

THE UNIVERSITY OF CALGARY

DEVELOPMENT OF A HIGH PRESSURE FLUID COLLECTION SYSTEM
FOR COMBUSTION TUBES

BY

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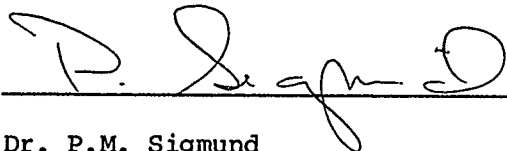
THE UNIVERSITY OF CALGARY

FACULTY OF GRADUATE STUDIES

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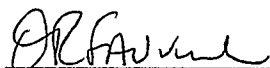
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ABSTRACT

The objectives of this study were two-fold:

- i) to design and construct a sampling system for the collection of fluid samples produced during a combustion tube test at the conditions of the production end of the tube, and
- ii) to study the phase equilibria of the produced fluid, using the developed system, at high pressure and temperature conditions, similar to those encountered in a steam bank.

The prime objective of the study, that being the development of the sampling system, was achieved. The thesis concentrates on the design of the apparatus and on screening tests performed to confirm the feasibility of the device. However, scheduling problems with the combustion tube test program did not allow for a successful test of the apparatus.

The sampling system consisted of a hydraulic piston, two sight glasses, four liquid cylinders, 300 cm³ each, in volume and four gas cylinders, 1 litre each in volume, all enclosed in a constant temperature air bath. The production from the combustion tube was collected in a floating piston cylinder, allowed to equilibrate, and

then displaced into high pressure collection cylinders. Dissolved gas was first flashed into expansion chambers, and then drawn by means of the Teopler pump into a volumetric burette for volume and composition analysis.

Part of the sampling system was successfully used to determine the solubilities of nitrogen in water and Athabasca bitumen.

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NOMENCLATURE

B	=	Ratio of number of moles of gas & liquid; n_G/n_L
B.C.	=	Bunsen Coefficient
f	=	Fugacity of pure component; kPa
\bar{f}	=	Fugacity of a component in a mixture; kPa
H	=	Henry's law constant, $p = Hx$; kPa
K	=	Equilibrium constant, $k = y/x$
M	=	Molecular weight; g/gmol
n	=	Moles
O.C.	=	Ostwald Coefficient
p	=	Total pressure; kPa
P_i	=	Partial pressure; kPa
R	=	Gas constant; $m^3 \text{ kPa/kmol K}$
S	=	Solubility; $\text{cm}^3(\text{ST})/\text{g}$
T	=	Temperature; K
V	=	Total volume; cm^3
v	=	Molar or specific volume; cm^3/gmol
\bar{V}	=	Partial molar or specific volume; cm^3/gmol
x	=	Mole fraction in the liquid phase
y	=	Mole fraction in the gas phase
γ	=	Activity coefficient
ρ	=	Density; g/cm^3

Subscripts and Superscripts

G	=	Gas phase
i	=	A subscript referring to any component in the mixture
L	=	Liquid phase
$^\circ$	=	A superscript designating a pressure p° , approaching zero
'	=	Primes designate separate phases

CHAPTER 1

INTRODUCTION

Increasing demands for alternate energy have prompted a greater effort in search for new sources of energy. Oil sands, also known as tar sands, provide a promising alternate energy resource. Considerable effort is now being expended to determine and utilize the energy stored in the bituminous sands, its prospects for recovery and the nature of its products.

Oil sands are sand deposits containing crude bitumen (viscous Petroleum) and other associated mineral substances. Crude bitumen is defined by the Alberta Energy Resources Conservation Board as:

"a naturally occurring viscous mixture mainly of hydrocarbons heavier than pentane that may contain sulphur compounds and that, in its naturally occurring viscous state, is not recoverable at an economic rate through a well".

Oil sands are often found in the same geographical area as conventional petroleum. Sixteen major oil sands deposits have been reported all over the world(1). Most of the known North American oil sand resource is located in Alberta, Canada, with sizeable deposits in Utah and smaller deposits scattered throughout the United States (2,3).

The Alberta tar sands reserves are estimated at about $1.59 \times 10^{11} \text{ m}^3$ (10^{12} bbl) bitumen, out of which $4.77 \times 10^{10} \text{ m}^3$ (3×10^{11} bbl) are considered recoverable. The extent of the Athabasca tar sands deposits, its properties and the recovery processes are covered in two reviews (4,5).

Because of the high viscosity of bitumen, about 100-1000 Pa-s at reservoir temperature and pressure, it will not flow into a well drilled into the formation and thus cannot be produced by conventional methods. As only 10 percent of the Athabasca bitumen can be surface mined, various techniques of lowering the viscosity with temperature, pressure and dissolved gases, to supplement the recovery of bitumen, are being developed. Experimental data on gas solubilities, gas-oil ratios and equilibrium constants (K-factors) of the major hydrocarbon components found in bitumen or heavy oils, therefore become increasingly important in the development of the various recovery techniques.

Thermal methods such as steam drive or steam flooding and in situ combustion have considerable potential for the recovery of heavy oils. Steam flooding has shown the most promise for bitumens such as those from Athabasca, Peace River and Cold Lake as a first step in the recovery process. In steam-flooding, the injected steam not only serves to lower the oil viscosity, but also supplies the drive energy. The steam saturated zone in the reservoir, whose temperature is approximately that of the injected steam, moves oil to the production well by steam distillation of the oil, solvent extraction, and gas drive. In situ combustion, also known as fire-flooding, appears to be an attractive process once bitumen mobility between the injectors and producers is established. In situ combustion also appears attractive for shallow reservoirs with 18 to 24 API gravity oils. This process involves the creation of a fire-front in the reservoir which is subsequently propagated by air injection. The burning front or combustion zone moves in the formation as a narrow band consuming or displacing the fluids encountered ahead of it. The process produces upgraded oil as a result of thermal cracking at the combustion front and produces carbon dioxide as a product of the combustion reactions. The combustion gases, together with the upgraded oil, come in contact with the virgin crude downstream of the front and tend to alter the properties of the crude. Natural surfactants are produced by reactions between the oxygen and oil, especially under

low temperature (less than 250°C) conditions. While the production of these surfactants is normally observed from produced water-in-oil emulsions, the presence of the surfactants may have some effect on the phase behaviour between the combustion gases (mainly N₂, CO₂ and CO) and the hydrocarbon phase (17).

This study was undertaken in an effort to investigate the phase behaviour of fluids produced during actual combustion tube tests under conditions equal to those at the outlet or production end of the tube. The basic design of the combustion tube effluent sampler, constructed for the collection of combustion tube products, was primarily intended to look at the phase behaviour of produced fluid samples and to compare it with what was predicted using numerical in situ combustion simulators. Combustion tube data are routinely used as a data base for a numerical simulator and it was felt that these data could be very useful. The equipment was thus designed to measure the solubility or gas-oil ratios and estimate the equilibrium constants of the lighter components found in the combustion tube products based on the assumption that the fluid samples were saturated. The imposition of tight time constraints due to the length of a single test was known to be a limitation, hence, it was realized at the outset that the experiments would result in somewhat crude phase behaviour measurements. However, the data produced were felt to be valuable for

comparison with those from more controlled experiments such as those reported by Svrcek and Mehrotra (6).

The major problems associated with the design were the presence of excess amounts of gas, and the presence of clays and sand grains in the normally highly viscous produced oils. In addition, conventional sight glasses could not be used as they are quickly coated and visual observation of the gas-hydrocarbon-oil interfaces becomes impossible. As mentioned earlier, a further problem was the real time operation of the tests as dictated by the burning front velocity. Typical combustion tube tests normally require 10 to 40 hours, hence turn around times had to be relatively short to allow for the gathering of more than one sample. Although not anticipated at the outset of the program to be a major problem, the separation of the gas and liquid phases within the cell was very difficult. As will be discussed in a later section, this latter problem prevented the successful completion of the second objective of the work.

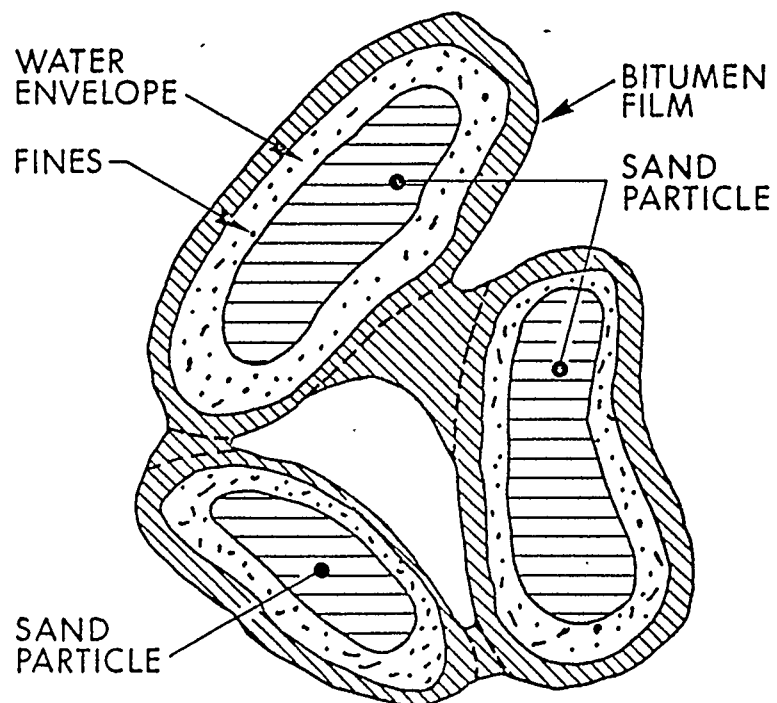
A portion of the apparatus was, however, calibrated by determining the solubility of nitrogen in Athabasca bitumen. The apparatus of Svrcek and Mehrotra (6) was utilized to saturate the bitumen samples. Nitrogen solubilities in water were also determined by saturating the samples within the collection system and analysing them using the volumetric apparatus constructed for the study.

CHAPTER 2

LITERATURE SURVEY

2.1 Bitumen Chemistry and Structure

Oil sand, as defined earlier, is a highly viscous petroleum which cannot be produced by conventional methods. It is a mixture of sand, water and bitumen, as depicted in Figure 2.1.

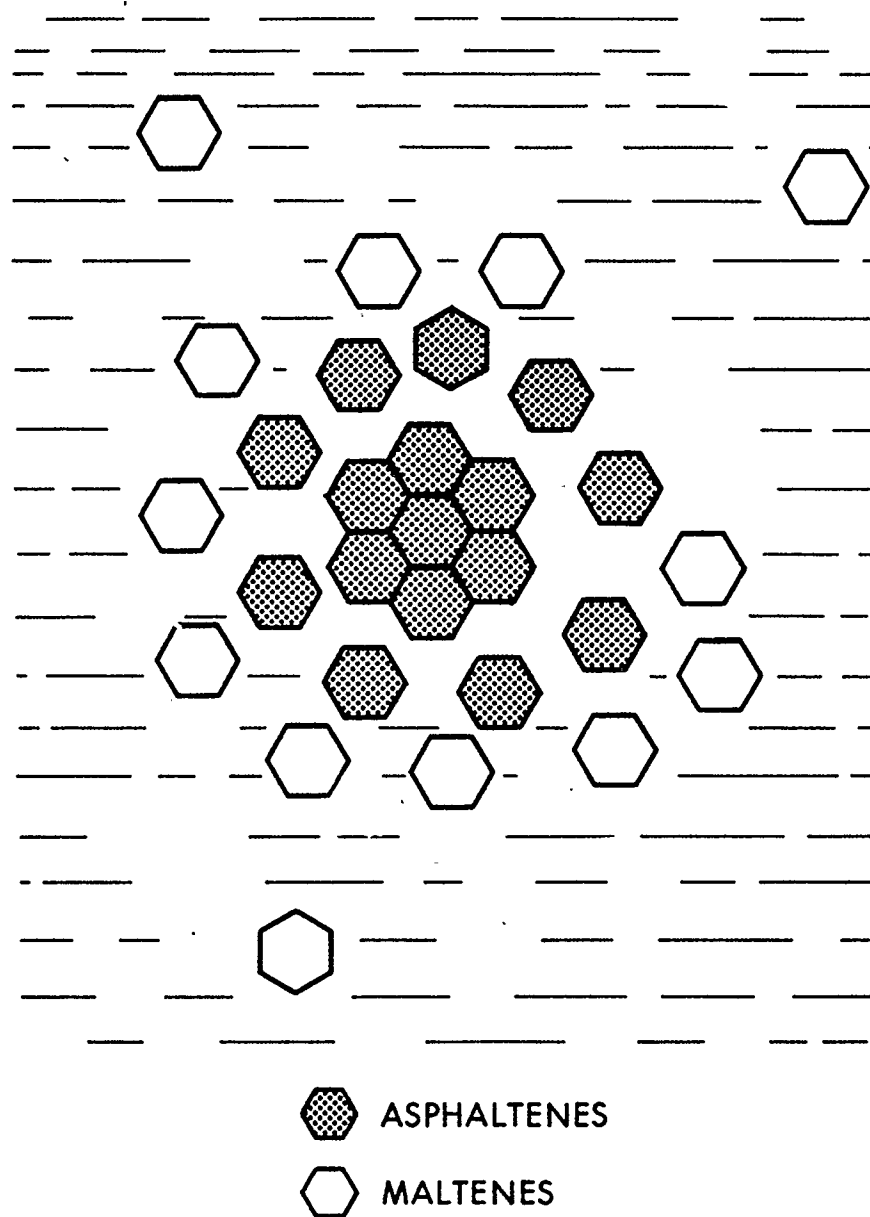


(5)

Fig. 2.1 - Typical Arrangement of Tar Sands Particle

Bitumens are among the most complex non-living organic matter found in nature. These differ from conventional petroleum because of the presence of a small concentration of low molecular weight hydrocarbons and the abundance of high molecular weight polymeric material.

Based on its solubility in a certain solvent (generally pentane) the bitumen constituents can be divided into soluble viscous oil, the "maltenes", and a heavier insoluble solid precipitate, asphaltenes. There is a third light hydrocarbon fraction, part of which is lost if bitumen is degassed or if it is prepared by solvent extraction (7). There are differing views whether bitumens are true solutions or colloidal in nature. Altgelt and Harle (8) suggest bitumens to be a molecular solution made up of maltenes as the solvent phase and asphaltenes as the solute phase. Pfeiffer and Saal (9) proposed bitumens to be colloidal in nature with asphaltenes forming the micellar dispersed medium and maltenes the dispersing medium. The structure of the micelle is such that substances with greater molecular weight and with the most pronounced aromatic nature are situated closest to the nucleus and are surrounded by lighter constituents of less aromatic nature (10). The transition of the intermicellar (dispersed or oil) phase is gradual and almost continuous as shown in Figure 2.2.



(10)
Figure 2.2 - Schematic Representation of the Physical
Structure of Petroleum

2.2 Composition of Alberta Oil Sand Bitumen

The elemental compositions of Athabasca and other Alberta oil sand bitumens are given in Table 2.1. Table 2.2 gives the overall gross composition.

Table 2.1

(11)

Overall Composition of Alberta Oil Sand Bitumen

	% of Whole Bitumen*			
	Cold Lake	Athabasca	Peace River	Wabasca
Asphaltenes	15.3	16.9	19.8	18.6
Deasphalted Oil	84.6	83.1	80.0	81.2
Acids	15.2	13.69	12.0	10.3
Bases	6.38	6.5	6.8	6.38
Neutral N-compounds	1.15	1.35	1.41	2.67
Saturates	21.3	18.3	15.15	14.60
Monoaromatics	8.3	8.1	8.57	7.61
Diaromatics	3.6	3.8		
Polyaromatics + Non-defined polar compounds	24.35	23.8		
Thiopheno-aromatics from mono and diaromatic fractions	0.8	0.88		
* Bitumen = 100%				

2.3 Phase Behaviour of Bitumen Systems:

One of the first works on gas-solubilities in the Athabasca bitumen was published by Svrcek and Mehrotra (6). They reported the viscosity, density and gas-solubility data for Athabasca bitumen saturated with CO_2 , CH_4 and N_2 for temperatures 25°C to 100°C and pressures up to 10 MPa. They observed that CO_2 had a high solubility in bitumen, causing a significant reduction in the bitumen viscosity. N_2 recorded a low solubility with CH_4 being in the intermediate range. Recently, they carried out further studies to include the effects of CO and C_2H_6 on the Athabasca bitumen at temperatures from 23°C to 118°C and pressures up to 10 MPa⁽¹⁸⁾. They observed that although the solubility of CO decreased with temperature, the extent of the reduction was very small. Comparison of their CO -bitumen data with the published solubility data for N_2 -bitumen revealed the solubility of CO to be twice as high as that of N_2 in bitumen at similar temperatures and pressures. The research further revealed that the solubility of C_2H_6 was much higher than that of CO_2 in the Athabasca bitumen. Mehrotra and Svrcek (19) have also carried out viscosity, density and gas-solubility studies for N_2 , CO , CH_4 , CO_2 and C_2H_6 in the Peace River bitumen. Recently the same group published viscosity, density and gas solubility data for CO_2 -saturated Marguerite Lake (from the Cold Lake region) bitumen⁽²⁰⁾. Dr. Robinson of the University of Alberta

generated solubility data for CO_2 and C_2H_6 in Athabasca and Cold Lake bitumen at temperatures between 100°C to 200°C and pressures up to 20.7 MPa. The study was submitted in the form of a report to AOSTRA during the 1980's and was never published⁽²¹⁾.

