6. LABORATORY ANALYSES OF RESERVOIR FLUIDS

Composition analyses is needed when the fluid properties should be described in the PVT simulator. Composition analyses of reservoir fluid samples and the principles of recombination calculations was described in part 4 and part 5.

The physical behavior of the fluids needs also to be analyzed in the laboratory to understand the fluid behavior in the reservoir and during the production process.

Reservoir fluids are exposed to many laboratory analyses, and some of the most important experiments will be described in this chapter, to give the reader an understanding of the methods used to collect the data needed to describe reservoir fluid properties and behavior.

The physical fluid properties observe in the laboratory is important input parameters used for tuning the PVT simulators, and are also needed in front of the design of reservoir production strategy, design and production capacity of the process plant, and quality of sales gas and oil.

FLUID SAMPLING

Hydrocarbon samples to be analyzed for the previously mentioned properties are normally collected at the first stage (field) separator. Representative samples of both the separator liquid and the separator gas streams are collected.

During exploration, samples may also be obtained from the bottom of the well, so called bottom hole samples. These are quite common today, however, representative samples could be questioned when they are collected from saturated reservoir fluids.

Before starting an extensive analysis it is important to evaluate the available samples and to choose the sample thought to be the most representative for the reservoir hydrocarbon fluids. Samples obtained during the most stable separator conditions are normally chosen. In the laboratory, the saturation pressure (bubble point) of the separator liquid is determined at separator temperature. The sample is considered to be representative if the saturation pressure is equal to the test separator pressure at the sampling time.

The opening pressure of the corresponding gas phase sample may also be checked. It should be equal to the separator pressure at sampling time.

If both of these pressures agree with the value of the separator pressure, further processing of the samples may take place.

FLASH SEPARATION OF FLUID SAMPLES

After quality control of the received fluid samples from the reservoir, the samples need to be subjected to compositional analysis as described previously.

In order to analyze bottom hole samples or separator liquid samples which has been collected under pressure, the fluid must be stabilized to atmospheric conditions by a single flash process. Fig. 6.1.
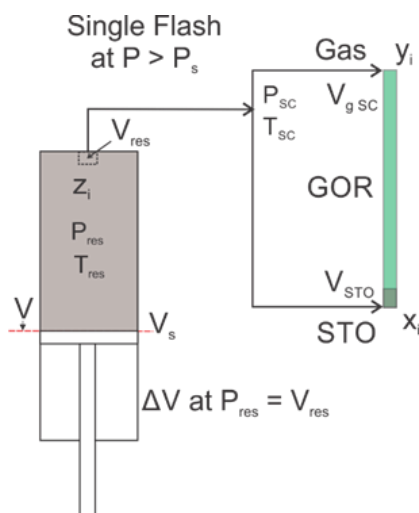
Fig. 6.1. Principle of Single flash apparatus.

The high-pressure sample container is, therefore, connected to the single-stage flash separator. The live fluid sample is thus allowed to separate into two phases, Gas and STO at Standard Conditions (SC).

The volume of the gas phase is determined. The liquid is allowed to settle in the bottom of the flash chamber, and the mass (m_{STO}) and density (ρ_{STO}) is determined.

The gas/oil ratio of the separator liquid sample, GOR_{sep}, may now be calculated:

$$GOR = \frac{volume\ gas\ (Sm^3)}{volume\ oil\ (Sm^3)}$$ (6.1)

where Sm^3 means the volume of fluids at standard conditions, normally 15°C and 1 atm (60°F, 14.7 psia). Flash experiments are described in detail in Part 4.

COMPOSITIONAL ANALYSIS OF FLUID SAMPLES

The dry gas or separator gas sample flask is heated to sampling temperature (ex. T_{sep}) and left to equilibrate. A sample of the gas is bled through a gas sampling valve and injected into the gas chromatograph. From the compositional analysis it is possible to detect whether the sample has been contaminated with, for example, air.

Composition analyses is performed on all fluid samples using GC analyses as described previously. Reservoir samples or Separator fluids samples are then recombined to reservoir fluid, for further PVT analyses on reservoir fluids.

PVT MEASUREMENTS

PVT measurements (often called PVT analyses) most commonly performed on fluid samples taken during reservoir production, or on representative reservoir fluid samples. In order to study the properties of the reservoir fluid, it could be necessary to recombine the separator gas and the separator liquid samples. This is done by mixing the two samples proportionally to their produced rates (GOR_{sep}). Reservoir fluid samples could also be available from downhole sampling in exploration or new production wells.

