor temperature differences in the vapor pressure measurement. Vapor pressure data for glycerol are easily available in the literature. Vapor pressure was measured by both using Pirani and barocel gauges in order to check for intra instrument differences. Measurements were made using maximum possible care and precision. However, differences are noticed between these two instruments as well. These observations led to as series of further exploratory experiments on the position of the thermocouple in the cell. Based on the experiments an attempt has been made to explain the observed behavior in the light of fundamental principles of heat transfer and kinetic theory.

Results and Discussion

The vapor pressures of trilaurin and trimyristin were measured using Pirani gauge and both the vapor and liquid temperatures were measured using thermocouples positioned as illustrated in *figure 1* and *2a* (thermocouple measuring liquid temperature is fully immersed in the liquid). The vapor pressure of tripalmitin was measured in a similar manner except with the addition of barocel to compare with the Pirani readings. The results are shown in *figures 3, 4* and *5* respectively. In both cases it was observed that both the vapor and liquid temperatures were significantly different in the experimental range of 7E-3mmHg to 3E-2mmHg for trilaurin and from 7E-3mmHg to 1mmHg for trimyristin. The experiments were repeated twice for trilaurin and four times for trimyristin with the same results. The difference between the vapor and liquid temperatures are quite significant and are larger at reduced pressure (higher vacuum).

Inspired by these observation subsequent experiments were conducted to explore the effects of thermocouple positioning in the sample bulb. These exploratory experiments are on both the vapor and liquid temperature measurements at the positions shown in *figures 2a* and *2b*. The sample was changed to glycerol because sufficient data on its vapor pressure is available in the literature for comparison (*Timmermanns; 1950* and *Lange's Handbook;1979*).

The vapor pressure measurements for the case illustrated in *figure 2a*, where the thermocouple just touches the liquid surface were made on four different days, the results are presented in *Table 1* and shown graphically in *figure 6*. The temperature measurements under these conditions indicate a small gap ($0°$ to $2°C$) between the liquid and vapor temperatures and are acceptable since it is within the thermocouples accuracy. However, when the thermocouple measuring liquid temperature was immersed into the liquid, a significant gap between the liquid and vapour temperature was observed as illustrated in *Table 2* and shown in *figure 7*. The differences varied from $0°$ to $5°C$, being higher at lower pressure.

In the beginning, it was thought that the differences between the liquid and vapor temperature could be due to the heat losses through the upper half of the heating mantle. Therefore, another experiment was conducted using silicon oil bath as a heating medium and keeping the vapor pressure cell completely immersed in the bath. The experimental conditions were exactly the same as before *(figure 2b)* and the observations were similar to the previous experiment using heating mantle under the same thermocouple positions *(figure 7, HB* - indicates heating method is silicone oil bath). These observation ruled out the possibility of the discrepancy between the liquid and vapor temperatures being due to the heating methods. It became imperative therefore, to seek an explanation for the observed temperature differences between the vapor and liquid.

The differences of vapor and liquid temperatures at equilibrium under these conditions could be due to the contribution of factors which may affect each other; i) the

various modes of heat transfer mechanisms under this experimental set-up, ii)instrumental effects i.e. the thermocouple and the pressure measurement principle, iii) the flow regimes; laminar and transition flow which is prevalent in this low pressure range and is well described by kinetic theory.

The effects of heat transfer mechanism which may contribute to the significant discrepancy between the liquid and vapor temperatures measured are first explored. The heat effects in the vapor pressure apparatus is governed by all the three modes of heat transfer mechanism. Heat is transferred by conduction from the heating element of the heating mantle through the glass wall to the liquid at the immediate surface of the wall. The same mechanism may govern the transfer of heat through the thermocouples. If a temperature gradient exist along a thermocouple, heat may be conducted into or out of the sensing element in accordance with the Fourier law of heat conduction.

Heat is then transferred by natural convection from the warmer/hot liquid near the wall of the glass bulb to the rest of the liquid. Heat is transferred by convection through the randomly moving molecules in the liquid to the immersed thermocouple. Heat is also transferred by convection to the thermocouple in the vapor phase. The molecules being in the vapor phase are spaced farther apart than the molecules in the liquid phase. Apart from conduction and convection that take place throughout within the glass sample bulb, heat transfer also occurs along the thermocouples which contributes significantly to the differences between vapor and liquid temperatures measured. All these modes of heat transfer phenomena occurring in the vapor pressure apparatus are illustrated in *figure 8*.

The measurement principle used in any instrument determines the accuracy of the readings. This is true with the two devices used in this experiment also. The thermocouple measuring heat is transferred to the thermocouple through the various heat transfer mechanisms. Temperature measurement using thermocouple is based on the principle of thermoelectric current and the current in the thermocouple circuit is

dependent on the electromotive force (emf) developed and the resistance of the circuit. For accurate temperature measurements, the measuring instrument is constructed so that a no-current emf is measured to eliminate the effects of circuit resistance. The thermal emf, as indicated in *Figure 9*, is a measure of the difference in temperature between T_2 and T_1.

When a thermocouple is exposed to an environment, the temperature is determined in accordance with the total heat energy exchange with the temperature sensing element. Heat transfer to the thermocouple sensing element may take place as a result of one or more of the three modes of heat transfer: conduction, convection and radiation. Referring to the experimental set-up shown in *figure 8*; the thermocouple measuring the liquid temperature is immersed to a depth of 1 to 2 cm. The liquid surrounding the thermocouple and the thermocouple wires are exposed to a convection environment. The thermocouple wires are covered with insulating material. Since the thermocouple is in contact with the liquid (molecules in the liquid are closer to each other in relation to molecules in the vapor phase), the temperature of the thermocouple junction is expected to be the same as the liquid temperature, T_1.

The thermocouple measuring the vapor temperature is also exposed to convection environment in the vapor phase. Heat received by the thermocouple junction by convection and radiation from the vapors and liquid surface may be less compared to the heat lost by the junction by conduction and radiation.