CHAPTER 3

EXPERIMENTATION

3.1 Process Selection and Description

Vapor-liquid equilibria have been measured at high pressures by dynamic and static methods. In dynamic methods a biphasic continuous flow of co-existing phases takes place to achieve mass transfer of components until equilibrium is reached. The phases should then be continuously separated without perturbing the equilibrium. Static methods simply use a closed cell filled with the gas-liquid mixture. The mixture is stirred continuously until pressure and temperature reach equilibrium values, then samples of both phases are withdrawn and analyzed. If sampling can be achieved in a simple and reproducible way, static methods provide the most economical, accurate laboratory apparatus. The method used in this study was a static method.

The experimental apparatus designed to collect the fluid samples produced during a combustion tube test is shown in Figure 3.1. It consisted of a floating piston, two sight glasses 25 cm long, 9 cm wide and 11 cm deep, four liquid cylinders 300 cm³ in volume four gas cylinders 1 000 cm³ in volume, all enclosed in a constant temperature oven. The oven measured 90 cm long, 120 cm wide and 60 cm deep.

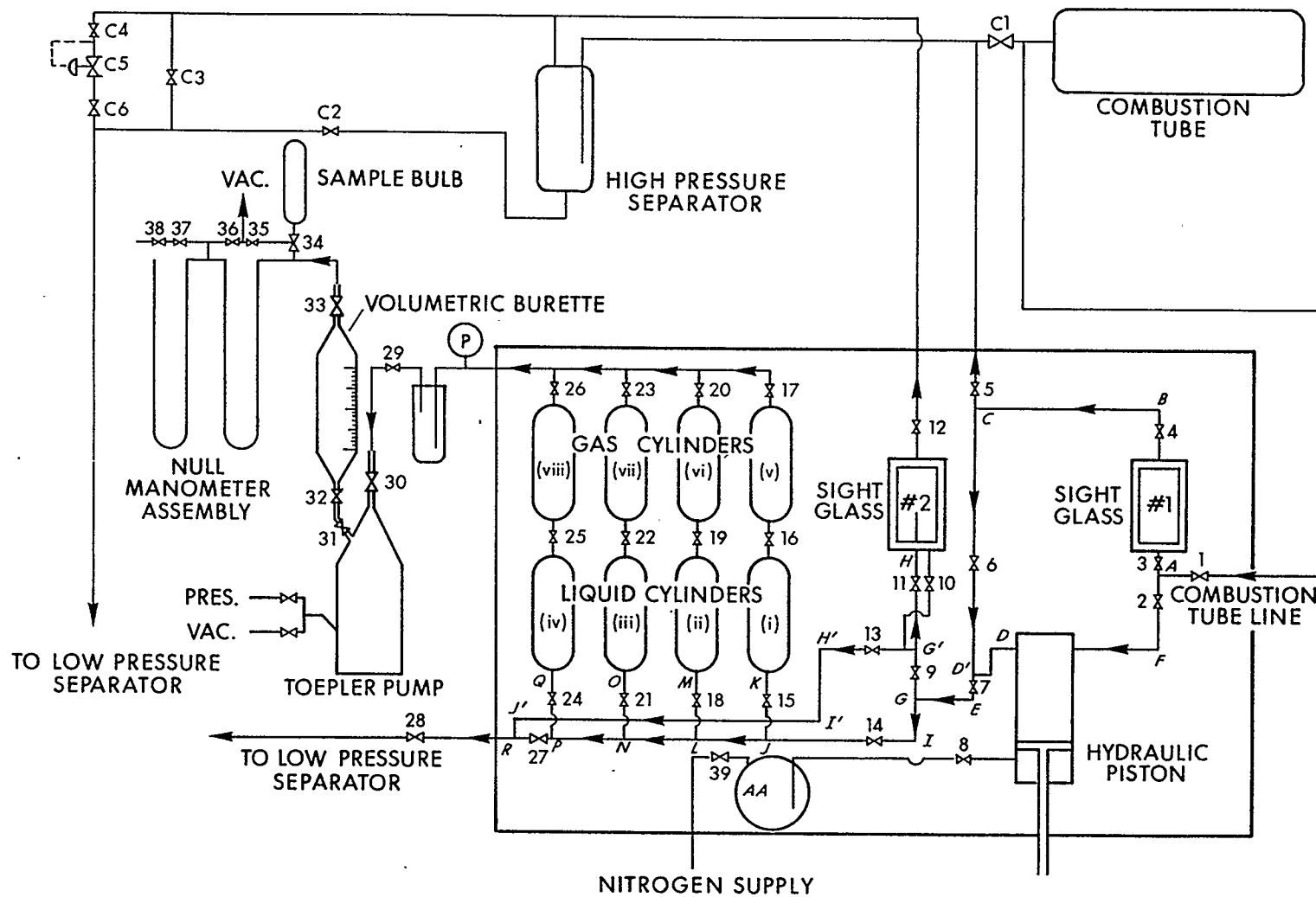


Figure 3.1 - Schematic of the Combustion Tube Effluent Sampler

The feed line to the floating piston was tied to the high pressure outlet of the combustion tube to collect the products. The other end of the experimental apparatus was connected to the Toepler pump assembly as shown, which was used to collect the solution gas at atmospheric conditions.

In both dynamic and static methods for measuring the phase behaviour of conventional oil or condensate systems the displacement of the phases is normally carried out by an immiscible fluid. Mercury or water is generally used as the displacing medium depending upon the composition of the phases. Because of the high temperatures (90°C - 100°C) and the presence of H₂S gas expected to be encountered during the experiments, use of mercury as the displacing medium was ruled out. Mercury was also not considered to be acceptable as it tends to emulsify following extended contact with heavy oils.

Use of water as the displacing medium was also considered undesirable because of the following reasons:

a) Water would be present in the form of an emulsion in the fluids produced during the combustion tube test and one of the proposed extensions of this study was to analyse the produced emulsions which had not undergone a sudden pressure expansion in the back pressure valves. Also, the original study called for accurate volume measurement of the liquid phase (containing water) under varying pressure conditions;

- b) Produced water in the combustion tube products would tend to mix in the displacement water phase;
- c) Experimental temperatures were as high as steam temperatures.

Therefore, because of the imposed limitations as described above, the use of mercury or water as a displacing medium was considered undesirable and a floating piston was installed for the fluid displacement.

Figure 3.2 shows a detailed arrangement of the floating piston cell. The original design was based on the information provided by an industrial laboratory. It was constructed of type 316 stainless steel, 46 cm in length and 6.3 cm in inside diameter. The two holes A and B drilled into the end cap of the cylinder were designed to provide for the passage of the fluids. The piston was driven by a hydraulic oil-gas system using port C to inject the driving fluid (oil). Reservoir AA (Figure 3.1) was filled with the hydraulic fluid (oil) with one end connected to a nitrogen gas cylinder and the other to the piston. In order to drive the piston upwards, nitrogen, under pressure, was introduced into reservoir AA which displaced the oil into the bottom part of the piston driving it upwards. The piston could be brought back to its original position by opening valve 39 (Figure 3.1) to release the gas pressure.

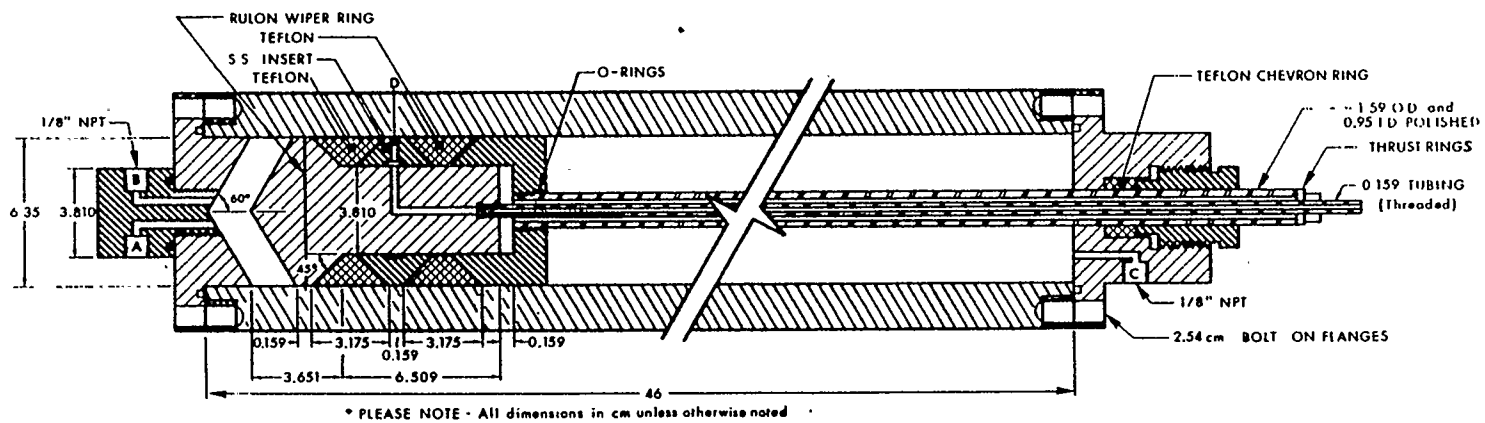


Figure 3.2 - Cross Section of the Floating Piston

The seal on the piston rod was achieved using teflon chevron rings as shown. In order to check for leakage between the produced fluid and hydraulic chambers, channel D was drilled to connect to the hollow inner stem (0.635 cm i.d.) of the piston rod. Any leakage drained through the hollow rod. Provision was made to stop the leak by tightening the nut over the special thrust rings provided at the bottom of the piston rod which caused an expansion of the seal rings.

The initial tests on the floating piston in the laboratory were marred by leakage problems. Produced fluid leaked past the seal and appeared at the base of the piston rod. Any amount of tension on the thrust rings was unable to stop the leakage. The piston was removed and, when dismantled for observation, it was seen that the presence of sand in the combustion tube products grooved the walls of the cylinder. This in turn gave rise to the leakage of the fluid under study. In order to rectify this problem, the interior of the cylinder was honed and a Rulon wiper ring was placed over the head of the piston rod as shown in Figure 3.2. The ring wiped away all the sand particles adhering to the walls of the cylinder, thereby preventing any subsequent damage to the cylinder walls. O-rings were also fitted at the hydraulic oil side of the piston (Figure 3.2), as a further protection against leakage at the piston rod connection. The floating piston operated successfully after these modifications. The modified

version of the floating piston is currently successfully employed at the Hycal Energy Research Laboratories Ltd. for phase behaviour measurements⁽¹⁷⁾.

Sight glasses are commonly used on conventional oils to assist in sampling of phases. Although the experimental apparatus did make use of a sight glass, it was somewhat modified to conform to the experimental needs and restrictions. The main reason a conventional sight glass was found impractical was that the fluid under study was black and viscous bitumen which, upon entering, would coat the sight glass, rendering it impossible to visually determine the gas liquid interface. The conventional sight glass was modified by inserting an inverted dip tube. The tube allowed for the passage of free gas and solution gas and the first drop of liquid coming out of it signalled the gas-liquid interface was reached.

Use of a thermal conductivity probe which would detect the position of the gas-liquid interface, was also investigated. This device was not useful because of its inability to withstand high temperatures.

In order to utilize the equipment to saturate liquid samples with gas (for calibration of the unit) a second sight glass was provided and situated in a position to complete a circuit FABCD'D (Figure 3.1). The

operation dealing with saturating the liquid samples using this sight glass is discussed in a later section.

The products coming out of the combustion tube were not a homogeneous mixture but rather a mixture of gas, oil and water phases. Therefore, once a sample from the combustion tube was collected in the floating piston it was felt necessary to divide the collected sample and channel it into more than one cylinder with the expectation of collecting a sample comprising only oil phase, one comprising only water phase and one comprising an oil-water emulsion. This would provide an opportunity to analyze oil and water/or emulsion separately. The apparatus was therefore equipped with four liquid cylinders with an internal capacity of 300 cm^3 each and four gas cylinders of $1\ 000 \text{ cm}^3$ each to separate the liquid and the gas phases.

The entire apparatus was enclosed in a thermostatically controlled oven. Electrical heaters rated at 1kW were provided in the forced-circulation heater box. The oven was also equipped with an electronic temperature controller to maintain it at a constant temperature. The controller operated on a type K thermocouple. The oven was insulated and the valves were mounted on extenders penetrating through the front panel. The rear panel was removable for easy access to all parts of the equipment.

A Toepler pump⁽²²⁾ was used to separate the solution gas from the parent liquid. This device was selected over the more conventional wet test meter because of the accuracy problems associated with low produced gas volumes. A wet test meter was also not used because of the long times required for separation of the solution gas from the bitumen.

A Toepler pump is a device for transferring gas from one vessel to another under reduced pressure. It operates by alternately raising and lowering a mercury level. Figure 3.3 shows a schematic of the separation apparatus. This consists of a liquid cylinder, a vacuum pump, a liquid trap, Toepler pump, a volumetric gas burette and a null manometer. The Toepler pump was constructed of glass with an approximate volume of 1 000 cm³ and was filled with mercury. Vacuum is applied to the line ABCDE (Figure 3.3) to evacuate the apparatus and the liquid cylinder valve is then opened allowing the solution gas from the liquid cylinder into the trap and the pump chamber 'aa'. The gas is trapped in this chamber by the check valve 'e'. Mercury is pushed into chamber 'aa' by introducing air into chamber 'bb'. This forces the collected gas out of 'aa' and into the burette where it is trapped by the check valve 'f'. The pump injection is repeated until no further gas is produced. The null manometer assembly connected to the tip of the gas burette records the pressure corresponding to the volume of the solution gas collected.