The reservoir fluid or recombined reservoir fluid is transferred to a PVT cell for fluid properties analyses, Fig. 6.2.
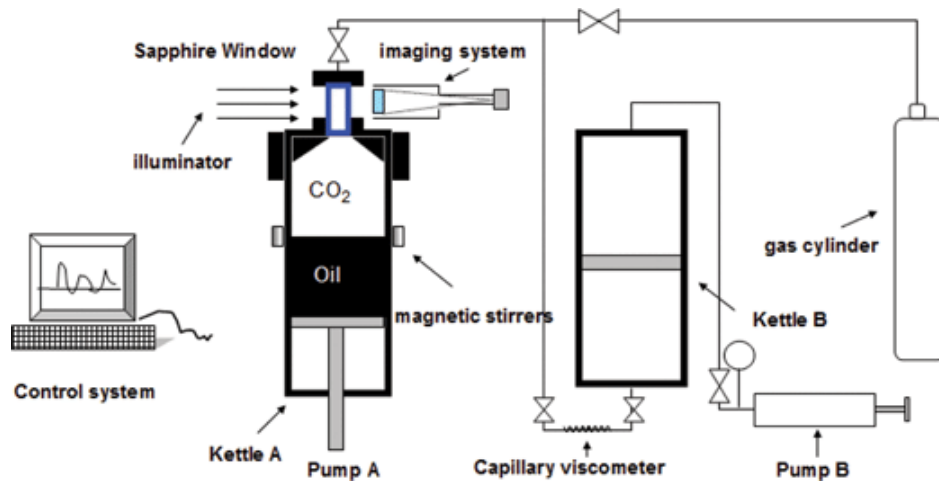
Fig. 6.2. Specific configuration of a laboratory PVT cell.

A lot of specialized laboratory PVT cells and equipment are available for different type of analyses, and different deliverers have different technical solutions.

Previously most of the equipment was mercury (Hg) based for pressure control on fluid samples, and the mercury also behaved as friction less piston, and supported sample mixing during agitation.

Mercury contamination of fluid samples and fluid sample cells have been a HSSE issue. Today more HSSE friendly PVT equipment solutions are available.

There are two main types of PVT equipment available in PVT laboratories:

- PVT test systems for black oils
- PVT test systems for gas condensates and volatile fluids.

They are discussed separately in this chapter.

6.1. PVT analyses on Oils with dissolved gas

Typical PVT analyses that are performed on Black oils and volatile Oils will be described in this section.

A typical schematic diagram of a black oil PVT system is shown in Fig. 6.3. The main parts of the system are a mercury pump, a calibrated steel cell, a heating chamber or bath (silicone oil), and a precision manometer. The principle of operation is as follows:
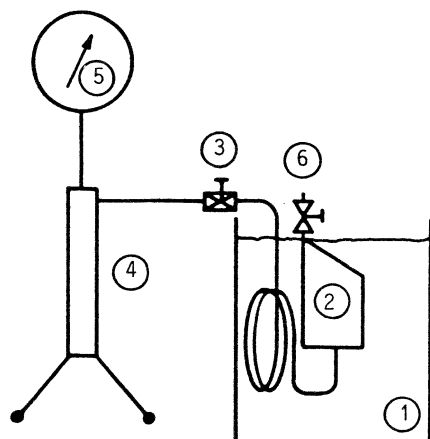
1. Heating bath with silicone oil
2. PVT cell (volume normally 0.6 – 1.0 l)
3. Valve
4. Graduated mercury pump
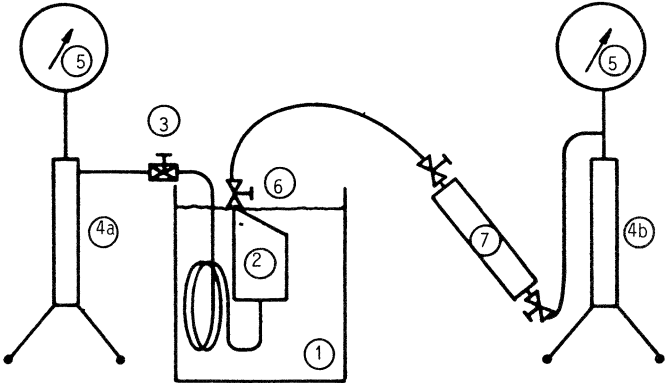5. Precision manometer
6. Cell entry valve

Fig. 6.3. Schematic diagram of black oil PVT apparatus.