Apart from the possible errors in the temperature recorded, the accuracy of pressure readings are also dependent on the principle of its operation; for instance the Pirani's gauge is based on the principle of the dependence of thermal conductivity of a gas on pressure. The pressure readings are recorded by a corrosion resistant Pirani gauge (shown in *figure 10*) in the range of 50 - 1E-3 mbar. Most Pirani gauges are calibrated for dry nitrogen but can also be used with gases having similar relative molecular mass (RMM) such as oxygen and carbon monoxide; however correction factors must be used

with other gases/vapors. It is reported that the readings may be off by 20 times on account of the differences in thermal conductivity of gases due to the different degrees of translational, rotational and vibrational energies of the gas molecules *(Fitch, 1987)*.

The pressure recorded by the Pirani gauge could not be corrected in any way as no correction curves for the triglycerides or glycerol were available. However, in one experimental run, the vapor pressure was measured using Pirani gauge calibrated against the barocel. The barocel or capacitance manometer is based on the deflection of a diaphragm and is thus independent of the composition of the gas. The accuracy of the barocel is reported to be in the range of +/-0.15% compared to +/-10% for Pirani. The results of the vapor pressure measurements using both Pirani and barocel are illustrated in *figure 7*. It is obvious that for glycerol, there is no significant difference between the vapor pressure measured by Pirani and the barocel.

Some of the observations made in these experiments may well be explained by the kinetic theory of gas in particular in the heat transfer mechanism and the principle of measurement of the pressure. The molecules in a gas are in constant random motion, periodically colliding with one another and moving off in new directions. The average distance travelled by a molecule between the collisions, the mean free path depends on the temperature and pressure of the gas and the size of the molecules. At atmospheric pressure, the mean free path of a gas molecule is about 100nm (100/P nm where P is the pressure in bar). According to the kinetic theory the mean free path, λ between elastic collisions of gas molecules of diameter d (assuming they are rigid spheres) is $1/(\sqrt{2}\sigma)(kT/p)$, where σ is the collision cross-sections, k is the Boltzman constant, T is the temperature and p is the pressure. (The mean free path is inversely proportional to the pressure). Thus the mean free path for glycerol molecules at 123°C and 1mmHg is $\lambda_1 =$ 2.90E-5m, while it is 4.89E-3m at a temperature of 61°C and 5E-3mmHg pressure.

Furthermore, in the vapor pressure apparatus, non-static conditions prevail, i.e. gas flows towards the pump as it is vaporised by heating. At moderately low pressures,

continuum behavior of the gas as a viscous compressible fluid exhibiting turbulent or laminar is replaced via a transition regime by its molecular behavior. The Knudsen number characterise these flow regimes as discussed by *Steckelmacher, 1987* and *Perry's Chemical Engineers' Handbook, 1985*. The Knudsen number, or the ratio of mean free path, λ to characteristic length, D and the parameter X given as $\sqrt{(8/\pi)}$ x (λ/D) in the vacuum system determines the type of flow, i.e. viscous-laminar, transitional or molecular *(Perry's Chemical Engineers Handbook, 1985)*.

For transitional (slip) flow X lies between 0.014 to 1.0, and if X is greater than 1.0 then the flow is molecular. It has been found that at the experimental pressure (1E-3 to 50mmHg), the laminar and transitional flow is prevalent. Calculations have shown that from 1to 4E-1mmHg the regime is laminar and from 4E-1 to 5E-3mmHg (0.014 to 0.694) transitional regime prevails. Therefore, in order to achieve molecular flow, the pressure should be further reduced. The calculated values for the mean free path, λ, the Knudsen number, (λ/D) and the parameter X for glycerol at different temperature and pressure are given in *Table 3*. At low pressure the chances of a molecule colliding with another is less due to the larger mean free path. As a result, heat transfer by convection from the vaporised glycerol molecule from the liquid surface to other molecules in the vapor phase is reduced which accounts for the bigger temperature gap. Energy (heat) received through convection by the thermocouple junction in the vapor phase is smaller (due to very few molecules colliding) than the energy radiated (which may be the same for both the thermocouples). Whereas the thermocouple immersed in the liquid records the true temperature due to convection through liquid molecules.

In the case where the liquid temperature is measured by inserting a thermocouple that just touches the surface of the liquid *(figure 2a)*, no difference in the liquid and vapor temperatures are observed. Both the thermocouples are entirely in the vapor phase and exposed to similar convection heat transfer as explained earlier. The temperature recorded is lower then the actual temperature in the liquid phase. The thermocouple in

the vapor phase therefore does not record the true temperature which must be theoretically the same as the liquid temperature at the boiling point.

Thus, the thermocouple positioning in measuring the vapor and liquid temperatures in the vapor pressure apparatus under vacuum is very important and determines the accuracy of measurement. This explains in part the discrepancies in the measurement of temperature and pressure at very low pressure in the vapor pressure apparatus. Therefore, in vapor-liquid equilibrium at very low pressures, the temperature measurements must be based on the liquid phase with the temperature sensor fully immersed and not in the vapor phase.

Conclusion & Perspectives

Liquid and vapor temperatures are different at equilibrium in the pressure range of 1 to 5E-3mmHg using the experimental set-up. The differences are attributed to a combination of factors, i) the various modes of heat transfer mechanisms under this experimental set-up, ii) instrumental effects i.e. the thermocouple and the pressure measurement principle, iii) the flow regimes; laminar and transition flow which is prevalent in this pressure region and is well described by kinetic theory

It is suggested that researchers should be aware of the effects of heat transfer mechanisms which together with kinetic theory of gases largely influence the temperature and vapor measurements at low pressures. As for the temperature measurement is concerned, it must be based on the temperature of the liquid phase with temperature sensor fully immersed in the liquid. This will ensure reliable temperature measurement. The results of the observations have been incorporated in the setup in our next phase of experiments which includes the vapor pressure measurement for pure triglycerides.