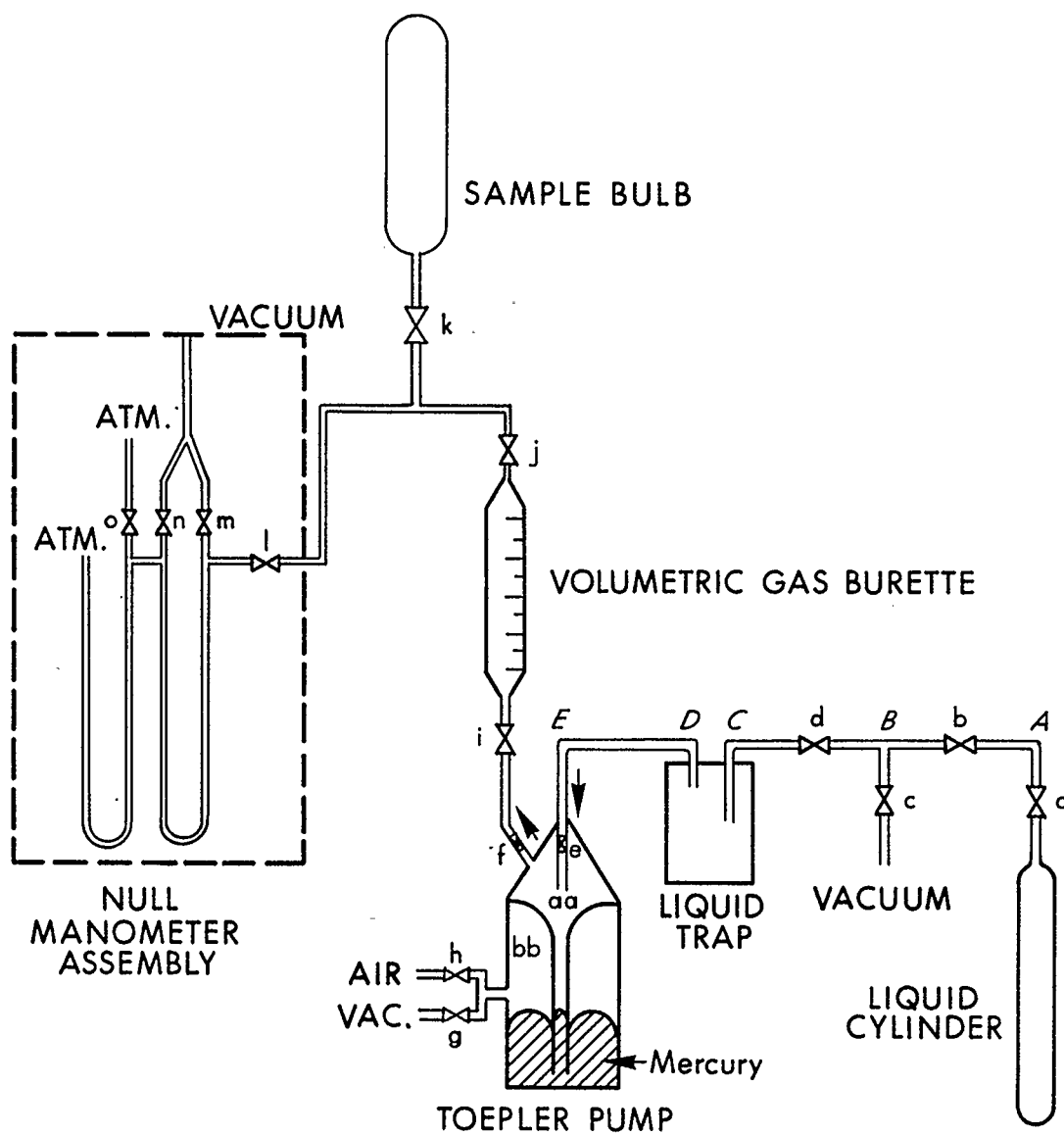
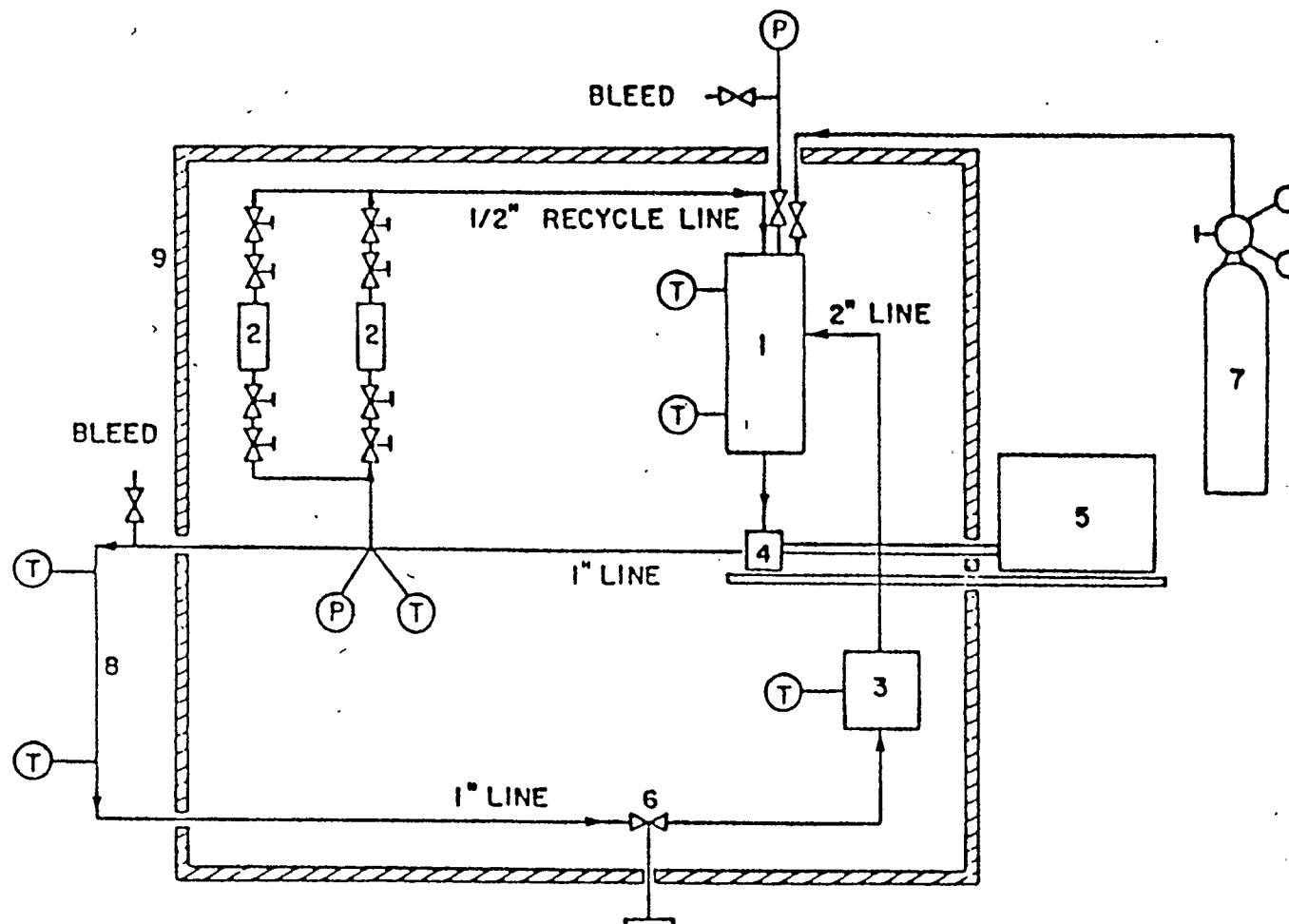


Figure 3.3 - Gas Separation Apparatus

3.2 Viscosity Apparatus of Svrcek and Mehrotra

This study was undertaken in an effort to investigate the phase behaviour of the fluids produced during actual combustion tube tests, however, as stated in the introduction, and further discussed in the following section, major problems prevented successful completion of this investigation. It was later considered appropriate to use a portion of the experimental apparatus to determine the solubility of nitrogen in the Athabasca bitumen and compare the results with the ones reported by Svrcek and Mehrotra (6).

In order to saturate the bitumen samples with the gas under study (N_2) a modified version of the viscosity apparatus of Jacobs (24) as reported by Svrcek and Mehrotra (6) was used. Figure 3.4 shows the detailed arrangement of the viscosity apparatus. It consisted of a gear pump, a mixing cell, a densitometer and a viscometer. The pump draws bitumen from the bottom of the mixing cell and divides the discharge into a recycle line and a circulation line. A pair of sample cells are placed, in parallel, in the recycle line, as shown. The recycle line supplies the bitumen to the top of the mixing cell, where a large contact area is provided between gas and liquid phases. The circulation line takes the bitumen through the densitometer and the viscometer. The entire apparatus sits in an electrically heated constant temperature air bath. Saturated bitumen samples are collected in the sample cells. These cells are then connected to the Toepler pump



LEGEND

1 - MIXING CELL ; 2 - SAMPLE CELL ; 3 - VISCOMETER

4 - GEAR PUMP ; 5 - MOTOR ; 6 - VALVE

7 - GAS SUPPLY ; 8 - DENSITOMETER ; 9 - HEATED AIR BATH

Figure 3.4 - Schematic of Bitumen Saturation Apparatus of Svrcek and Merhotra (6)

assembly for the collection of solution gas. It should be noted that the densitometer and the viscometer were not utilized as the equipment was solely used for saturation purposes.

3.3 Solubility of Nitrogen in Water

Nitrogen - water solubility measurements were done to confirm the operation of the Toepler pump. The test program was as follows:

The empty liquid cylinder was weighed and connected to the experimental apparatus (Figure 3.1) which was pressure tested and evacuated. Nitrogen gas was introduced into the floating piston. Water was then fed into sight glass #1. At this stage, the system contained only nitrogen gas and water. Nitrogen gas @ 4826 kPa and room temperature (22°C to 25°C) was then circulated through the water in sight glass #1 using line FABCD'D (Figure 3.1) by the inward and outward motion of the floating piston. This process was repeated several times and water was then drawn from sight glass #1 to the piston. The system was left undisturbed for a period of 24 hours to achieve equilibrium and saturation.

All the free gas was expelled through the line DD'EGG'H (Figure 3.1) using sight glass #2 as the monitor. This operation was performed by opening valves 7, 9, 11 and 12 and driving the piston upwards. At the sight of the first drop of liquid from the inverted dip tube in

sight glass #2, valves 9 and 11 were closed and the vapor in the sight glass expelled through the top and into the high pressure separator line. To confirm the expulsion of all the free gas had occurred, valves 9, 13 and 28 were opened and the products from the piston were driven through line DD'EGG'H'I'J'R and at the sight of the first drop of liquid from the low pressure separator line valves 9, 13 and 28 were shut off. Liquid cylinder (i) was then filled with the saturated water. Valve 16 was opened to let the solution gas expand into the gas cylinder (v). The volume of the gas cylinder was selected to be large enough ($1\ 000\text{ cm}^3$) to allow the system to attain near atmospheric conditions. The system was left undisturbed for a period of 24 hours to achieve equilibrium at low pressure conditions. The gas cylinder was connected to the Toepler pump assembly for the collection of dissolved gas. The total system (Toepler pump and null manometer assembly (Figure 3.3) was evacuated to the cylinder valve 'a', creating vacuum conditions. Valve 'a' was opened slowly, allowing the solution gas to flow into the trap and the pump chamber 'aa'. Here, the gas was trapped and backflow was prevented by the check valve 'e' (the arrow pointing in the direction the valve opens). Entrained liquid with the solution gas was collected into the trap provided. Air was now introduced to chamber 'bb' using valve 'h', forcing mercury into chamber 'aa' and into the base of the gas burette. Mercury was brought to a pre-set volume in the gas burette and the gas was displaced from chamber 'aa' into the burette. The null manometer, which was connected to the tip

of the gas burette, was zeroed and the pressure corresponding to the volume of the gas collected recorded.

Chamber 'bb' was now evacuated using valve 'g', withdrawing mercury from the pump body 'aa' to chamber 'bb' and once again creating vacuum in the line ABCDE. This in turn forced some more solution gas out of the cylinder which was displaced as described above. Similarly, the solution gas was forced out of the cylinder, in succession, until the manometer recorded constant pressure readings. These constant readings signalled that all the solution gas had evolved out of the liquid. The pressure reading gave the corresponding volume (using ideal gas relationship) of gas collected. The volume of the gas collected by the Toepler pump represented the volume of the nitrogen gas in solution in water at the experimental conditions. Based on the mass of water, the solubility of nitrogen gas in water, in terms of cm^3 gas per g water was calculated directly.

This process of saturating the liquid with gas was recognized as inefficient because of poor contact conditions between the gas and the liquid phase as any effective continuous stirring of the phases was absent. It was, however, felt to be adequate to test the liquid transfer operations and to test the Toepler pump assembly.

3.4. Mode of Operation of Combustion Tube Effluent Sampler

AOSTRA test 115 was the first run on which collection of the combustion tube products was attempted. The combustion tube sampler (Figure 3.1) was opened to the combustion tube as soon as the liquid production had started.

The apparatus (Figure 3.1) was first pressure-tested, the piston was pushed all the way up and the oven temperature set to 100°C. Combustion tube products, containing liquids and free gas, were directed into the floating piston cylinder (line AFD of Figure 3.1) and the piston was lowered. It was known that the combustion tube products would contain both gas and liquid phases in varying amounts. In order to ensure that the collected sample contained significant amount of liquid, valves 7, 9, 11 and 12 (Figure 3.1) were opened and the piston driven upwards, driving the products through the line DD'EGG'H (using sight glass #2 as a monitor) until liquid phase appeared in the sight glass. The collected gas was expelled through the top and into the high pressure separator line. Valves 7, 9, 11 and 12 were closed and additional combustion tube products were channelled into the floating piston cylinder. This process was repeated several times until it was felt that significant amount of liquid sample was collected. The collected products were allowed to equilibrate in the sampling cylinder by leaving them undisturbed for a couple of hours. The first major operation was to expel all the free gas from the system. This was

performed by opening valves 7, 9, 11 and 12 and driving the piston upwards. At the sight of the first drop of liquid from the inverted dip tube in the sight glass #2, valves 9 and 11 were closed and the vapor in the sight glass expelled through the top and into the high pressure separator line. To confirm the expulsion of all the free gas had occurred, valves 9, 13 and 28 were opened and the products from the piston were driven through line DD'EGG'H'I'J'R and at the sight of the first drop of liquid from the low pressure separator line valves 9, 13 and 28 were shut off.

The system, at this stage, was assumed to be free of all the free gas. The four liquid cylinders (i), (ii), (iii) and (iv) were now filled, one at a time, using line DD'EGIJLNP. Valves 16, 19, 22 and 25 were opened to let the solution gas expand into the gas cylinders (v), (vi), (vii) and (viii). The volume of these cylinders was selected to be large enough to allow the system to attain near atmospheric conditions. The system was then left undisturbed for a period of 10-15 hours to achieve equilibrium at the low pressure conditions. The pressure of individual gas cylinders was measured to ensure atmospheric conditions prevailed. Under these conditions, the Toepler pump could be connected directly to the gas cylinders to collect the dissolved gas. It was observed that the gas cylinders registered high pressures, hence, valves 15, 16, 18, 19, 21, 22, 24 and 25 were closed and the liquid cylinders were dismantled and connected, individually, to the

Toepler pump assembly for the collection of the dissolved gas as described in Section 3.3. The volume of the gas collected in the gas cylinders and that collected by the Toepler pump should have represented the total volume of gas in solution in the liquid sample. The mass of the liquid in the individual cylinders was measured. Following correction, the ratio of the volume of the gas collected, to the corresponding mass of liquid collected in the cylinders should have given the gas-oil ratio.

It was intended to analyze the dissolved gas by gas chromatography for the measurement of its composition, and hence the mole fractions. The information on the free gas composition was available from the combustion tube tests. From this the equilibrium constant, K , being the ratio of the mole fraction of a component in the gas phase to the mole fraction of the same component in the liquid phase, for lighter components could be calculated. As will be discussed, useful dissolved gas composition data were not obtained as the high pressures indicated that both free and dissolved gas were present in the sample cylinders.

3.5 Solubility of Nitrogen in Bitumen

The bitumen samples used for solubility measurements were obtained by toluene extraction of oil-sands mined in 1976 from the face of Suncor Great Canadian oil Sands. Details of the extraction

procedure have been reported by Vorndran et al (25).

The experimental set-up for the solubility determination was divided into two parts using two separate apparatus. The viscosity apparatus of Svrcek and Mehrotra, as shown in Figure 3.4, was used to prepare gas-saturated samples. The Toepler pump assembly, as shown in Figure 3.3, was used to analyze the volume of the dissolved gas.

The entire viscosity apparatus was thoroughly cleaned with toluene and dried with nitrogen gas. The sample cells were thoroughly cleaned with toluene, dried, weighed and their volumes determined before installation in the 1.27 cm recycle line (Figure 3.4). The apparatus was then filled with bitumen and pressure tested with the gas under study at about 10 MPa. The system was then brought to the desired pressure and temperature conditions and maintained there for 5-days. After 5-days of gas circulation through bitumen, it was expected the bitumen would be saturated with the gas under study.

Saturated bitumen samples were trapped by closing all the four valves around the sample cells without disturbing the gas-bitumen equilibrium.

The sample cells containing saturated bitumen were then weighed, and the mass of the trapped bitumen was determined by difference. The

density of bitumen was calculated from the mass and volume of the bitumen sample.

The sample cell containing the saturated bitumen was then connected to the Toepler pump assembly through which the dissolved gas was collected as discussed in Section 3.3. The solubility of the gas in bitumen was calculated in terms of cm^3 of gas per cm^3 bitumen, and cm^3 of gas per g bitumen.

CHAPTER 4

EXPERIMENTAL RESULTS AND DISCUSSION

4.1 Nitrogen - Water Solubility Tests

To determine the reliability and accuracy of the combustion tube effluent sampler and the Toepler pump (Figure 3.1), preliminary tests for the solubility of nitrogen in water were carried out. Tests were performed at temperatures of 22, 24 and 25°C at an absolute pressure of 4826 kPa. Table 4.1 presents the measured solubility data along with literature reported values at 25°C and 5050 kPa. The 5050 kPa data are presented for reference only and a more valid comparison is provided by Figure 4.1 which presents solubility as a function of pressure. It is seen that the solubility of nitrogen in water measured about 5.0 - 6.0 percent lower than the published values. This could be the result of the conditions under which water was saturated with nitrogen gas. As mentioned earlier any effective continuous stirring of the two phases was absent resulting in poor contact conditions between the gas and the liquid phase. Therefore, total saturation might not have taken place, resulting in a lower nitrogen solubility in water.

TABLE 4.1NITROGEN - WATER SOLUBILITY

TEMP.	SOLUBILITY	SOLUBILITY	SOLUBILITY	SOLUBILITY
	cm ³ N ₂ /g H ₂ O	cm ³ N ₂ /g H ₂ O	cm ³ N ₂ /g H ₂ O	cm ³ N ₂ /g H ₂ O
°C	@ 5050 kPa (26)	@ 5050 kPa (27)	@ 5050 kPa (28)	TEST RESULTS @ 4826 kPa
22	-	-	-	0.666
24	-	-	-	0.647
25	0.711	0.680	0.712	0.643

NOTE: cm³ N₂ reported at 15°C and 101.325 kPa.