A reservoir oil or a recombined reservoir oil is charged to the cell at constant pressure through valve 6 at the top of the cell. The cell may be equipped with one or more windows for monitoring the charging and subsequent operations.

The charging process is performed at the pressure in the sample cylinder. Constant pressure is maintained using the mercury pumps shown in Fig. 6.4.

The mercury pumps can be either hand or machine operated. In both cases the pumps must be graduated and calibrated to a volumetric scale. By retracting the cell pump and advancing the charge pump, a known volume of sample can be transferred to the cell.

The cell is immersed in a thermostat and heated to the reservoir temperature, or any other required test temperature, before the cell is charged. This is important because heating after charging could, without proper monitoring of the oil pressure, lead to excess cell pressures due to thermal expansion of the mercury and the sample. If the sample has been brought into the two-phase region, heating after charging is normally safe but should be monitored.


```
1. Heating bath - with silicone oil
2. PVT cell
3. Isolating valve
4. Graduated mercury pumps (a) cell (b) charging
5. Precision manometers
6. Cell entry valve
7. Hydrocarbon sampling bottle or recombination cell
```

Fig. 6.4. Black oil PVT apparatus rigged for sample transfer.

6.1.1. Bubble-Point Determination

Once the fluid has been equilibrated at the desired temperature (usually reservoir), the PVT analyses can start.

The first analysis performed is typically the saturation (P_s) or bubble point (P_b) determination. The P_b is defined as the pressure where, at constant temperature, the oil system is in equilibrium with an infinite small gas bubble.

The PVT cell is accessed by opening valve 3 shown in Fig. 6.3, and reservoir fluid pressure and volume are changed by mercury injection. After the system is equilibrated, the mercury volume is recorded at the resulting pressure. Based on the amount of mercury injected into the cell, and the amount of sample charged to the cell, the sample volume in calculated at this pressure.

This process is repeated several times, and the resulting volume pressure data is plotted as shown in Fig. 6.5.
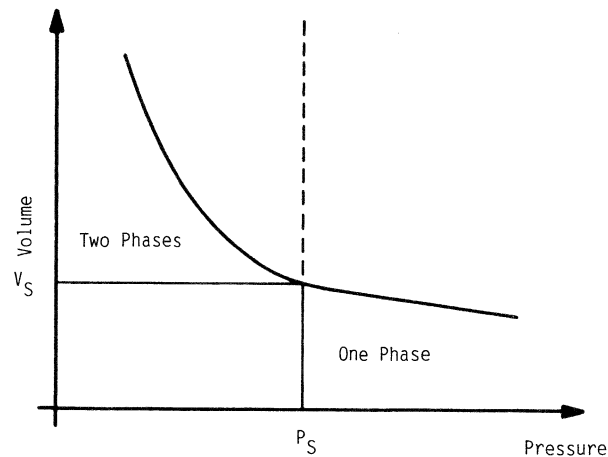
Fig. 6.5. Saturation point (P_s)/bubble point (P_b) determination of a Black oil.

Normally, a clear discontinuity is found. This point is the bubble point of the mixture at the given temperature.

Several factors influence the accuracy by which the saturation pressure can be determined by the graphical technique. The change of slope in Fig. 6.5 depends on the compressibility difference between the two-phase system and the single-phase system. At high pressures and temperatures, and when the system approaches the critical region, this difference is not very large.

6.1.2. Constant Mass Expansion

In order to achieve a representative reservoir fluid, separator samples of Oil and Gas is recombined at measured GOR to a PVT cell. With a representative reservoir fluid in the PVT cell at reservoir temperature, the system is compressed to above the reservoir pressure (P_{res}) and equilibrated (usually overnight). The fluid is checked to see it is all in single phase (Liquid), and the fluid volume recorded. A constant mass expansion experiment can then be performed. A schematic diagram of this process is shown in Fig. 6.6.
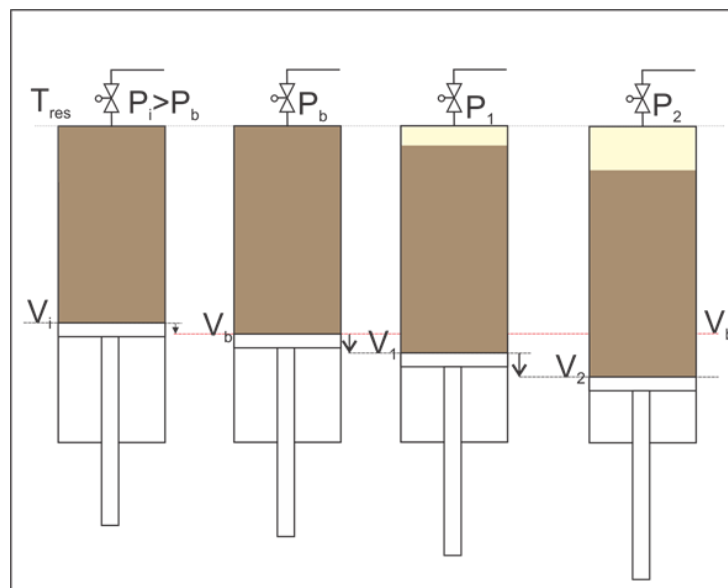