REFERENCES

Bailey's Industrial Oil and Fat Products, Ed. D. Swern, Vol. 1, 4th Ed., John Wiley and Sons, 1979.

Daubert, T.E. and D.K. Jones, *Pure Component Liquid Vapor Pressure Measurements*, AIChE Symposium Series, **86** (275); 29-39, 1990.

Dean J. A., Lange's Handbook of Chemistry, 12th Ed., Mc Graw Hill, 1979.

Hickman, K.C.D., J.C. Hecker and N.D. Embree, *Direct Determination Of Low vapor Pressure*, Industrial and Engineering Chemistry, Analytical Edition, 9(6); 264-267, 1937.

Fitch R.K., *Total pressure gauges*, Vacuum, **37** (8/9); 637-641, 1987.

Osborn, A.G. and D.R.Douslin, *Vapor Pressure Relations Of 36 Sulfur Compounds Present In Petroleum*, J. Of Chem.& Engg. Data, 11(4); 502-509, 1966.

Perry, E.S., W.H. Weber and B.F. Daubert, *Vapor Pressures Of Phlegmatic Liquids. I. Simple And Mixed Triglycerides*, J. Amer. Che. Soc., **71**; 3720-3726, 1949.

Perry, R.H., *Perry's Chemical Engineers Handbook*, 6th. Edition, Mc Graw Hill Publisher, 1985.

Reid, R.C., J.M. Prausnitz and B. E. Poling, *The Properties of Gases and Liquids*, 4th Ed., Mc Graw Hill, 1988.

Rosen, J.M. and C. Dickinson, *Vapor Pressure And Heats Of Sublimation Of Some High Melting Organic Explosives*, J. Of Chem. & Engg. Data, **14**(1); 120-124, 1969.

Steckelmacher, W., The calibration of vacuum gauges, Vacuum, 37(8/9); 651- 657, 1987.

Tilinski and H.Puderbach, *Experiences With The Use Of DSC In The Determination Of Vapor Pressure Of Organic Compounds*, J. Of Thermal Analysis, **35**; 503-513, 1989.