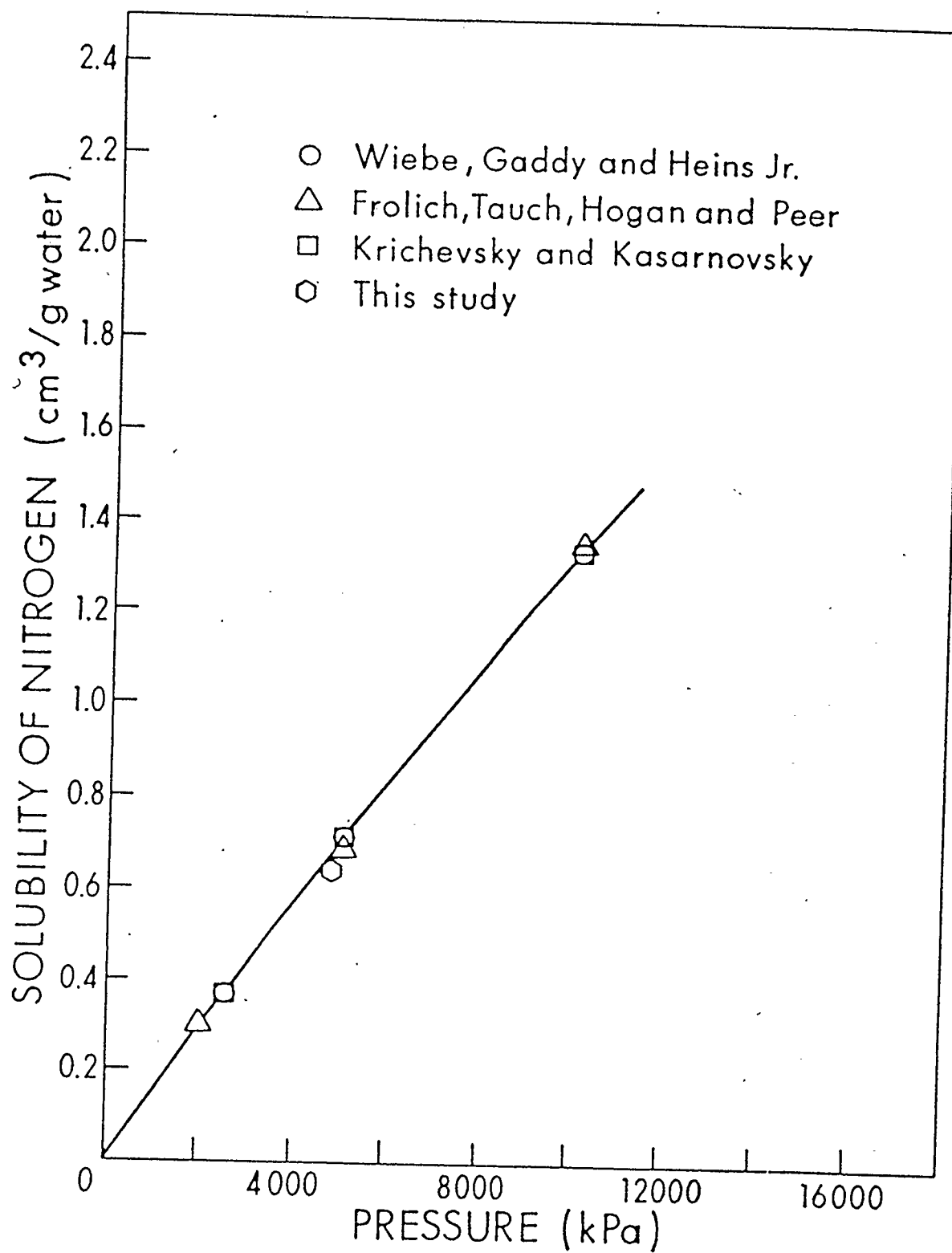


Figure 4.1 - Solubility of Nitrogen in Water at 25°C
(cm³ N₂ reported at 15°C and 101.32 kPa)

4.2 Nitrogen - Bitumen Solubility Test

In order to determine the solubility of nitrogen in Athabasca bitumen, the viscosity apparatus of Svrcek and Mehrotra (6) (Figure 3.4) was used to saturate bitumen samples with nitrogen gas and the Toepler pump was then used to collect the solution gas released by the saturated samples. In carrying out these solubility runs the pressure was maintained constant while the temperature was varied. The solubility (expressed as cm^3 gas at S.T.P. per cm^3 of saturated bitumen, and cm^3 per g of saturated bitumen), Henry's constant, equilibrium constants and density data for nitrogen - bitumen systems are summarized in Tables 4.2 and 4.3. The calculations utilized to evaluate the solubility, Henry's constants and equilibrium constants are summarized in Appendices A and B.

The nitrogen-bitumen solubility experiments were carried out at three different temperatures: 64°C , 96°C and 115°C while the pressure was kept constant at 3.0 MPa. The solubility results are compared with the ones reported by Svrcek et al (6) in Figure 4.2. It is seen that with increasing temperatures the solubility of nitrogen in bitumen is reduced. The curve levels off at high temperatures indicating the solubility of nitrogen in bitumen is not affected significantly at these temperatures. The solubility data of Figure 4.2 when replotted in terms of the logarithm of Henry's constant against

TABLE 4.2NITROGEN - BITUMEN SOLUBILITYP = 3000 kPa

T	DENSITY	S O L U B I L I T Y	
(°C)	(g/cm ³)	(cm ³ N ₂ /cm ³ Bitumen)	(cm ³ N ₂ /g Bitumen)
64.0	1.0031	1.789	1.783
96.0	0.9852	1.704	1.729
115.0	0.9572	1.607	1.679

NOTE: (cm³ N₂ reported at 15°C and 101.32 kPa)

TABLE 4.3NITROGEN - BITUMEN SOLUBILITYP = 3000 kPa

T	SOLUBILITY	B	x	K	H
(°C)	(cm ³ /g)	(moles solute) (moles liquid)	(fraction)		(kPa)
64.00	1.783	4.6754×10^{-2}	0.04467	22.389	67167
96.0	1.729	4.5337×10^{-2}	0.04337	23.057	69170
115.0	1.679	4.4027×10^{-2}	0.04217	23.714	71141

NOTE: (cm³ N₂ reported at 15°C and 101.32 kPa)

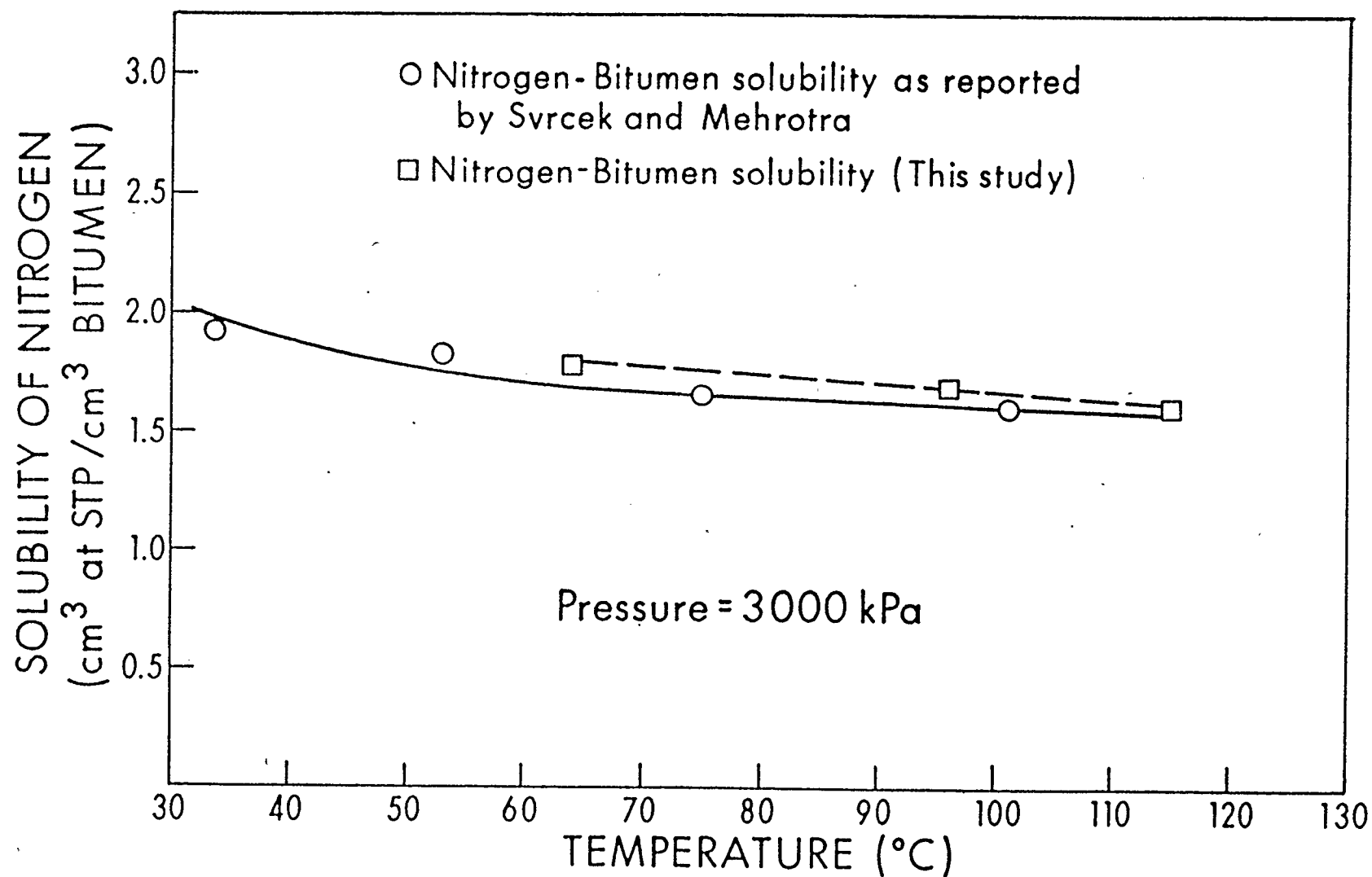


Figure 4.4 - Solubility of Nitrogen Bitumen

the inverse of absolute temperature resulted in a straight line, as shown in Figure 4.3. Figure 4.4 shows a plot of equilibrium constants against temperature for the nitrogen-bitumen system. Equilibrium constants increase with increasing temperatures. Figure 4.5 shows a plot of density versus temperature for the nitrogen saturated bitumen system. As seen, an increase in temperature decreases the density of nitrogen-saturated bitumen.

4.3 Bitumen - Phase Equilibria Tests

The high pressure sampler was used to collect combustion tube products in order to determine the product gas solubility and estimate the equilibrium constants for a number of the lighter components. Due to completion of the test program, high pressure collection of the liquid products was performed on AOSTRA runs 115 and 118 only. Run 116 was scheduled for product collection but various equipment problems with the newly designed system prevented high pressure sampling during this test.

Test 115 was a dry (no water injection) combustion tube test which utilized normal air (21 percent oxygen) injection at a back pressure of 2760 kPa. The sand pack for this test was mined and toluene extracted Athabasca oil sands containing 2.6 mass percent clay. A nominal air injection flux of $47.31 \text{ m}^3(\text{ST})/\text{m}^2\text{h}$ (injection rate of $0.367 \text{ m}^3(\text{ST})/\text{h}$) was used for the test. Total air injected over the