Fig. 6.6. Schematic representation of constant mass expansion (CME) experiment on a Black Oil (Oil with dissolved gas)..

6-5

A stepwise pressure reduction is performed. The system is observed visually, and the total fluid volume in the PVT cell is recorded at each pressure level, or typically by reading the volume in the mercury pump (incompressible fluid).

The bubble point pressure (P_b) as the first presence of free gas can be difficult to observe, therefore the stepwise pressure reduction is continued below the dew point, and the total fluid volume (Gas and Liquid) at each pressure step is determined. The results could be tabulated in the first 2 columns of Tbl. 6.1.

Tbl. 6.1. Constant mass expansion on a Black Oil system

PRESSURE BAR		REL VOL V/V_b	COMPRESSIBILITY 1/BAR	Y-FACTOR
401.7		0.9811	1.05E-04	
380.1		0.9836	1.08E-04	
362.S		0.9853	1.11E-04	
343.8		0.9873	1.14E-04	
325.3		0.9895	1.16E-04	
307.4		0.9915	1.19E-04	
291.4		0.9934	1.21E-04	
274 .9		0.9955	1.24E-04	
254.3		0.9981	1.27E-04	
P_b = 239.0		1.0000	1.29E-04	
235.0		1.0033		5.10
215.1		1.0230		4.84
182.4		1.0678		4.58
142.8		1.1651		4.08
113.3		1.2946		3.77
91.7		1.4568		3.52
77.1		1.6193		3.39
65.7		1.8158		3.23

Based on the results, the compressibility of the single-phase Black Oil system could be calculated:

$$c = -\frac{1}{V}\left(\frac{dV}{dP}\right)_T \qquad (6.2)$$

The Y-factor for the 2-Phase fluid system at $P<P_b$ could be calculated:

$$Y = \frac{P_b - P}{P\left(\frac{V}{V_b} - 1\right)} \qquad (6.3)$$

and should be a straight line in a Y-P diagram and is used as a quality check of the fluid.

6.1.2. Differential Depletion

Other important properties of the oil system can be derived through a differential depletion or differential liberation experiment. These properties are:

1. Shrinkage factor (B_o).

This is a measure of the ratio of the volume of the hydrocarbon system at reservoir conditions to the volume at stock tank conditions:

$$B_o = \frac{V_{res}}{V_{STO}} \left[m^3 / Sm^3 \right] \tag{6.4}$$

2. Solution gas/oil ratio (R_S).

This is a measure of the volume of gas in solution at given pressures (P) (see also Eq. 6.8):

$$R_S = \frac{V_{gas,P}}{V_{STO}} \left[Sm^3 / Sm^3 \right] \tag{6.5}$$

3. Density of the reservoir fluid at different pressures (P), including the saturation pressure:

$$\rho_{o,P} = \frac{m_{o,P}}{V_{o,P}} \left[kg / m^3 \right] \tag{6.6}$$

4. Real gas deviation factor Z, i.e., compressibility factor, for the gas phase at given T and P:

$$Z = \frac{PV}{nRT} \tag{6.7}$$

where V is the volume and n the number of moles

A schematic diagram of the differential depletion experiment is shown in Fig. 6.7.

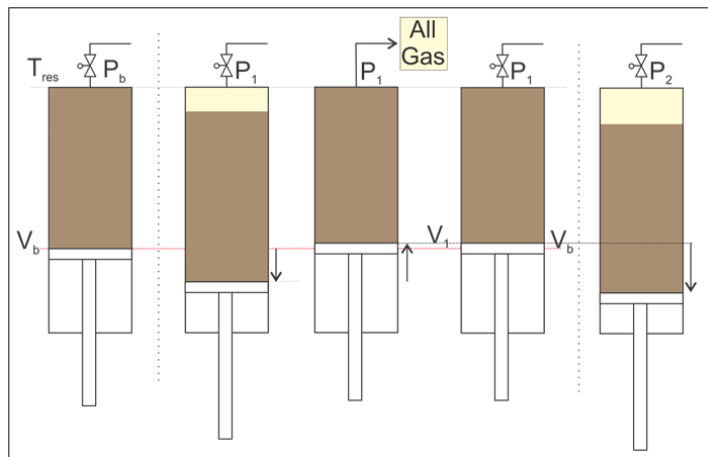

Fig. 6.7. Schematic representation of a differential liberation experiment

The reservoir fluid at constant temperature (T_{res}) is compressed to a pressure above the saturation pressure and equilibrated in front of the experiment.