Timmermans, J., *"Physico-Chemical Constants Of Pure Organic Compounds"*, Vols. 1 & 2, 1st. Ed., Elsevier Publishing Co., New York, 1950.
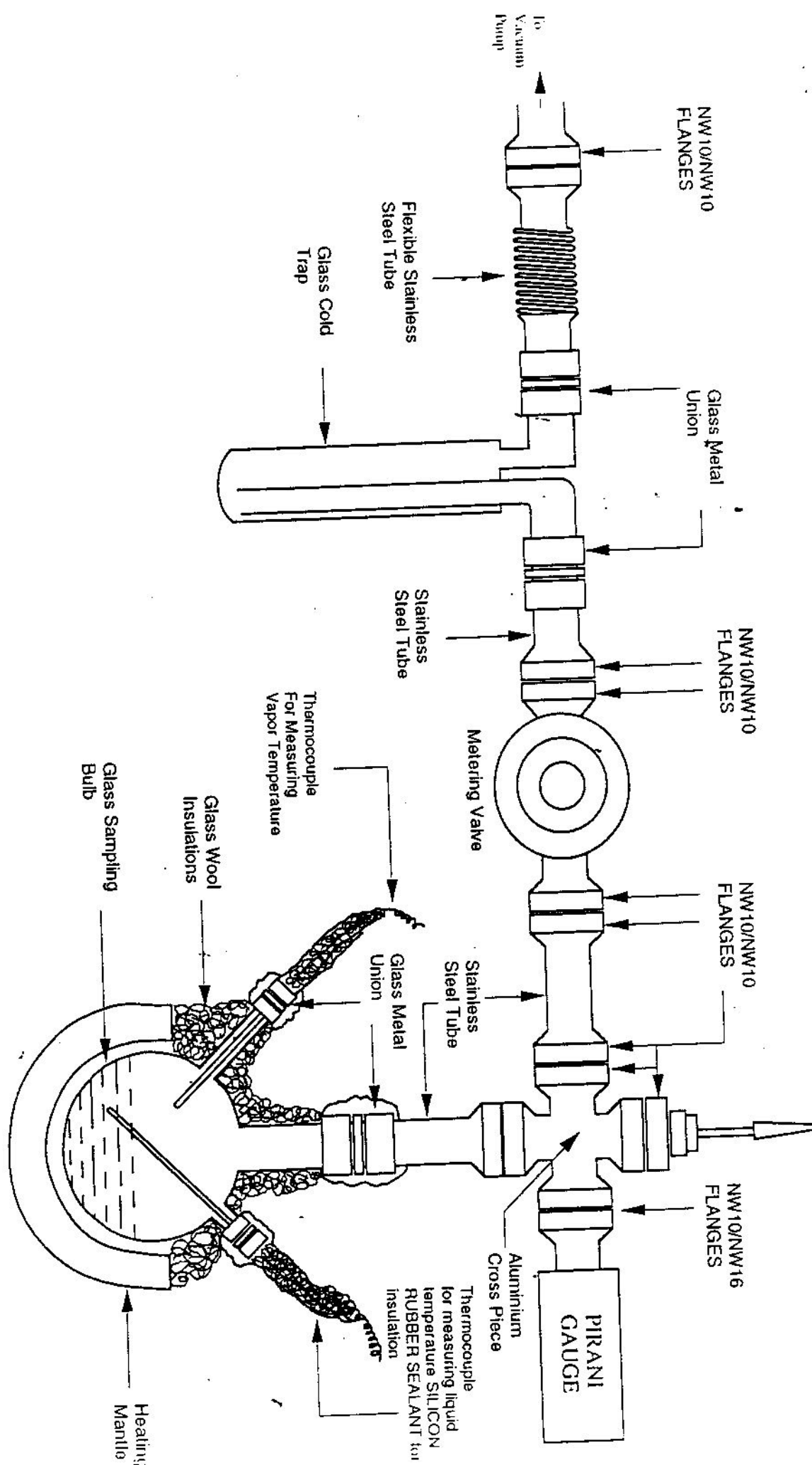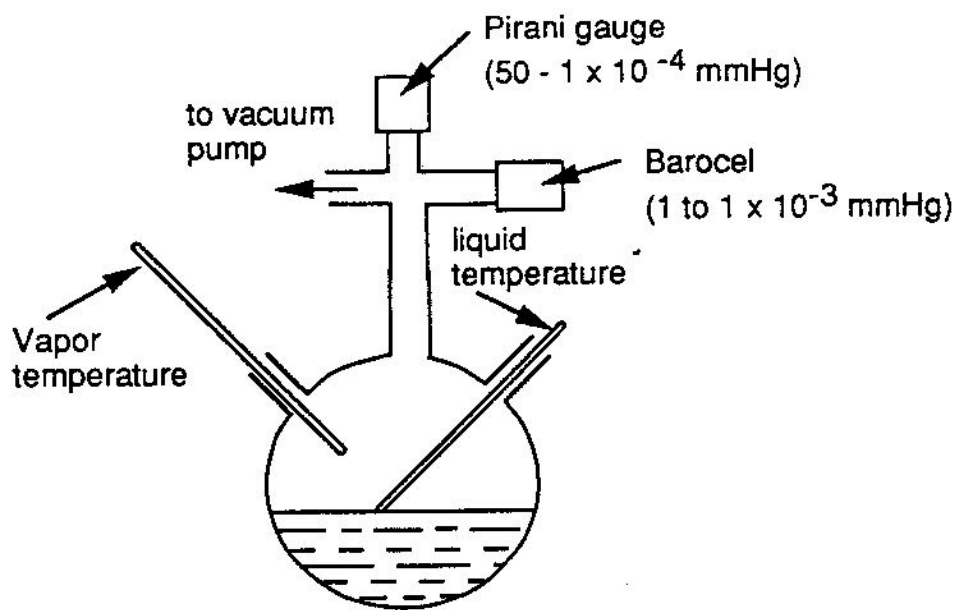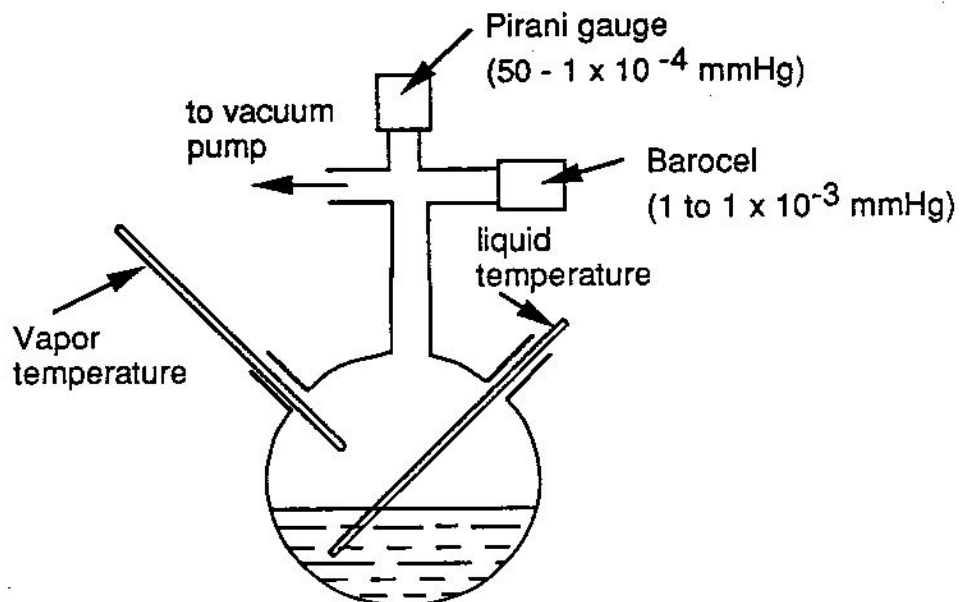
FIGURE 1 - APPARATUS FOR MEASURING VAPOR PRESSURE
OF PURE COMPONENTS - VACUUM RANGE 50 m bar - 10⁻⁴ mbar,
TEMPERATURE RANGE 100 °C - 450 °C.

FIGURE 2a - VAPOR AND LIQUID TEMPERATURE MEASUREMENTS: THERMOCOUPLE MEASURING THE LIQUID TEMPERATURE JUST TOUCHING THE SURFACE OF THE LIQUID.