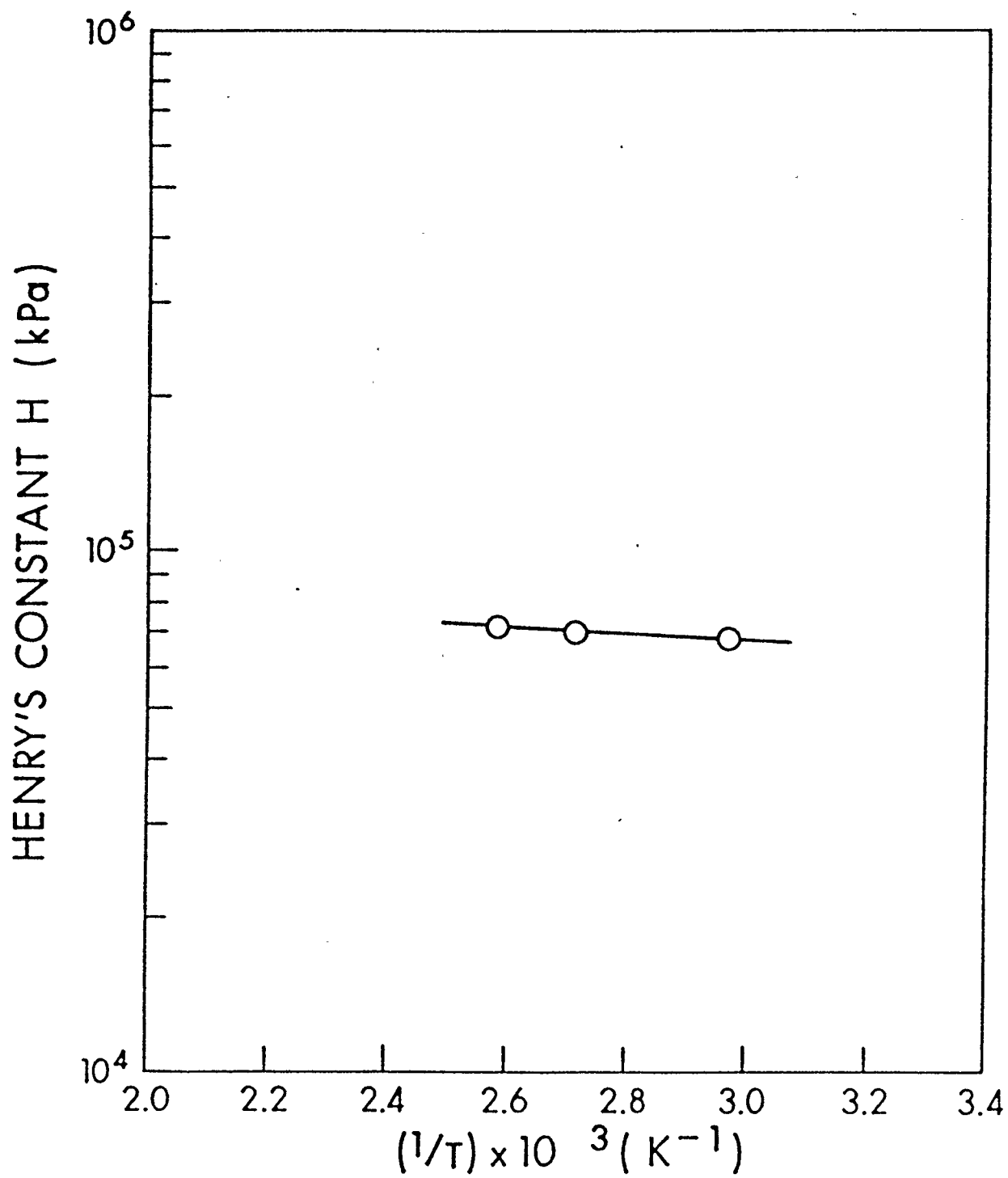


Figure 4.3 - Henry's Constant for Nitrogen - Bitumen System

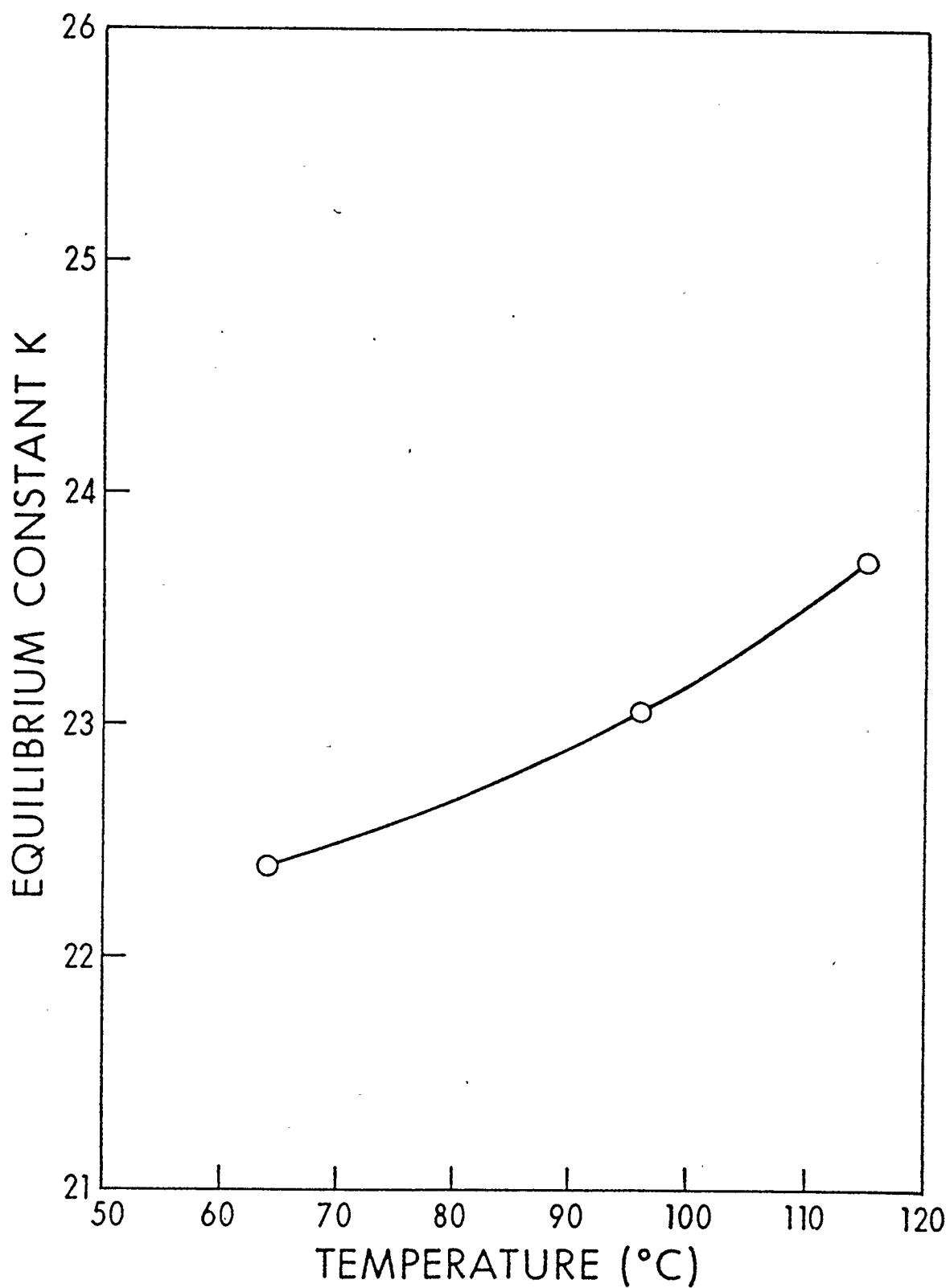


Figure 4.4 - Equilibrium Constant of Nitrogen - Bitumen System

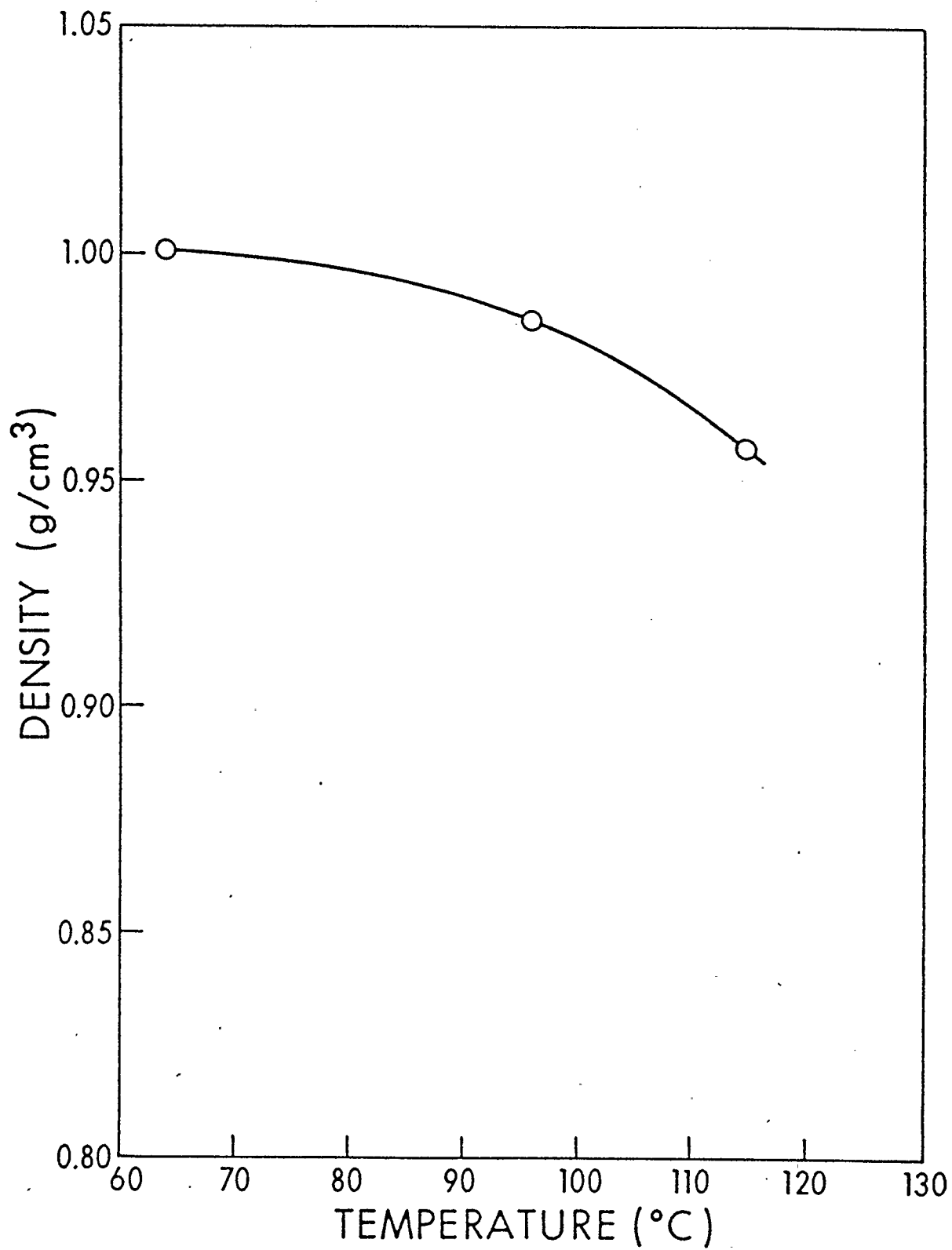


Figure 4.5 - Temperature Dependence of Nitrogen - Saturated Bitumen Density

duration of the test was $4.44 \text{ m}^3(\text{ST})$ where $\text{m}^3(\text{ST})$ are measured at 15°C and 101.325 kPa .

Combustion test 118 was also a dry test utilizing normal air at a back pressure of 2670 kPa . The sand pack was mined Athabasca oil sands containing 4.4 mass percent clay. The air injection flux was $33.42 \text{ m}^3(\text{ST})/\text{m}^2\text{h}$ which corresponds to an air injection rate of $0.260 \text{ m}^3(\text{ST})/\text{h}$. Total air injected was $3.92 \text{ m}^3(\text{ST})$.

The volume of the production gas was approximately equal to the volume of injection gas for both tests. Total oil and water masses initially present in the cores were 5349 g and 669 g respectively for test 115 and 4497 g and 1554 g respectively for test 118. Fluid production was expected to be relatively evenly distributed over the course of each test.

While the fluid production rates were anticipated to be uniform, the (oil/water ratio) of the produced fluids was expected to change considerably. The change in produced fluid composition is illustrated in Tables 4.4 and 4.6 for tests 115 and 118 respectively.

Table 4.4 provides the oil and water production rates and Table 4.5 gives the oil viscosity and water pH measurements for test 115. Tables 4.6 and 4.7 give the corresponding data for test 118.

TABLE 4.4

AOSTRA TEST RUN #115

TIME (h)	OIL PROD. (g)	CUM. OIL (g)	WATER PROD. (g)	CUM. WATER (g)	WOR
0.50	528.20	528.20	98.80	98.80	0.19
2.08	454.30	982.50	16.40	115.20	0.04
3.08	434.80	1417.30	7.00	122.20	0.02
4.42	707.70	2125.00	12.50	134.70	0.02
6.25	178.10	2303.10	0.40	135.10	0.00
7.75	719.80	3022.90	37.70	172.80	0.05
8.75	59.20	3082.10	0.70	173.50	0.01
10.75	620.30	3702.40	183.60	357.10	0.30
11.75	352.80	4055.20	36.10	393.20	0.10

TABLE 4.5

AOSTRA TEST RUN #115

TIME (h)	OIL VISCOSITY (Pa-S)			WATER pH
	80°C	95°C	110°C	
0.50	1.10	0.36	0.18	2.52
2.08	1.10	0.37	0.19	-
3.08	1.20	0.39	0.23	-
4.42	0.89	0.30	0.15	-
6.25	-	-	-	-
7.75	0.44	0.18	0.099	3.34
8.75	-	-	-	-
10.75	0.28	0.12	0.24	2.65
11.75	0.10	0.052	0.029	-

TABLE 4.6

AOSTRA TEST RUN #118

TIME (h)	OIL PROD. (g)	CUM. OIL (g)	WATER PROD. (g)	CUM. WATER (g)	WOR
2.00	738.50	738.50	0.50	0.50	0.00
3.50	612.30	1350.80	0.70	1.20	0.00
4.50	333.80	1684.60	47.20	48.40	0.14
6.17	272.60	1957.20	153.40	201.80	0.56
7.50	90.10	2047.30	0.70	202.50	0.01
10.00	341.10	2388.40	355.90	558.40	1.04
15.00	387.60	2776.00	530.40	1088.80	1.37
16.50	261.70	3037.70	145.30	1234.10	0.56

TABLE 4.7

AOSTRA TEST RUN #118

TIME (h)	OIL VISCOSITY (Pa-S)			WATER pH
	80°C	95°C	110°C	
2.00	0.47	0.21	0.12	-
3.50	0.58	0.26	0.15	-
4.50	0.72	0.31	0.17	6.12
6.17	0.52	0.23	0.13	7.93
7.50	0.51	0.23	0.13	7.39
10.00	0.21	0.11	0.065	4.74
15.00	0.041	0.025	0.017	1.82
16.50	-	-	-	-

Graphical presentation of the data are provided in Figures 4.6 to 4.15 respectively. The changing viscosity and pH suggest that the liquid samples undergo a marked variation in their quality over the course of a test. The WOR for the test runs are plotted in Figures 4.10 and 4.13. The highly fluctuating path traversed by these curves confirm the variation of the liquid quality. Oil and water production rates for test 115 are plotted in Figures 4.11 and 4.12 respectively, while Figures 4.14 and 4.15 present the corresponding data for test 118. As seen, the production rates of the liquids at different time intervals also varied.

It was in anticipation of the changing composition of the liquid phase that four sample cylinders were installed in the apparatus. It was hoped that at least one cylinder would contain oil only and at least one would contain only water.

The data on the high pressure combustion tube products collected in the four different cylinders are presented in Tables 4.8 and 4.9. The tables provide the liquid and gas volumes collected along with gas pressures registered by individual cylinders and GOR for tests 115 and 118 respectively. As seen, each cylinder registered high pressures instead of the expected atmospheric pressures. Based on our assumptions of 40 to 100 scf/bbl bitumen, a GOR of 7 to 18 cm³/g bitumen was expected. As seen from Tables 4.8 and 4.9, measured GOR's for the

tests were unrealistically high. The excessive gas volumes indicated the presence of free gas in the collection cells. Tables 4.10 and 4.11 give the product gas and solution gas analyses for tests 115 and 118 respectively. The gas analyses do not show any definite trend. Based on the CO_2 and N_2 compositions in cylinders #3 and #4, test #115, it can be discerned that the solution gas is representative of the free gas composition. However, the rest of the compositions suggest internal inconsistencies between the free gas and the solution gas compositions as exemplified by H_2 and O_2 (cylinders #3 and #4), test 115; and C_3H_8 , N_2 (cylinder #2) and H_2 , O_2 and CH_4 (cylinder #4), test #118 (Tables 4.10 and 4.11). Also the essential absence of CO in the solution gas (test #115) does not seem logical given the finite composition of CO in the free gas. In light of the above, no firm conclusions can be drawn from the gas analyses.

The volume of collected liquid was very low as seen from Tables 4.8 and 4.9. Assuming a cylinder volume of 300 cm^3 , the expected liquid mass should have been approximately 295 g in each cylinder. The significantly lower mass in each cylinder shows that insufficient liquid was collected in the sampler. Given the very small liquid masses and the high pressures in the sample cylinders it can be concluded that the floating piston contained large amounts of free gas which was pushed into the cylinders.

The large gas volumes and small liquid volumes negated the validity of the tests. Both the tests, AOSTRA runs 115 and 118 ended with the gas cylinders registering excessive volumes of gas, thereby rendering the experiments inconclusive.

The most probable explanation for the presence of free gas, despite the efforts to expel the gas through the sight glass, is that gas bubbles were trapped in the highly viscous bitumen. Thus, when the first drop of bitumen did appear at the tip of the tube in the sight glass, it was interpreted, erroneously, to mean the line leading to the sight glass from the piston and the cylinder chamber were full of saturated liquid only. It is highly probable that pockets of trapped gas developed in the liquid and were not expelled from the system. The test results indicated that much longer equilibration times are required to allow for gas-liquid separation.

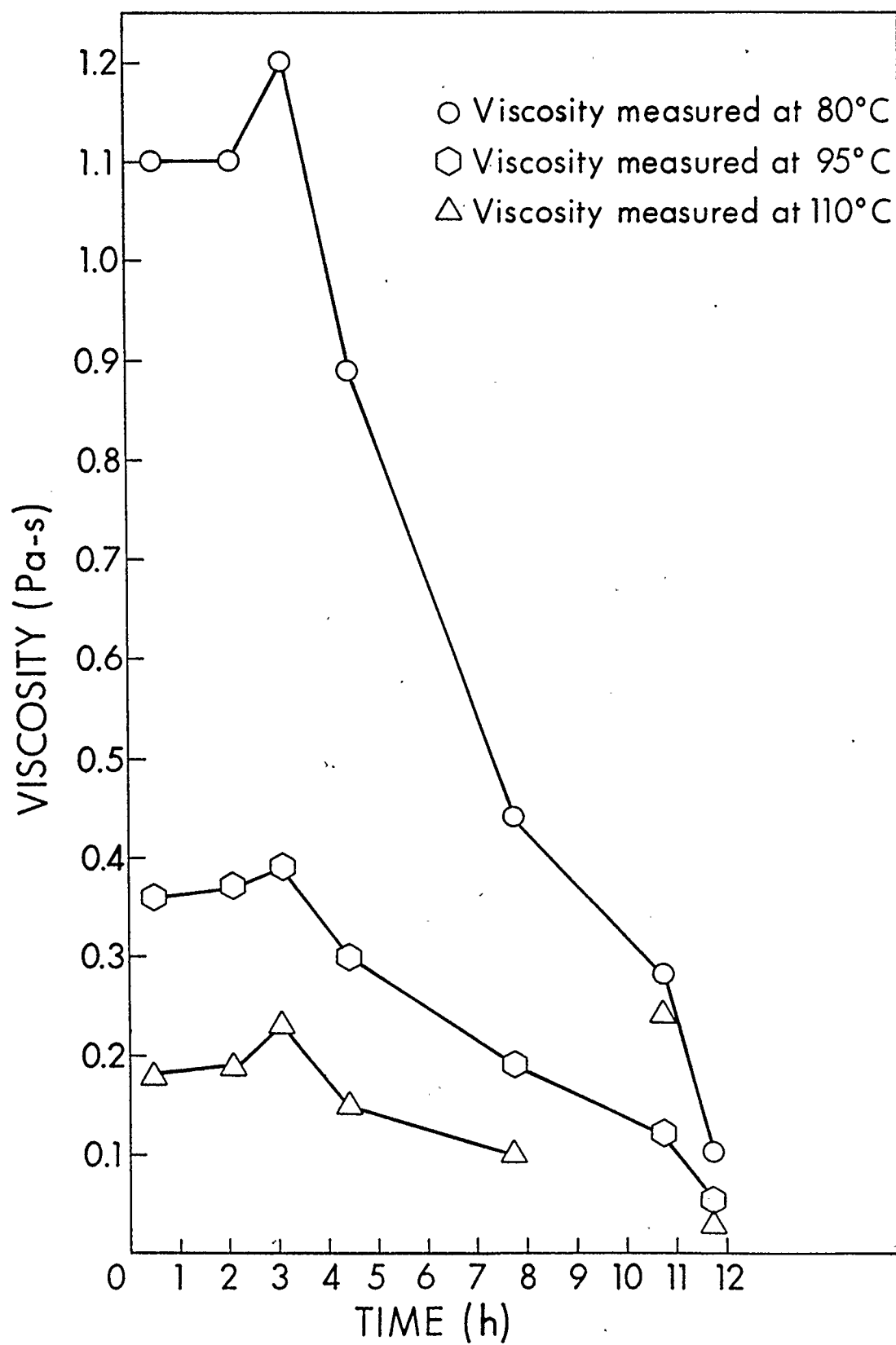


Figure 4.6 - Viscosity of the Produced Fluid (AOSTRA Test Run #115)