The pressure is decreased to saturation pressure $P_s = P_b$ and $V_s = V_b$ is measured.

A new pressure reduction is performed below P_s and equilibrated at constant pressure P_1. The fluid system will then be separated in a gas and oil phase. The gas phase is produced from the cell at constant pressure P_1. The amount of gas is measured with a gasometer and sampled.

The new oil volume V_1 is calculated from the readings on the mercury pump/PVT-cell before and after the gas discharge. These readings will also give the gas phase volume at P_1 and T_{res}.

The hydrocarbon system is again brought into the two-phase region, this time at a lower pressure P_2 and equilibrated. The gas discharge procedure is then repeated.

The pressure step intervals are repeated through 8-10 stages between P_s and P_{atm}. At the last stage, all the remaining gas is discharged with the residual oil left in the cell.

The pressure of the residual oil is increased stepwise, and the oil volumes are recorded. Normally, one records volumes at each 50 bar up to 300 bar. The plot of these volumes can be extrapolated back to P_{atm} , so that a measure of the residual oil volume at T_{res} (normally) can be determined, V_{RT}.

Then the cell temperature is reduced to T_{SC} (15°C) at P_{atm}, and the oil volume is determined. This volume is the reference residual volume V_R. The oil is then discharged from the cell, and density measured.

The data recorded during differential depletion can be represented as shown in Fig. 6.8.
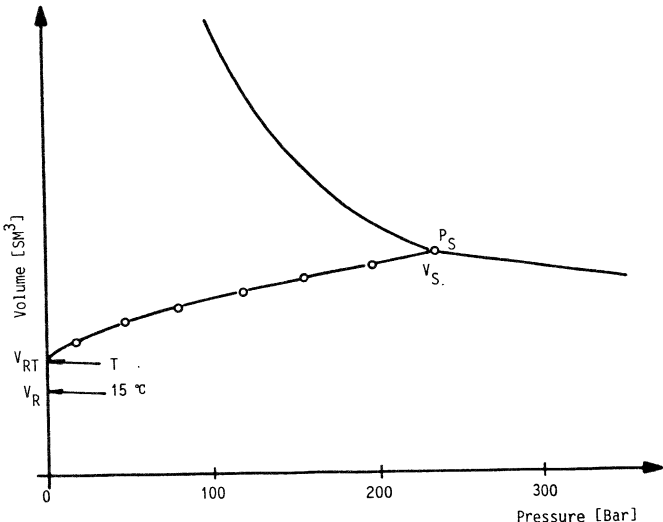

Fig. 6.8. Determination of saturation pressure and volume from a differential depletion experiment.

P_s and V_s are the saturation pressure and volume, respectively; V_{RT} the liquid volume at one atmosphere and temperature, T_{res}; and V_R is the reference liquid volume at 15°C. From these data the shrinkage factor of the system at the saturation pressure may be calculated:

$$B_{o,s} = \frac{V_s}{V_R} \left[m^3/Sm^3\right]$$
(6.8)

The whole B_o-curve (see Fig. 6.9) may be calculated as follows:

$$B_o = \frac{V}{V_R} \left[m^3/Sm^3\right]$$
(6.9)

The solution gas/oil ratio of the reservoir fluid, R_s, at pressure stage N can be obtained from:

$$R_S = \sum_{n=N+1}^{NSTEP} \frac{V_{gas,n}}{V_R} \left[Sm^3/Sm^3\right]$$
(6.10)