FIGURE 2b - VAPOR AND LIQUID TEMPERATURE MEASUREMENTS. THERMOCOUPLE MEASURING THE LIQUID TEMPERATURE IS FULLY IMMERSED IN THE LIQUID .
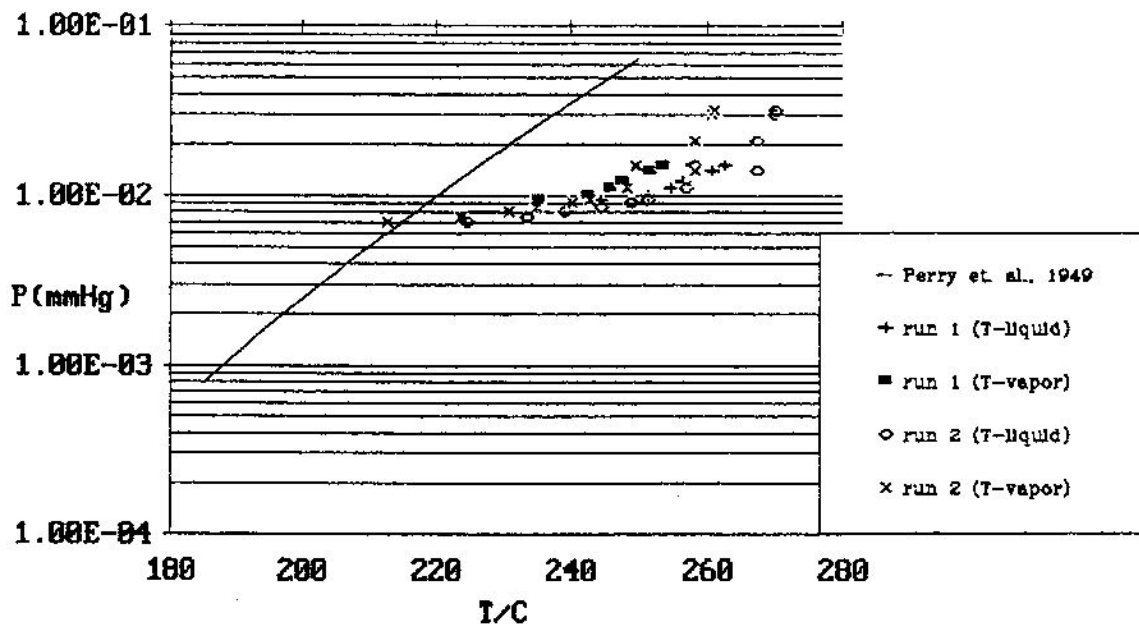
FIGURE 3. MEASUREMENT OF VAPOR PRESSURE OF TRILAURIN: VAPOR AND
LIQUID TEMPERATURES ARE OBSERVED TO BE DIFFERENT AT BOILING CONDITIONS.
— the thermocouple measuring the liquid temperature is immersed below
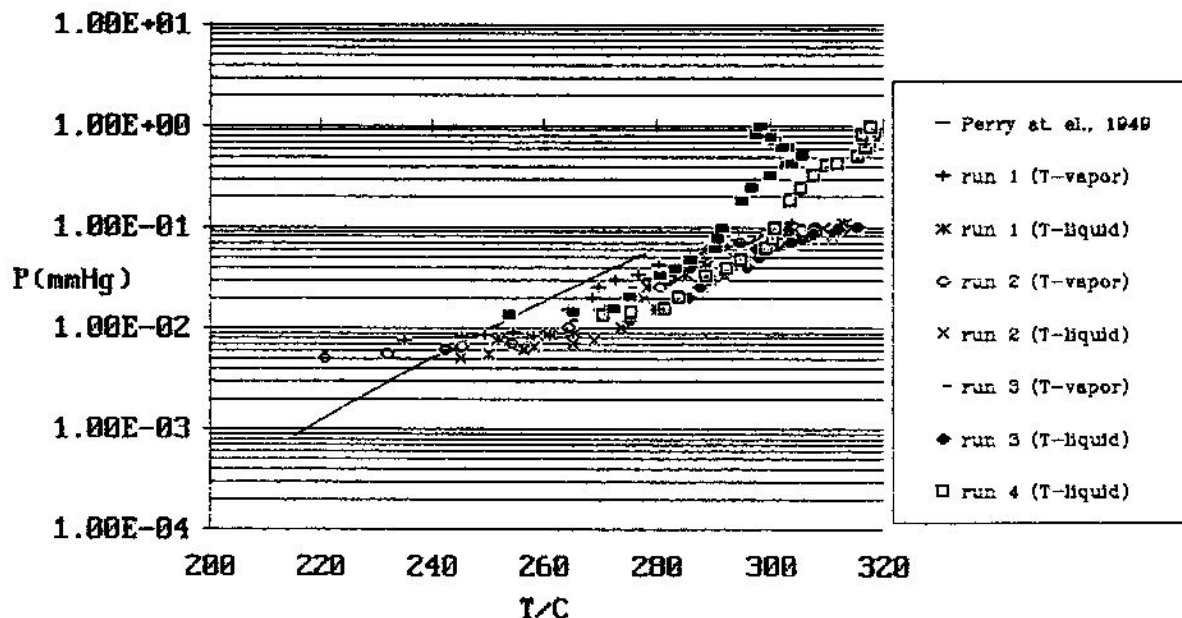the liquid surface, the vapor pressures are measured using Pirani gauge.

FIGURE 4. MEASUREMENT OF VAPOR PRESSURE OF TRIMYRISTIN: VAPOR
AND LIQUID TEMPERATURES ARE OBSERVED TO BE DIFFERENT AT BOILING CONDITIONS
— the thermocouple measuring the liquid temperature is immersed below
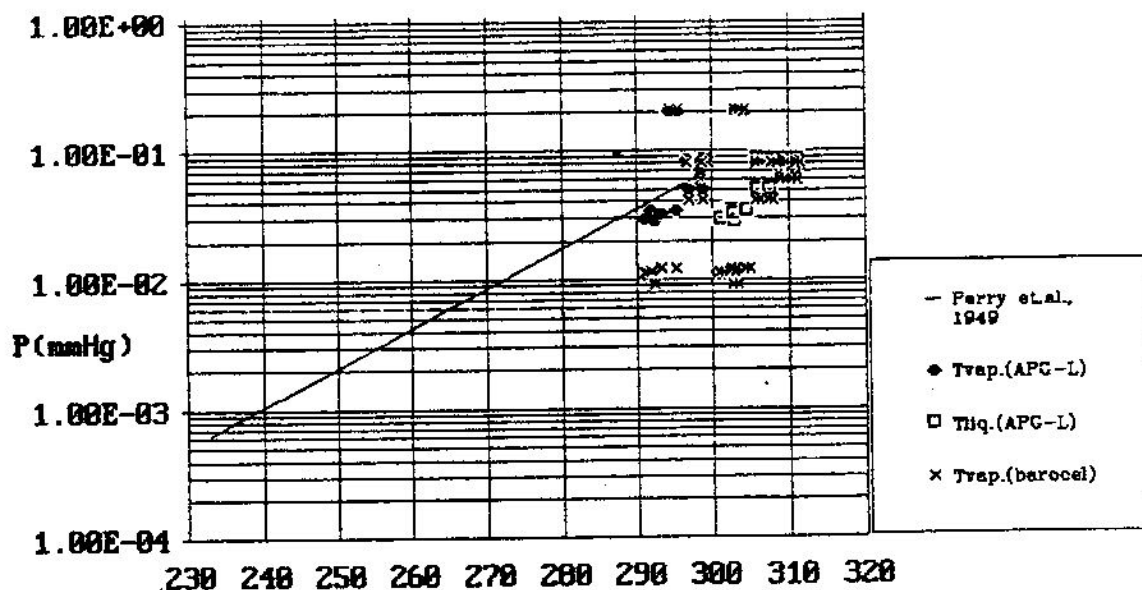the liquid surface, the vapor pressures are measured using Pirani gauge.