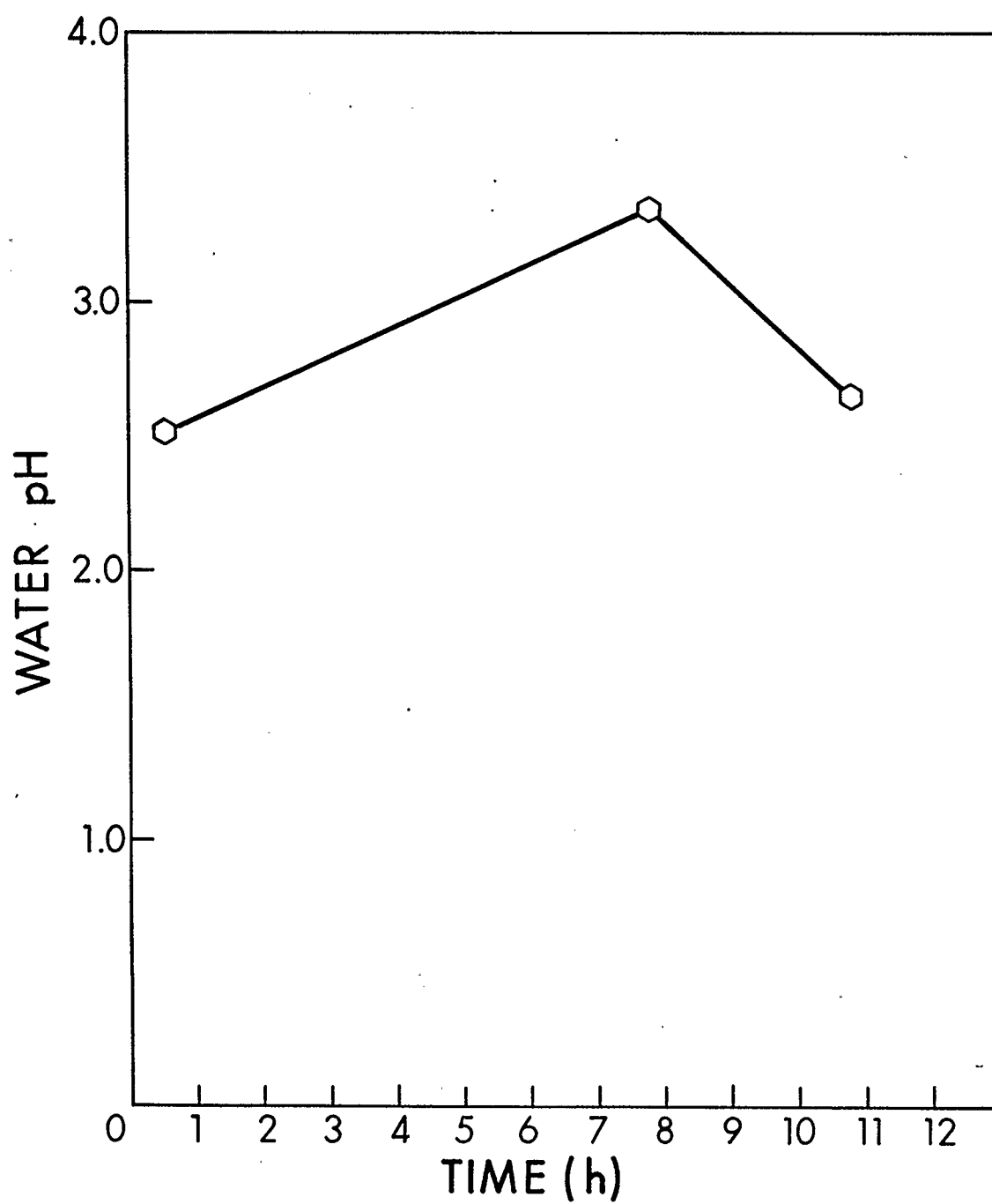


Figure 4.7 - Water pH of the Produced Fluid (AOSTRA Test Run #115)

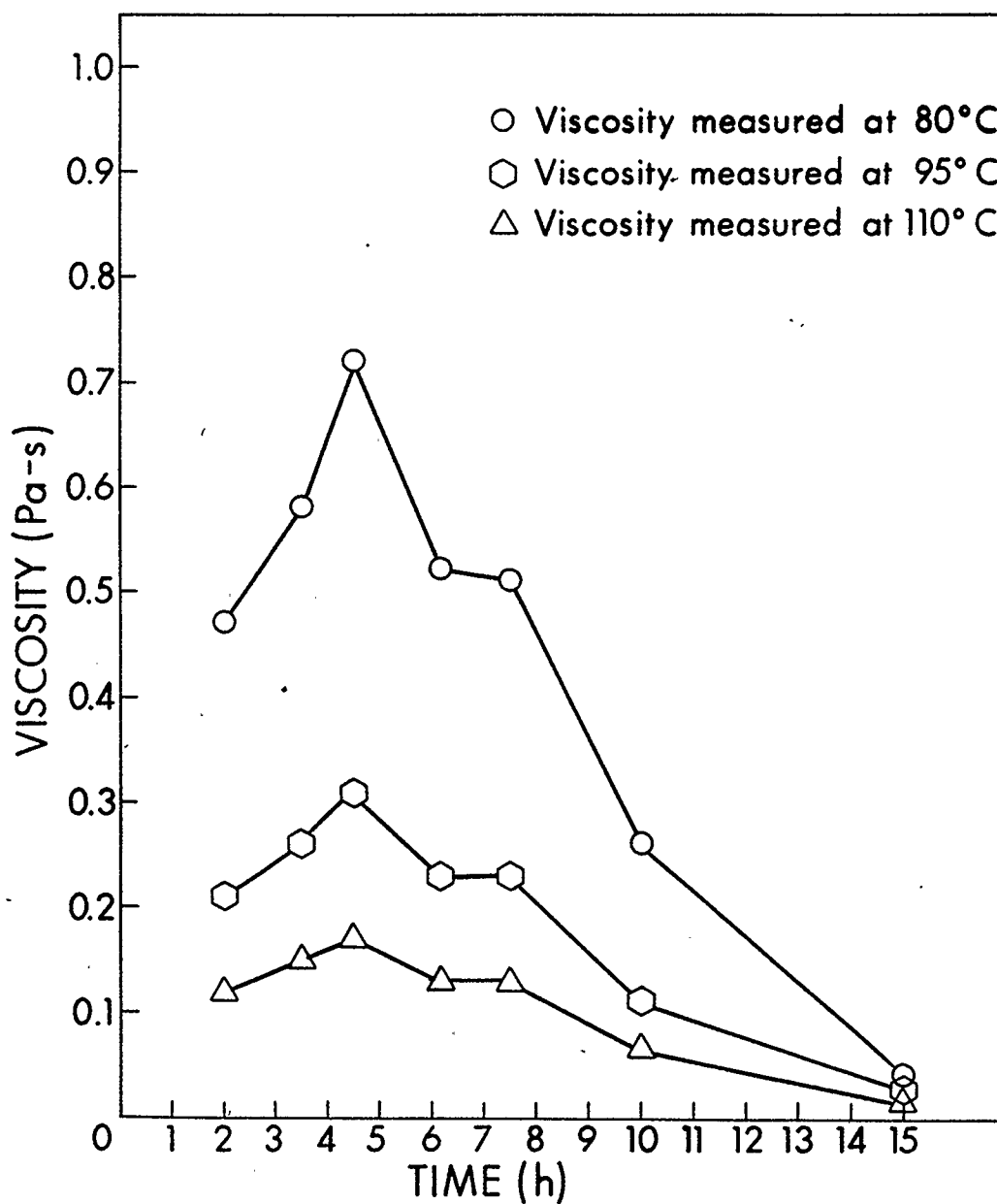


Figure 4.8 - Viscosity of the Produced Fluid (AOSTRA Test Run #118)

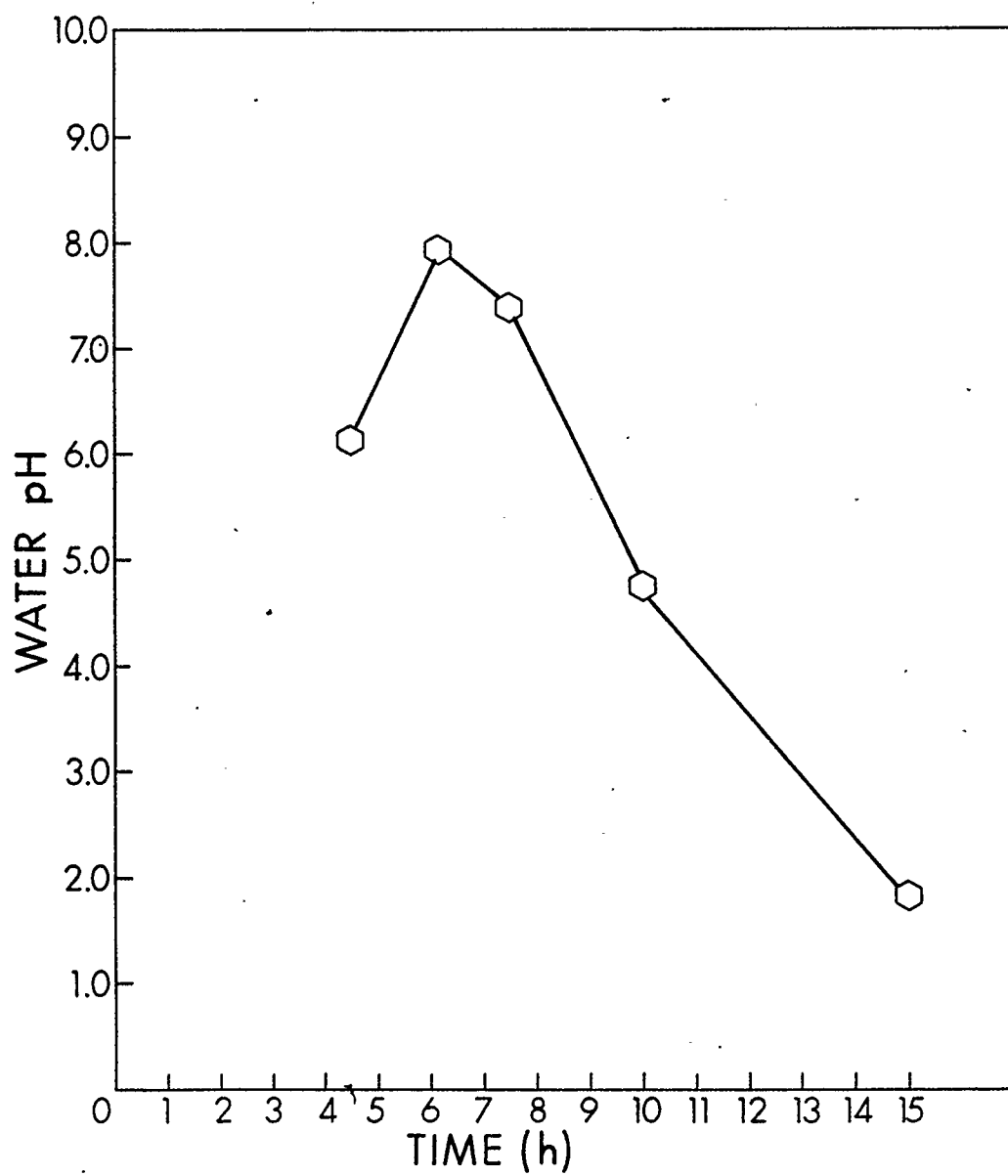


Figure 4.9 - Water pH of the Produced Fluid (AOSTRA Test Run #118)

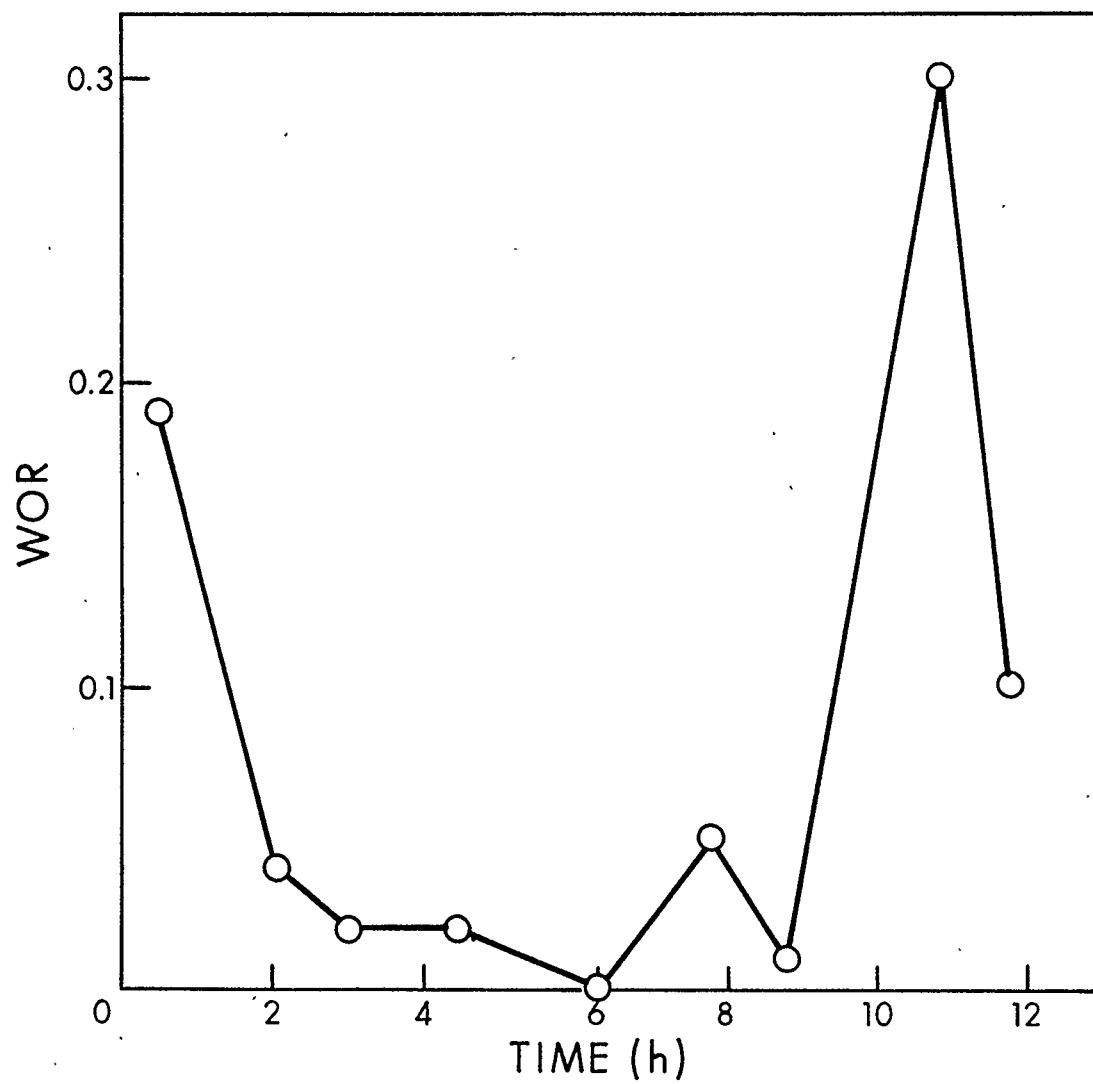


Figure 4.10 - WOR of the Produced Fluid (AOSTRA Test Run #115)

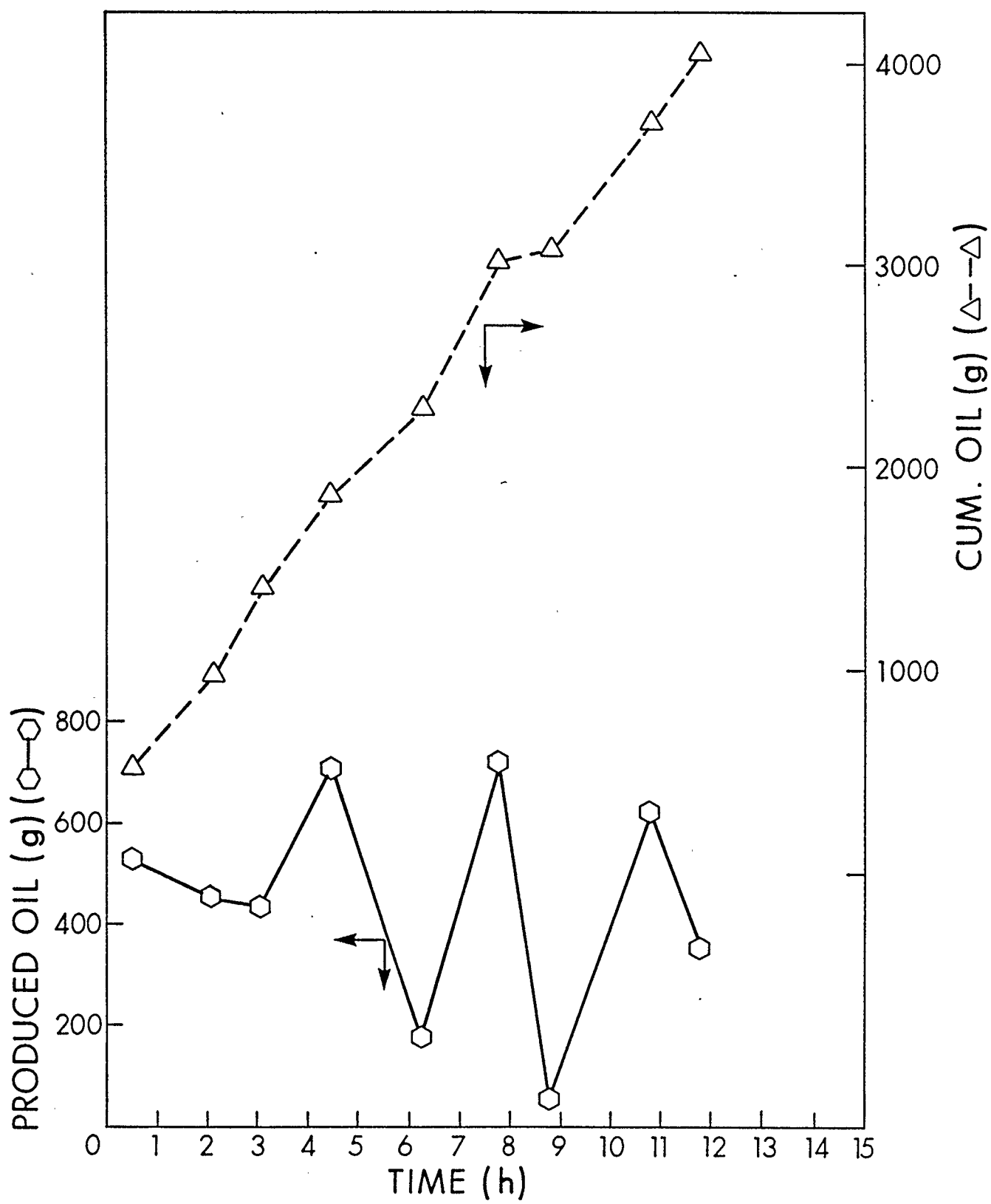


Figure 4.11 - Oil Production Rate (AOSTRA Test Run #115)