where NSTEP is the total number of flash stages and $V_{gas,n}$ is the volume of gas (Sm^3) liberated at flash stage n. These data can be represented as shown in Fig. 6.10.
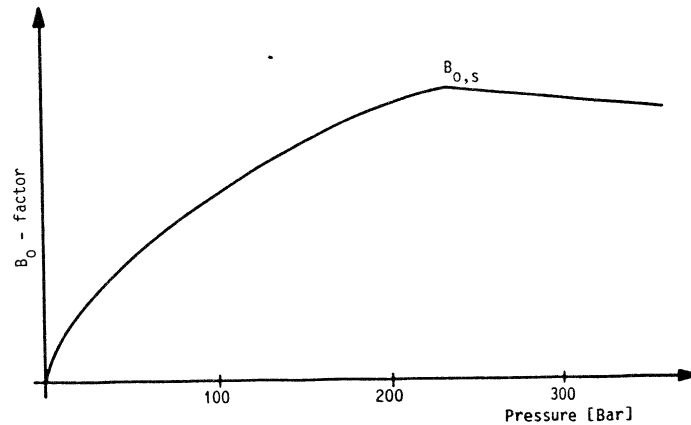
Fig. 6.9. The differential liberation B_o-factor as function of pressure.
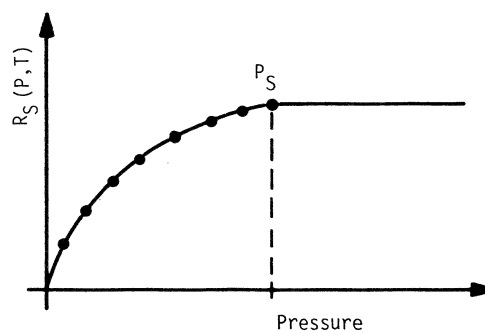

Fig. 6.10. The solution gas/oil ratio (R_S) as function of pressures.

The density of the reservoir fluid at each pressure reduction step can be determined from the known density at 15°C, the liquid volume, and the volume and molecular weight of the gas. The density versus pressure data may be presented as shown in Fig. 6.11.
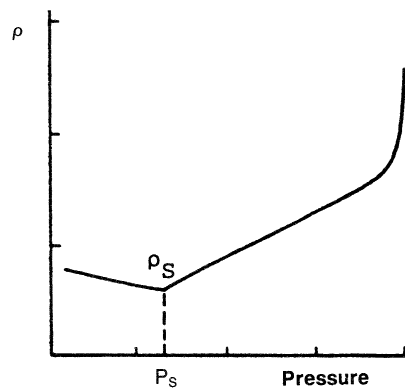

Fig. 6.11. Density of reservoir fluid as function of pressure.

Deviation from ideal gas behavior may be expressed via the compressibility factor, Z, as defined in Eq. 6.5. Employing Eq. 6.5 twice., i.e., at two different pressures and temperatures and for the same number of moles, will result in:

$$Z_1 = \frac{P_1 V_1 T_2 Z_2}{P_2 V_2 T_1}$$

(6.11)

Eq. 6.11 relates a compressibility factor at condition 1, where it is unknown, to the compressibility factor at condition 2, where it is assumed to be known. Z_2 is normally the compressibility factor at ambient conditions, and it is usually close to unity.

6-9

6.1.3. Separator test

A three-stage flash can be performed in order to furnish support data for process simulation. Such a flash sequence is shown in Fig. 6.12.
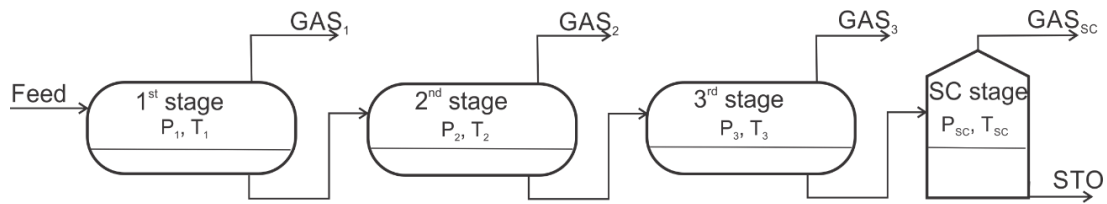

Fig. 6.12. A 3-stage flash separation train, including a last stage stabilized to SC.

The last stage is the stock tank stage at standard conditions, where the pressure is one atm and the temperature is 15°C. For the other three stages, temperature and pressure can be chosen as desired.

The three first stages are accomplished in the same PVT cell as was used in the differential liberation experiment; and the last stage is carried out by transferring the third stage fluid to a single flash apparatus (see "Flash Separation and Compositional Analysis " discussed earlier). From this experiment the overall GOR, GOR at individual stages, compositions of the gas and liquid phases, properties of the stock tank fluid such as density and molecular weight and also the B_o factor of the oil can be obtained. Tbl. 6.2 and Tbl. 6.3 show a typical laboratory result of a separator test experiment.