FIGURE 5. MEASUREMENT OF VAPOR PRESSURE OF TRIPALMITIN: VAPOR
AND LIQUID TEMPERATURES ARE OBSERVED TO BE DIFFERENT AT BOILING CONDI'
the thermocouple measuring the liquid temperature is immersed below
the liquid surface, the vapor pressures are measured using Pirani and barocel.

FIGURE 6. VAPOR PRESSURE OF GLYCEROL: VAPOR AND LIQUID
TEMPERATURES ARE OBSERVED TO BE DIFFERENT WITHIN 0 - 2 C
AT BOILING CONDITIONS.
- the thermocouple measuring the liquid temperature just touches
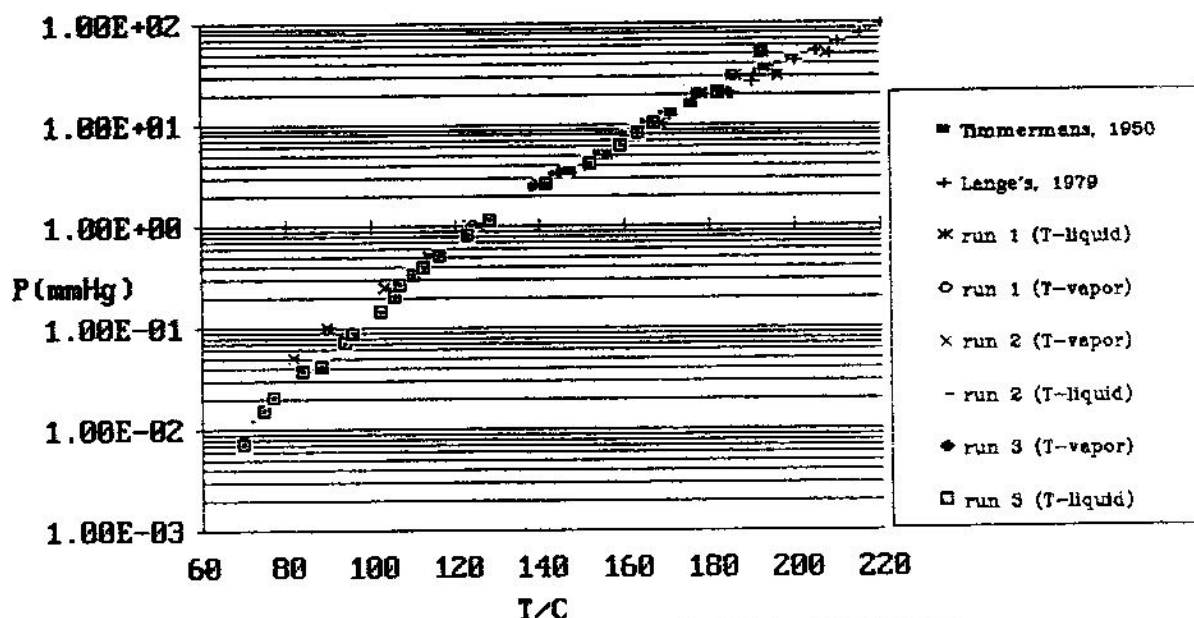the surface of the liquid, the vapor pressures are measured
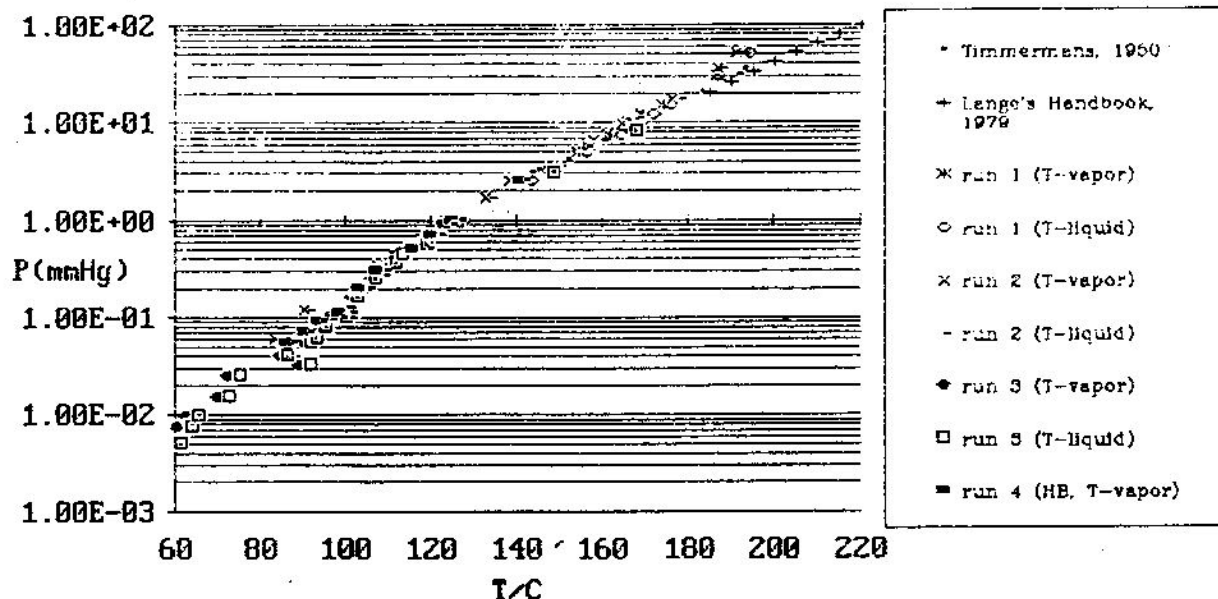using the Pirani gauge