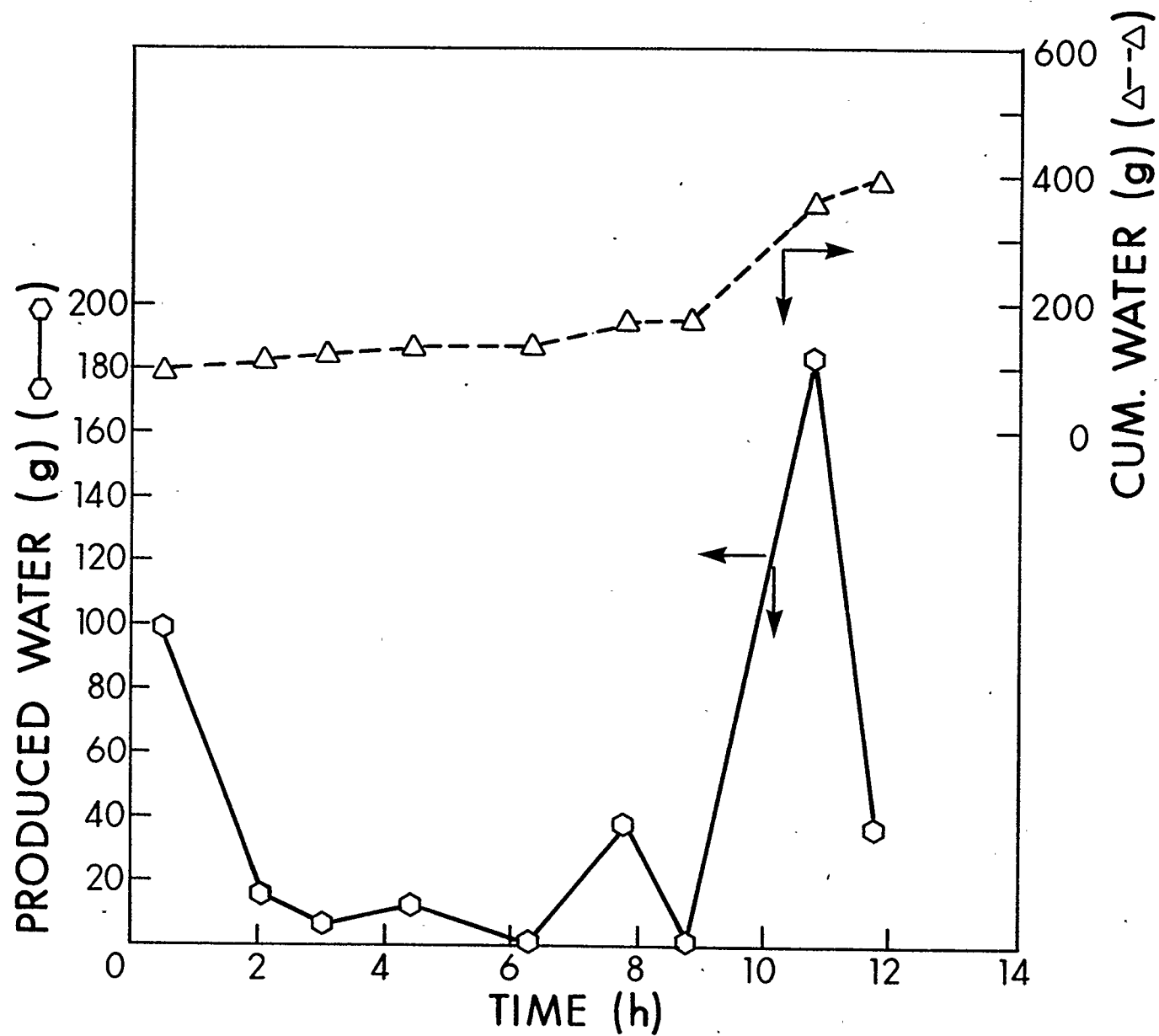


Figure 4.12 - Water Production Rate (AOSTRA Test Run #115)

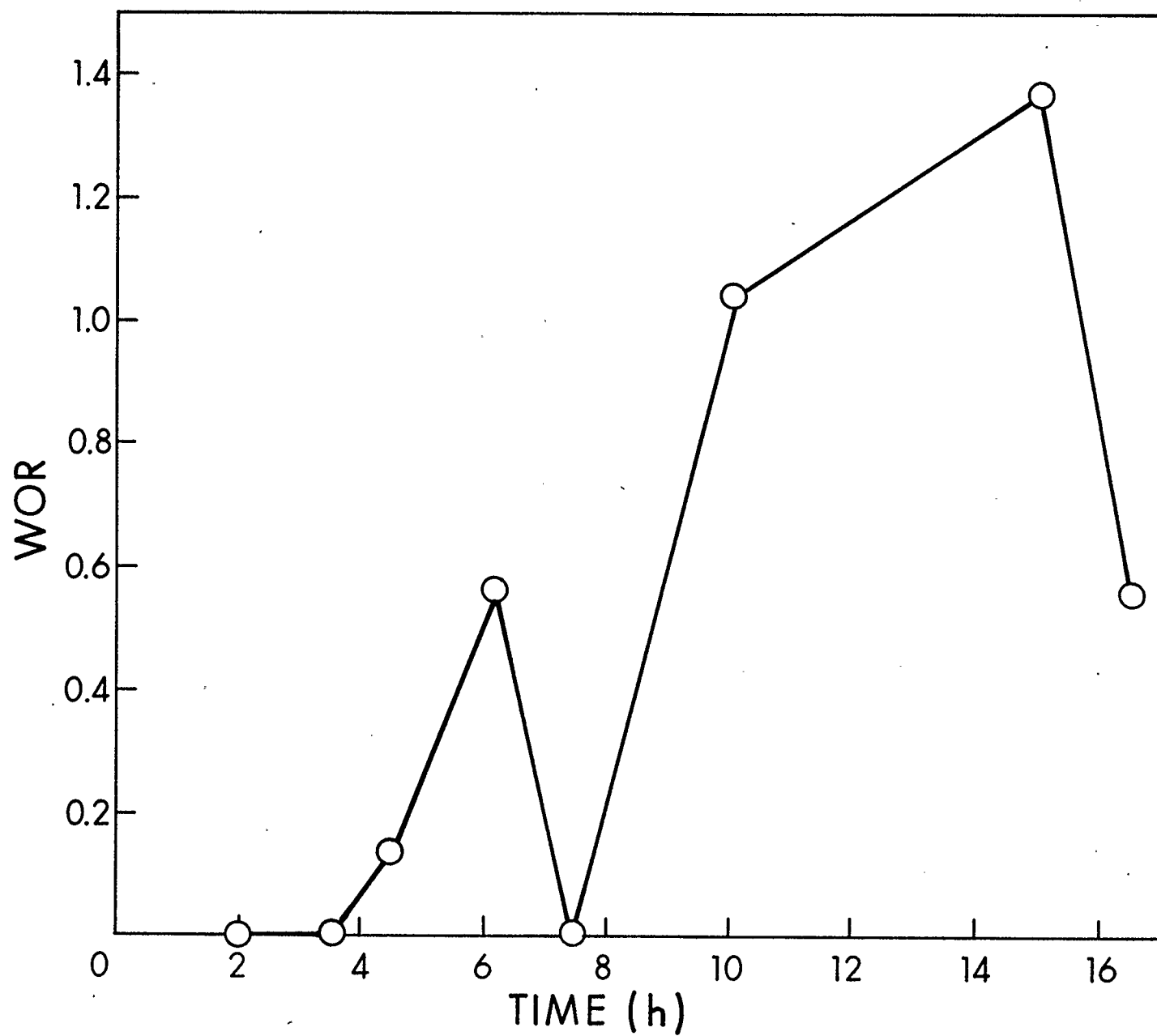


Figure 4.13 - WOR of the Produced Fluid (AOSTRA Test Run #118)

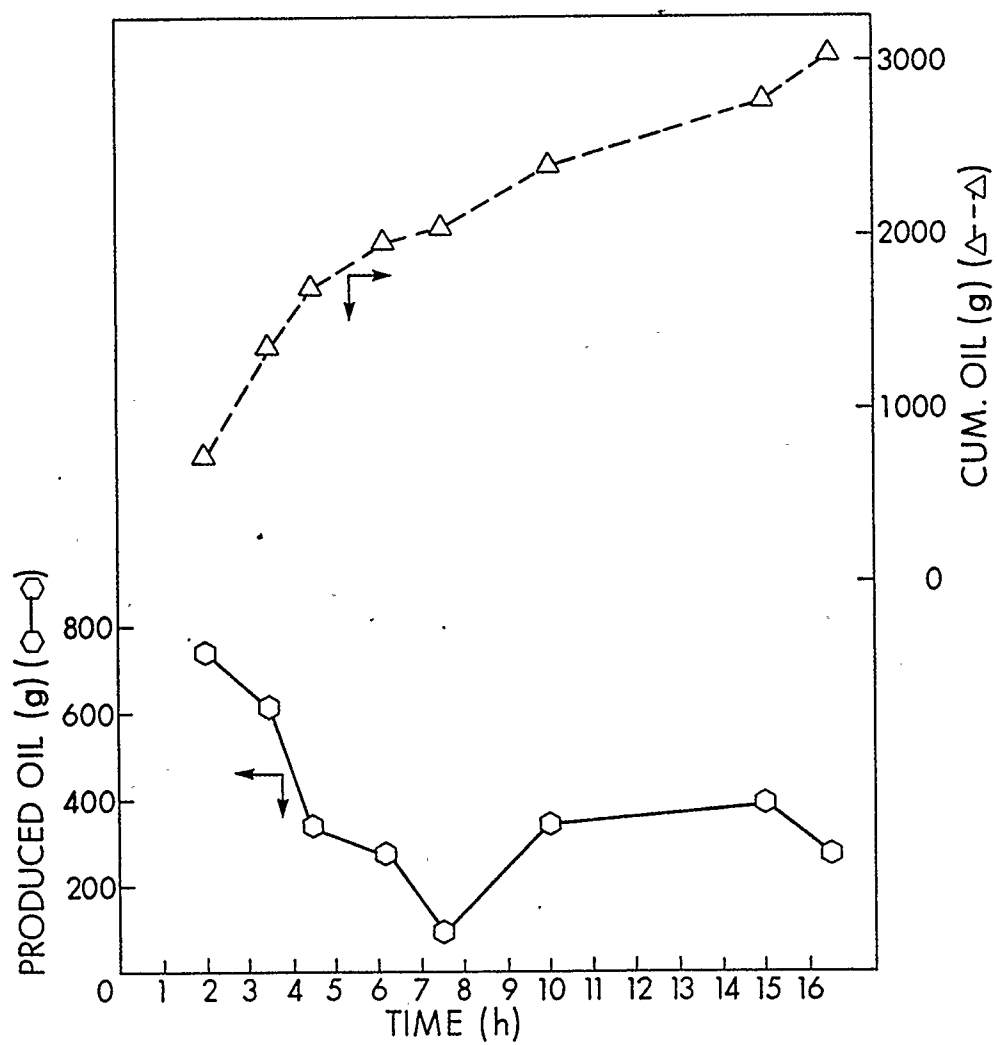


Figure 4.14 - Oil Production Rate (AOSTRA Test Run #118)

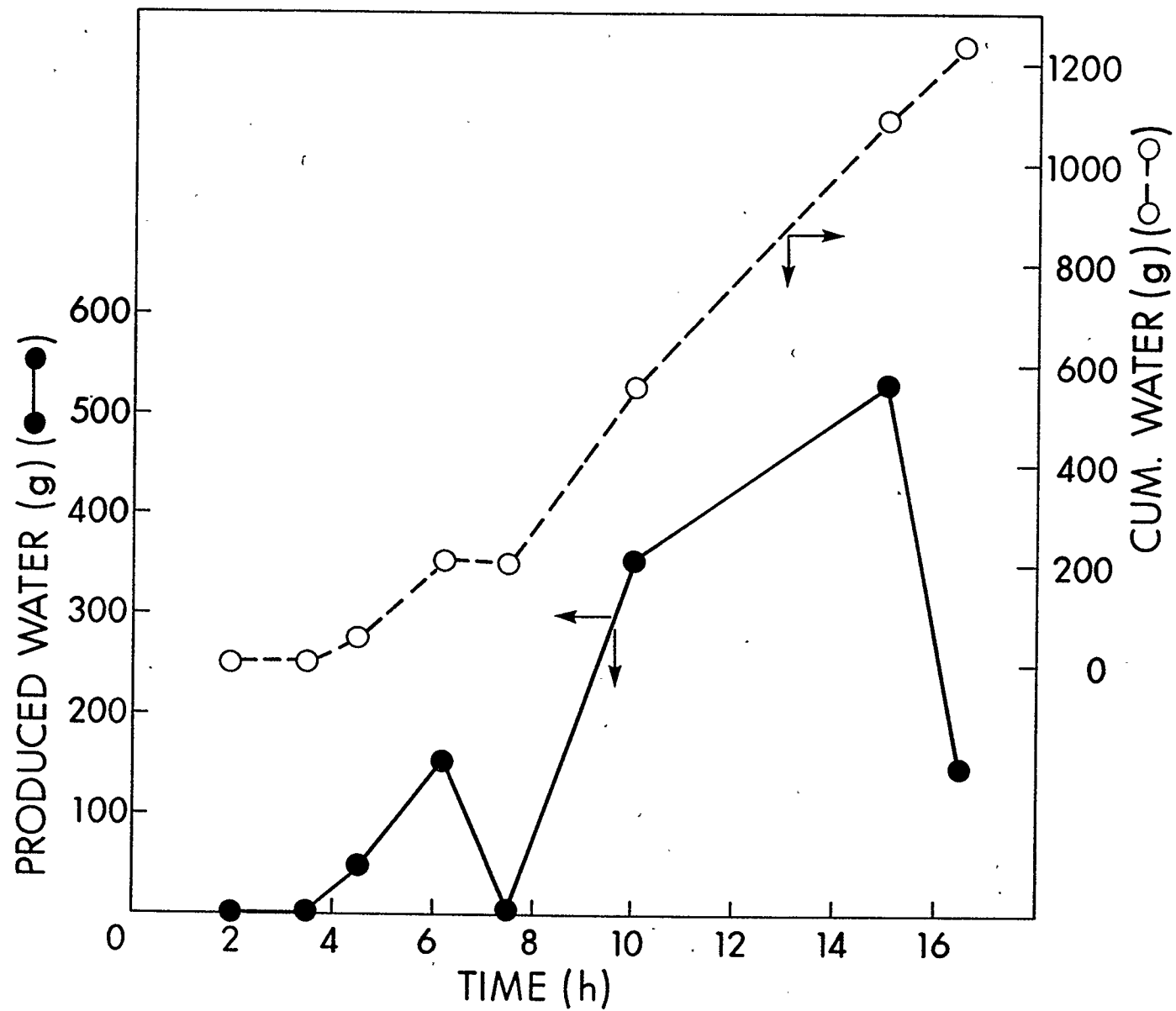


Figure 4.15 - Water Production Rate (AOSTRA Test Run #118)