Tbl. 6.2. Separator Test Results for a Black Oil

Stage	P_{sep} Bar	T_{sep} °C	GOR [1]	GOR [2]	ρ_{STO} at 15°C	$B_{o,f}$ [3]	$B_{o,sep}$ [4]	Flashed Gas γ_g
1	68.9	41.2	91.6	105.2			1.148	0.641[5]
2	22.4	85.6	21.6	24.3			1.125	0.675[5]
3	1.7	77.9	10.9	11.8			1.084	0.930[5]
	1.013	15	0.1	0.1	0.8822	1.360	1.000	[6]

[1] Gas/oil ratio in m^3 of gas at SC (15°C and 1.0132 bar) per m^3 of oil at stage P and T.

[2] Gas/oil ratio in m^3 of gas at SC (15°C and 1.0132 bar) per m^3 of STO at 15°C.

[3] Formation volume factor ($B_{o,f}$) in m^3 of saturated oil at 333.5 bar and 73.0°C per m^3 of STO at 15°C.

[4] Separator volume factor ($B_{o,sep}$) in m^3 of oil at indicated P and T per m^3 of STO at 15°C.

[5] Gas collected for specific gravity and hydrocarbon composition analyses.

[6] Insufficient gas for analysis

Tbl. 6.3. Analyses of Separator Gases (Mole%) from Separator Tests

Component	Composition (Mole%)		
	Stage 1	Stage 2	Stage 3
Hydrogen sulfide	0	0	0
Carbon dioxide	1.56	2.05	2.60
Nitrogen	1.65	0.55	0.23
Methane	88.49	85.44	61.49
Ethane	5.79	7.72	17.38
Propane	1.01	1.95	7.70
iso-Butane	0.35	0.57	2.75
n-Butane	0.47	0.66	3.47
iso-Pentane	0.23	0.25	1.44
n-Pentane	0.16	0.30	0.94
Hexanes	0.12	0.15	0.82
Heptanes plus	0.17	0.36	1.18
∑	100.00	100.00	100.00

6.1.4. Gas Reinjection related analyses

In order to understand the reservoir fluid behavior under gas injection processes, two different laboratory experiments are performed:

1. Swelling test

2. Slim tube minimum miscibility pressure determination

Swelling Test.

When gas is injected into a reservoir containing a reservoir oil undersaturated of gas, the injected gas can dissolve into the oil, swelling the oil, and the volume of the reservoir oil increases.

Simulation of this effect can be performed in an ordinary PVT cell, starting with the original reservoir fluid in question. A small known volume of compressed injection gas from a separate steel cell is transferred into the PVT cell. The new saturation pressure of the reservoir oil is determined as described earlier, and the new corresponding saturation volume is recorded.

This process is repeated until the saturation pressure of the fluid is equal to the estimated injection pressure of the system. The data from this test can be presented as shown in Fig. 6.13.
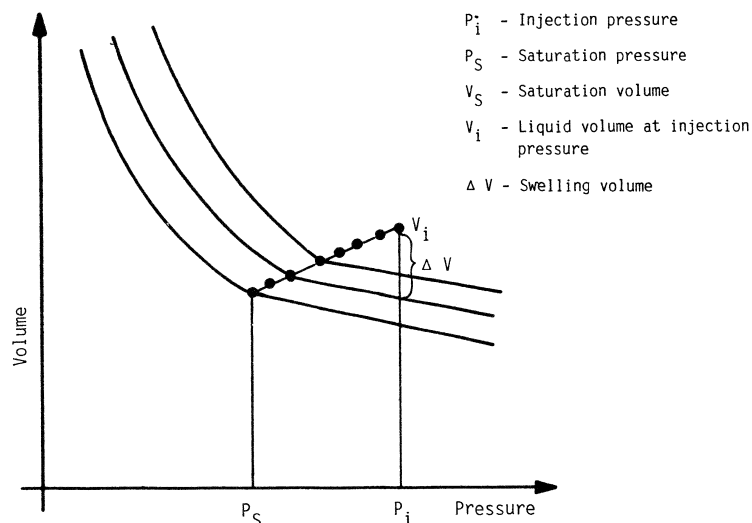

Fig. 6.13. Graphical representation of swelling test data.

Slim Tube Test.

One method of improving oil recovery involves injection of gas into the oil reservoir. The gas may be nitrogen, carbon dioxide, flue gas, or natural gas.