FIGURE 7. VAPOR PRESSURE OF GLYCEROL: VAPOR AND LIQUID TEMPERATURES ARE OBSERVED TO BE DIFFERENT WITHIN 0 - 5 C AT BOILING CONDITIONS
- the thermocouple measuring the liquid temperature is immersed below the surface of the liquid, the vapor pressures are measured using the Pirani gauge. Similar experiment were conducted using heating bath (HB) instead of the heating mantle.
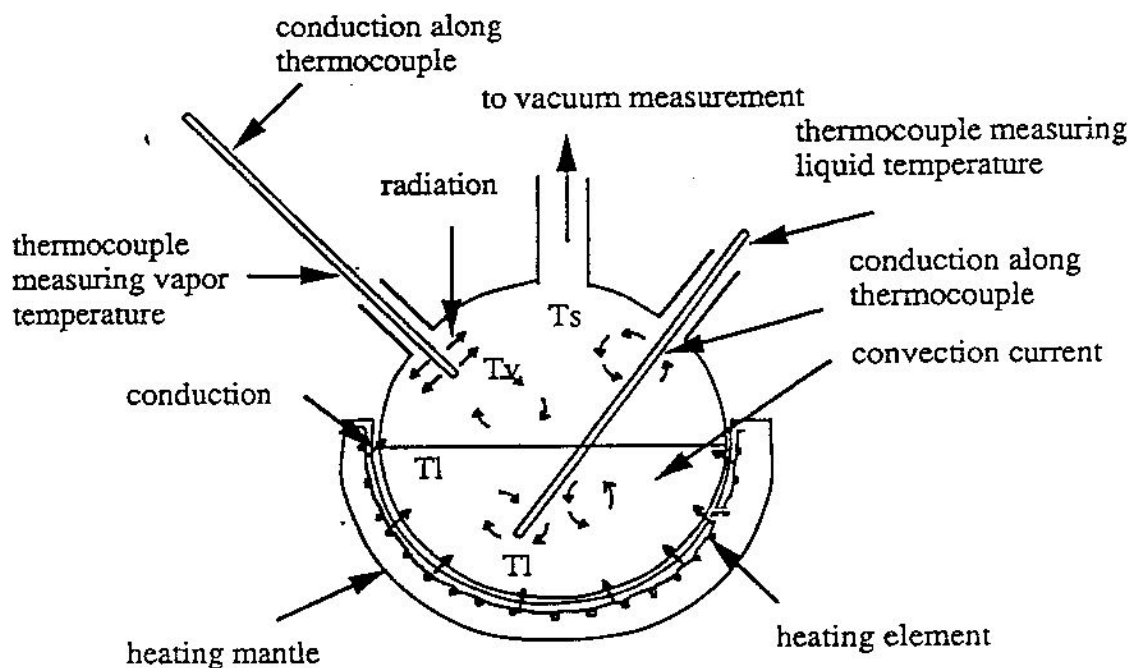
Figure 8. Heat Transfer phenomena that takes place in the vapor pressure apparatus. Conduction occurs from the heating mantle through the glass wall. Heat is transferred by convection from the hot to cold fluid. Heat is radiated from the thermocouple to the surrounding.

(Tl - liquid temperature as measured by the thermocouple uniproceed in the liquid.
Tv - vapor temperature as measured by the thermocouple placed in the vapor phase.
Ts - temperature of the vapor around the thermocouple in the vapor phase).
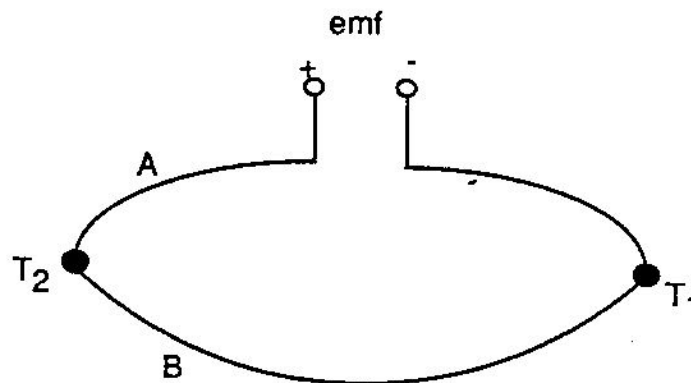
FIGURE 9 - THE THERMAL EMF, IS A MEASURE OF THE DIFERENCE
IN TEMPERATURE BETWEEN T_2 AND T_1.

For calibrating
under atmospheric
(10.000v) & vacuum
conditions (2.000v)

Gauge set point trip

Circlip retaining filter
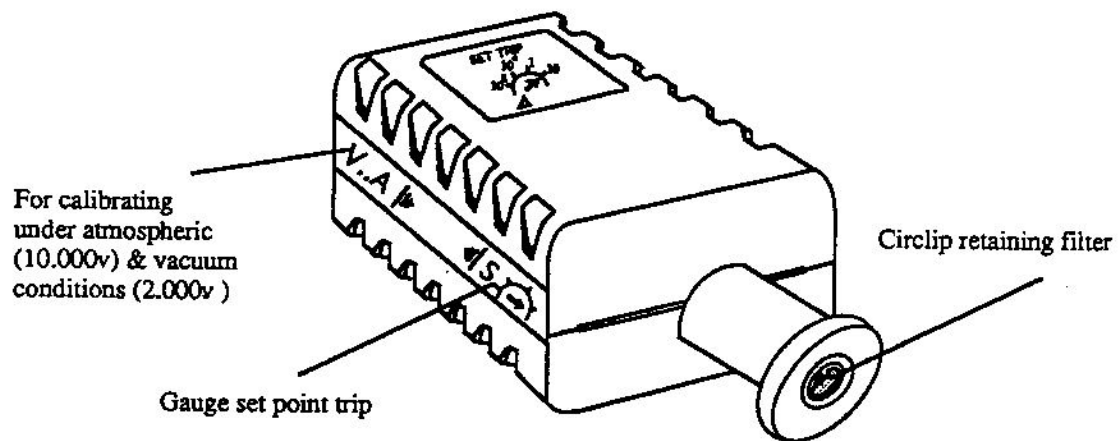
FIGURE 10 - GENERAL VIEW OF AN ACTIVE PIRANI GAUGE
(PRESSURE IN THE RANGE OF 50 mbar - $1X10^{-4}$ mbar)