TABLE 4.8
AOSTRA TEST RUN #115
(LIQUID SAMPLE)

	BITUMEN (g)	WATER (g)	GAS (cm ³)	GOR (cm ³ /g)	Pressure (kPa)
Cylinder #1	105.3	0.2	9 025.86	85.71	862
Cylinder #2	72.8	0.2	15 514.83	213.12	1 448
Cylinder #3	15.6	0.2	18 941.93	1 214.23	1 689
Cylinder #4	16.5	0.2	19 288.72	1 169.01	1 724
Lines	27.1	0.2	-	-	-

TABLE 4.9
AOSTRA TEST RUN 118
(LIQUID SAMPLE)

	BITUMEN (g)	WATER (g)	GAS (cm ³)	GOR (cm ³ /g)	Pressure (kPa)
Cylinder #1	-	-	-	-	-
Cylinder #2	18.1	0.4	19 516.92	1 078.28	1 827
Cylinder #3	2.8	0.2	3 413.44	1 219.08	310
Cylinder #4	1.0	0.1	1 488.74	1 488.74	138
Lines	20.9	2.1	-	-	-

TABLE 4.10
AOSTRA TEST RUN #115
(PRODUCT GAS AND SOLUTION GAS)

	TIME (h)	AVG.	CO ₂		C ₂ H ₆		H ₂ S		COS		C ₃ H ₈		C ₄ ⁺		H ₂		O ₂		N ₂		CO		CH ₄		C ₃ H ₆	
			F.G.	S.G.	F.G.	S.G.	F.G.	S.G.	F.G.	S.G.	F.G.	S.G.	F.G.	S.G.	F.G.	S.G.	F.G.	S.G.	F.G.	S.G.	F.G.	S.G.	F.G.	S.G.	F.G.	S.G.
Cylinder #2	6.55	1	15.17	30.20	0.17	0.58	0.54	0.11	-	-	0.21	0.94	0.09	3.96	1.04	1.52	0.09	1.09	79.34	60.29	2.73	-	0.64	1.33	-	-
Cylinder #3	8.68	6	14.37	11.12	0.05	0.26	-	0.07	-	-	0.13	1.65	-	2.93	-	2.74	0.08	4.75	81.18	75.82	3.74	0.04	0.45	0.52	-	-
Cylinder #4	9.78	6	19.93	16.05	0.72	0.31	0.59	2.25	0.07	-	0.23	2.33	0.01	1.91	-	4.39	0.14	1.60	71.98	69.35	6.22	0.02	0.67	1.49	-	0.27

TABLE 4.11
AOSTRA TEST RUN #118
(PRODUCT GAS AND SOLUTION GAS ANALYSIS)

	TIME (h)	AVG.	CO ₂		C ₂ H ₆		H ₂ S		COS		C ₃ H ₈		C ₄ ⁺		H ₂		O ₂		N ₂		CO		CH ₄		C ₃ H ₆	
			F.G.	S.G.	F.G.	S.G.	F.G.	S.G.	F.G.	S.G.	F.G.	S.G.	F.G.	S.G.	F.G.	S.G.	F.G.	S.G.	F.G.	S.G.	F.G.	S.G.	F.G.	S.G.	F.G.	S.G.
Cylinder #2	7.83	1	16.42	18.27	-	-	-	2.76	-	-	0.08	39.60	-	39.64	0.67	0.62	0.07	0.40	80.49	37.83	1.92	0.10	0.32	0.40	-	-
Cylinder #3	8.55	3	15.21	2.85	-	-	-	0.25	-	-	0.06	2.40	-	2.56	-	-	0.65	1.35	81.43	92.30	2.39	0.50	0.25	0.20	-	-
Cylinder #4	9.58	1	15.23	5.42	-	-	-	-	-	-	0.08	-	-	-	0.58	9.00	0.12	12.62	80.99	61.17	2.73	1.49	0.28	10.36	-	-

NOTES:
F.G. - Free Gas
S.G. - Solution Gas

CHAPTER 5

CONCLUSIONS

1. The combustion tube effluent sampler, designed to collect the bitumen samples from the combustion tube, was able to operate in the harsh environment associated with high gas volumes, produced emulsions and solids.
2. Liquid samples were successfully collected and channelled into separate cylinders for the separation of gas and liquid phases, and therefore, the basic design was proven.
3. The very tight time frame dictated by the combustion tube test program and a failure to recognize the presence of free gas in the sample cylinder, even though liquid appeared in the sight glass, prevented successful achievement of the desired objective of measuring phase equilibria data on the produced fluids.
4. In view of the problem of trapped gas in sample cylinder, the collected liquid samples should be left untouched for at least 10-12 hours to allow the gas to separate.

5. The Toepler pump proved to be a credible device for measuring the solubility of gases in liquids.
6. The experimental gas solubility values of nitrogen gas in both Athabasca bitumen and water compared well with the published values.

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APPENDIX - ASolubility of Nitrogen in BitumenSample Calculation

T_{STD}	=	$15^{\circ}\text{C} = 288.15 \text{ K}$
P_{STD}	=	101.325 kPa
T_{system}	=	$96^{\circ}\text{C} = 369.15 \text{ K}$
P_{system}	=	$3.0 \text{ MPa (Absolute)}$
T_{room}	=	$27^{\circ}\text{C} = 300.15 \text{ K}$
$P_{barometer}$	=	$668 \text{ mmHg} = 89.06 \text{ kPa}$
Wt. of empty cell	=	305.681 g
Wt. of cell + bitumen	=	311.789 g
Wt. of bitumen	=	6.108 g
Volume of cell	=	6.200 cm^3
Density of bitumen	=	0.9852 g/cm^3

Toepler Pump Readings

Volume of gas (constant)	=	95 cm ³
p ₁ (cm.Hg) - p ₂ (cm.Hg)	=	Δp (cm.Hg)
70.5 - 8.8	=	61.7
70.1 - 9.5	=	60.6
69.7 - 10.0	=	59.7
69.3 - 10.4	=	58.9
69.0 - 10.6	=	58.4
68.9 - 10.7	=	58.2
68.8 - 10.8	=	58.0
68.8 - 10.8	=	58.0
68.8 - 10.8	=	58.0

$$p = 58.0 \text{ cm.Hg} = 77.33 \text{ kPa.}$$

$$V_{\text{STD}} = \frac{95 \times (89.06 - 77.33) \times 288.15}{101.325 \times 300.15} = 10.5581 \text{ cm}^3 \text{ N}_2 \text{ gas}$$

$$\text{Solubility (S)} = \text{cm}^3 \text{ gas/g liquid}$$

$$= \frac{10.5581 \text{ cm}^3 \text{ N}_2}{6.108 \text{ g bitumen}}$$

$$S = 1.729 \text{ cm}^3 \text{ N}_2/\text{g bitumen}$$

APPENDIX - B

The following set of equations were utilized to calculate Henry's constants and K-factors for the nitrogen-bitumen system.

$$\text{Solubility (S)} = \frac{\text{cm}^3 \text{ gas}}{\text{g liquid}} \quad (\text{@ } 288.15 \text{ K and } 101.325 \text{ kPa})$$

Mole fraction of component i in the liquid phase is given by,

$$x_i = \frac{n_G}{n_G + n_L} \quad \text{..... (B-1)}$$

or,

$$\frac{n_G}{n_L} = \frac{x_i}{1 - x_i} = B_i \quad \text{..... (B-2)}$$

where,

n_G = moles of dissolved gas (solute)

n_L = moles of liquid hydrocarbon (solvent)

B_i = mol gas/mol liquid

Rewriting Equation (B-2),

$$B_i = \frac{n_G}{n_L} = \frac{S(\text{cm}^3 \text{ gas})}{(\text{g liquid})} \times \rho_g \frac{(\text{g mol gas})}{(\text{cm}^3 \text{ gas})} \times M \frac{(\text{g liquid})}{(\text{g mol liquid})} \quad \text{..... (B-3)}$$

where,

ρ_g = molar density; g mol/cm³

M = molecular weight of liquid hydrocarbon,
assumed to be 620 g/g mol (Table 2.1)

Specific molar volume is defined by the equation

$$v_g = \frac{RT}{P} \quad \text{..... (B-4)}$$

where,

v_g = specific molar volume; cm³/g mol

R = gas constant; 8.31434 m³ kPa/k mol K

At standard conditions (288.15 K and 101.325 kPa)

$$v_g = 8.31434 \frac{(\text{m}^3 \text{ kPa})}{(\text{k mol K})} \times \frac{(10^6 \text{ cm}^3)}{(\text{m}^3)} \times \frac{(\text{k mol})}{(10^3 \text{ g mol})} \times \frac{(288.15 \text{ K})}{(101.325 \text{ kPa})}$$

$$v_g = 23644 \text{ cm}^3 \text{ gas/g mol}$$

$$\rho_g = \frac{1}{v_g} = 4.2293 \times 10^{-5} \text{ g mol/cm}^3$$

$$B_i = S \rho_g M$$

or,

$$B_i = 2.6222 \times 10^{-2} \text{ s} \quad \text{..... (B-5)}$$

From the above calculations the mole fraction, x_i , equilibrium constant, K_i , and Henry's constant, H_i , for component i can be calculated by the following equations:

$$x_i = \frac{1}{1 + 1/B_i} \quad (\text{from B-2}) \quad \text{..... (B-6)}$$

$$K_i = \frac{y_i}{x_i} = \frac{1}{x_i} \quad \text{..... (B-7)}$$

where,

y_i = mole fraction of component i in the gas phase (since we have only one gas in the system, $y_i = 1$),

$$H_i = \frac{P}{x_i} \quad \text{..... (B-8)}$$

APPENDIX C

THEORETICAL CONSIDERATIONS

C.1 Vapor-Liquid Equilibria

The main criterion for vapor-liquid calculations is the concept of equilibrium i.e. no change in the composition of the vapor and liquid in contact with each other will take place with respect to time. The concept of equilibrium does not indicate that the system is static, merely that the rates of vaporization and condensation of a given molecular species is equal so that no net change in composition occurs. Therefore, a necessary condition for equilibrium between two phases dictates that the temperature and pressure of both phases be the same. At low pressures ideal-gas behaviour is often assumed to be valid. However, at higher pressures the vapor pressures of the components are affected by the total pressure of the system, and the vapor phase departs appreciably from ideal-gas behaviour. Up to several thousand kPa these effects may be taken into account by using the fugacity concept to calculate equilibrium ratios. The concept of fugacity can be defined by the equation,

$$RT \, d(\ln f) = v \, dp \quad \text{.....(C-1)}$$

where,

v = molar or specific volume

f = fugacity of pure substance

As the pressure approaches zero, all substances behave as an ideal gas. Hence at very low pressures,

$$d(\ln f) = d(\ln p) \quad \text{.....(C-2)}$$

which upon integration, and setting the constant of integration equal to zero, yields,

$$f^o = p^o \quad \text{.....(C-3)}$$

Equation (C-3) completes the definition of fugacity and states that the fugacity of a substance is equal to the pressure when the substance is in the state of an ideal gas or at a pressure near zero (as represented by the superscript 'o'). Equilibrium of component i among various phases in equilibrium, in terms of fugacities, can then be represented by,

$$\bar{f}_{i_L} = \bar{f}_{i_L} = \bar{f}_{i_V} \quad \text{.....(C-4)}$$

where the subscripts refer to the different phases.

From the above equations, it can be developed that,

$$\ln \frac{\bar{f}_i}{\bar{p}_i} = \frac{1}{RT} \int_{p^\circ}^p \bar{v}_i dp \quad \dots\dots\dots(C-5)$$

where,

\bar{f}_i = fugacity of component i in the mixture

\bar{v}_i = partial molar volume of component i in the mixture

Applying Equation (C-5) to a liquid and a gas phase for component i, we have

$$\ln (\bar{f}/\bar{p}^\circ)_L = \frac{1}{RT} \int_{p^\circ}^p \bar{v}_{i_L} dp \quad \dots\dots\dots(C-6)$$

$$\ln (\bar{f}/\bar{p}^\circ)_G = \frac{1}{RT} \int_{p^\circ}^p \bar{v}_{i_G} dp \quad \dots\dots\dots(C-7)$$

For pressures approaching zero, the liquid phase becomes an ideal gas and we can write,

$$\bar{p}_L^\circ = p^\circ x_i \quad \dots\dots\dots(C-8)$$

$$\bar{p}_G^\circ = p^\circ y_i \quad \dots\dots\dots(C-9)$$

Substituting Equations (C-8) and (C-9) into Equations (C-6) and (C-7) respectively, we have,

$$\ln (\bar{f}_L/p^\circ x_i) = \frac{1}{RT} \int_{p^\circ}^P \bar{v}_{iL} dp \quad \dots\dots\dots(C-10)$$

$$\ln (\bar{f}_G/p^\circ y_i) = \frac{1}{RT} \int_{p^\circ}^P \bar{v}_{iG} dp \quad \dots\dots\dots(C-11)$$

Subtracting Equation (C-11) from Equation (C-10), we have,

$$\ln \left(\frac{\bar{f}_L/x}{\bar{f}_G/y} \right)_i = \frac{1}{RT} \int_0^P (\bar{v}_L - \bar{v}_G)_i dp \quad \dots\dots\dots(C-12)$$

At equilibrium, $f_L = f_G$, therefore,

$$\ln (y/x)_i = \ln K_i = \frac{1}{RT} \int_0^P (\bar{v}_L - \bar{v}_G)_i dp \quad \dots\dots(C-13)$$

where,

$$\bar{v}_{iL} = \text{partial molar volume of } i \text{ in the liquid phase}$$

$$\bar{v}_{iG} = \text{partial molar volume of } i \text{ in the gas phase}$$

and (y/x) is termed the phase equilibrium constant, K , a function of composition, temperature and pressure, defined as the ratio of the mole fraction, y_i , of the component i in the gas phase of the mixture to the mole fraction, x_i , of the same component in the liquid phase of the mixture when the gas and the liquid phases are in equilibrium.

C.2 Solubility of Gas

Solubility is defined as the amount of gas or solute dissolved in a unit amount of solvent. Gas solubilities have been expressed in terms of a variety of units. Two of the most common are the two dimensionless coefficients, Bunsen coefficient and Ostwald coefficient. Bunsen coefficient is defined as the volume (corrected to 0°C and 101.325 kPa) of gas dissolved per unit volume of solvent at system temperature T (K) when the partial pressure of the solute is 101.325 kPa. Ostwald coefficient is defined as the volume of gas at system temperature T (K) and partial pressure p dissolved per unit volume of solvent. For an ideal gas phase with a low gas solubility the

Ostwald coefficient is independent of p and the two coefficients are related by the following expression,

$$\text{O.C.} = \text{B.C.} \times \frac{(101.325)}{p} \times \frac{T}{273} \quad \text{.....(C-14)}$$

In recent years, it has become a common practice to report gas solubilities in units of mole fraction, or Henry's constants. When the solubility is small, Henry's Law provides a good approximation. To establish a relationship in terms of Henry's constant, we go back to the equilibrium relations expressed by Equation (C-4),

$$\bar{f}_{i_L} = \bar{f}_{i_G} \quad \text{..... (C-4)}$$

where,

$$\begin{aligned} \bar{f}_{i_L} &= \text{fugacity of component 'i' in a liquid mixture.} \\ \bar{f}_{i_G} &= \text{fugacity of component 'i' in a gaseous mixture} \end{aligned}$$

Applications of Lewis and Randall rule for the gas phase, expressed as,

$$\bar{f}_{i_G} = y_i f_{i_G} \quad \text{..... (C-15)}$$

and the definition of the activity coefficient for liquid phase,

$$\bar{f}_{i_L} = x_i \gamma_i f_{i_L} \quad \dots\dots\dots(C-16)$$

into equation (C-4), yields,

$$x_i \gamma_i f_{i_L} = y_i f_{i_G} \quad \dots\dots\dots(C-17)$$

where,

- f_{i_L} = fugacity of pure component i in the liquid phase
- f_{i_G} = fugacity of pure component i in the gas phase
- γ_i = activity coefficient of component i

For ideal solutions (for which $\gamma_i=1$), the solubility of the gas depends on its partial pressure (or gas-phase fugacity), and not on the liquid or liquid mixture into which it dissolves and this solubility is termed the ideal solubility of the gas.

When a gas is only sparingly soluble in a liquid or a liquid mixture (i.e. $x_i \rightarrow 0$), it is observed that the liquid phase mole

fraction of the solute species is linearly proportional to its gas phase fugacity, at a fixed temperature, and is expressed as,

$$x_i H_i = \bar{f}_{i_G} = y_i f_{i_G}, \text{ as } x_i \rightarrow 0 \quad \text{..... (C-18)}$$

or,

$$\bar{f}_{i_L} = x_i H_i \quad (\text{by virtue of equation...C-4})$$

where H_i is the Henry's Law constant of component 'i', rigorously defined as,

$$H_i = \lim_{x_i \rightarrow 0} \frac{\bar{f}_{i_L}}{x_i} \quad \text{..... (C-19)}$$