TABLE 1: DIFFERENCES BETWEEN VAPOR AND LIQUID TEMPERATURES AT EQUILIBRIUM. THE THERMOCOUPLE MEASURING THE LIQUID TEMPERATURE JUST TOUCHES THE SURFACE OF THE LIQUID AS ILLUSTRATED IN (*Figure 2a*). Results are for glycerol.

Tliq	Tvap	Papg (mm Hg)	Del T
Run 1			
123.5	123.8	1	-0.3
140.3	140.3	2.5	0
154.1	154.1	5	0
160.4	160.4	7.5	0
165.4	165.4	10	0
177.3	177.1	20	0.2
185.5	185.2	30	0.3
192.2	192.2	50	0
Run 2			
81.1	81.3	0.05	-0.2
89.2	89.0	0.1	0.2
102.5	102.5	0.25	0
113.9	113.3	0.5	0.6
140.9	140.9	2.5	0
155.8	155.8	5	0
162.2	162.2	7.5	0
168.2	168.2	10	0
183.4	183.3	20	0.1
196.2	196.1	30	0.1
207.3	207.2	50	0.1
Run 3			
69.6	68.2	7.00E-03	1.4
74.6	73.4	1.50E-02	1.2
83.7	82.9	3.60E-02	0.8
87.9	87.3	4.00E-02	0.6
93.6	93.2	7.00E-02	0.4
95.5	95.1	8.50E-02	0.4
105.4	105.0	2.00E-01	0.4
116.1	115.9	5.00E-01	0.2
123.0	123.0	8.00E-01	0.0
141.6	141.6	2.50E+00	0.0
152.0	152.0	4.00E+00	0.0
163.2	159.0	6.00E+00	0.0
166.9	166.9	1.00E+01	0.0
Run 4			
80.8	79.9	3.8E-02	0.9
84.1	83.2	4.4E-02	0.9
96.0	95.2	8.0E-02	0.8
100.1	99.3	1.0E-01	0.8
104.1	103.4	2.0E-01	0.7
110.0	109.3	3.0E-01	0.7
114.2	113.3	4.0E-01	0.9
123.0	121.9	7.5E-01	1.1
126.1	125.4	9.5E-01	0.7
134.2	133.1	1.5E+00	1.1
143.0	141.4	2.5E+00	1.6
158.3	158.2	5.5E+00	0.1

N.B   Tliq - Liquid temperature $^{\circ}C$

Tvap - Vapor temperature $^{\circ}C$

del T - Difference between the vapor and liquid temperature $^{\circ}C$

Papg - Vapor pressure recorded on the Pirani gauge

TABLE 2 DIFFERENCES BETWEEN VAPOR AND LIQUID TEMPERATURES AT EQUILIBRIUM - THE TERMOCOUPLE MEASURING THE LIQUID TEMPERATURE IS IMMERSED INTO THE LIQUID AS ILLUSTRATED IN *Figure 2b*. Result are for glycerol

Tliq	Tvap	Papg (mm Hg)	Del T
Run 1			
127.4	123.4	1	4
143.3	138.5	2.5	4.8
156.1	154.3	5	1.8
169	166.2	10	2.8
171.6	169.1	12	2.5
186.8	186.8	30	0
194	193.8	50	0.2
Run 2			
84.1	83.1	0.06	1
108.2	107.2	0.34	1
117.7	117.6	0.65	0.1
122.6	121.6	0.95	1
149.8	148.2	3.6	1.6
156.6	157.6	6.5	2
177.8	175.9	36	1.9
191.5	191.1	50	0.4
Run 3			
61.4	56.2	5.00E-03	5.2
65.4	62.1	9.50E-03	3.3
86.4	84.2	4.00E-02	2.2
91.9	90.2	5.50E-02	1.7
100	98.9	1.00E-01	1.1
101.3	99.2	1.10E-01	2.1
103	101.3	1.60E-01	1.7
109.2	108.2	3.00E-01	1.0
113.4	111.4	4.40E-01	2.0
118.9	117.4	5.50E-01	1.5
148.8	147.8	3.00E+00	1.0
167.8	166.4	8.00E+00	1.4
Run 4			
87.9	85.9	5.50E-02	2
95	93.4	9.00E-02	1.6
101.8	98.2	1.10E-01	3.6
105.7	102.6	1.90E-01	3.1
109.8	107.1	3.00E-01	2.7
119.6	115.5	5.00E-01	4.1
122.6	119.6	7.00E-01	3
127	124.6	1.00E+00	2.4
156.9	156.8	5.50E+00	0.1

TABLE 3 THE MEAN FREE PATH, THE KNUDSEN NUMBER AND THE PARAMETER X. CALCULATED FOR GLYCEROL.

$T/^0C$	P/mmHg	Mean Free Path λ (m)	Knudsen no. λ/D	$X = \sqrt{8/\Pi} * \lambda/D$	Flow type
123.0	1E-0	2.90E-5	2.58E-3	0.004	Laminar
114	5E-1	5.67E-5	5.04E-3	0.008	Laminar
110	3E-1	7.71E-5	6.85E-3	0.011	Laminar
91	12E-1	2.2E-4	2.0E-2	0.030	Slip
81	5E-2	5.19E-4	0.0461	0.0735	Slip
61	5E-3	4.89E-3	0.435	0.694	Slip