It is advantageous to have a miscible displacement. This means that at the gas/oil front only one phase is achieved no matter in what proportion the oil and the gas are mixed. The injected gas and the reservoir oil may be miscible by first contact or miscibility may be achieved as a result of a multiple contact process. If the gas and oil become miscible, complete displacement of the reservoir fluid will be accomplished, and the recovery may be larger than 90 %. It is, therefore, of great practical and economic interest to find out if the gas plus the oil form one phase, i.e., are miscible. If so, it becomes important to know the lowest pressure at T_{res} a complete miscibility occurs in the displacement process. This is called the minimum miscibility pressure and could be experimentally verified in a slim tube test.

The minimum miscibility pressure may be determined from visual observations of the displaced fluid. Usually, it is determined as the breakover point in the recovery curve from a series of displacement experiments. An example of a displacement curve is illustrated in Fig. 6.14, showing oil recovery as a function of pressure at a fixed temperature.
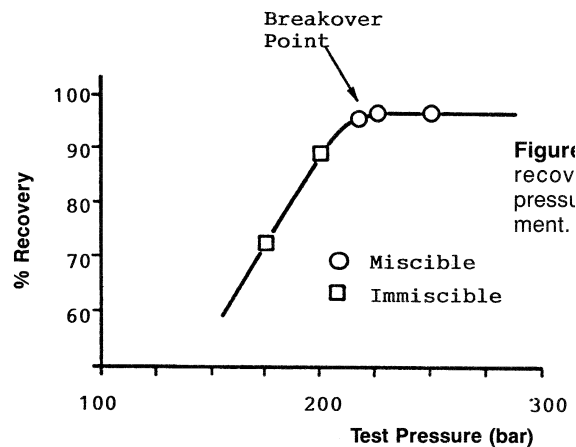

Fig. 6.14. Oil recovery as a function of pressure in a typical slim tube experiment

The main part of the equipment is a approximately 10 m long ¼ -in. steel tubing packed with sand. Two high pressure steel cells are connected, one for the injection gas and one for the reservoir oil , both pressure supported from mercury pumps. Using the pumps the reservoir fluid and the gas may be forced to flow through the steel pipe. A sight glass to observe the produced fluids and a flash separator to determine the amount of fluids produced are provided.

The sand pack is first saturated with the oil sample to be studied, and the initial volume of fluid in the coiled tubing is recorded. The pressure of the system is set, and gas is allowed to displace oil through the sand pack. The amount of produced fluid is monitored as time proceeds.

A schematic diagram of a slim tube apparatus is shown in Fig. 6.15.

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GAS
↑

        ⑤         ⑧        ② ③

        ⑥

   ⑦              ④
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1. – Mercury pump
2. – Oil reservoir
3. – Gas reservoir
4. – Slim tube – steel tubing 1/4" approx. 10 m
5. – Sight glass – visual flow cell
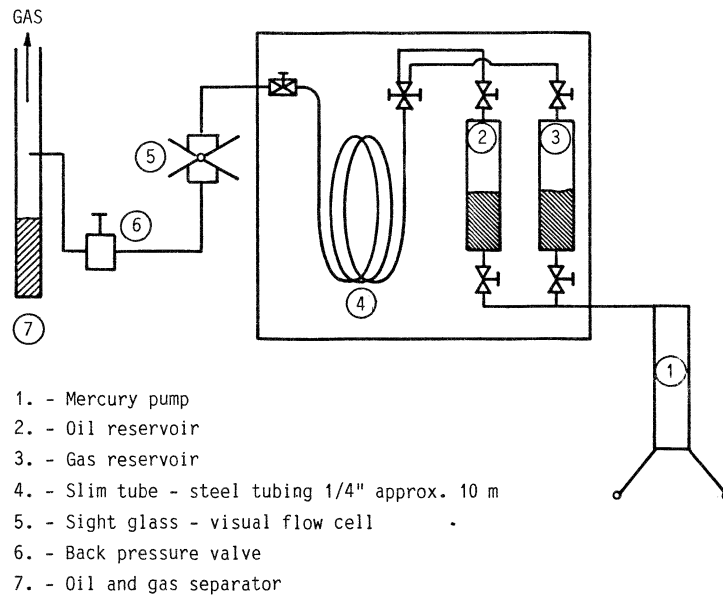6. – Back pressure valve
7. – Oil and gas separator

Fig. 6.15. Schematic diagram of slim tube apparatus.

The sequence is repeated for several pressures, and the recovery, (produced oil)/(initial oil), is recorded for each pressure. The resulting data may be plotted as shown in Fig. 6.16.
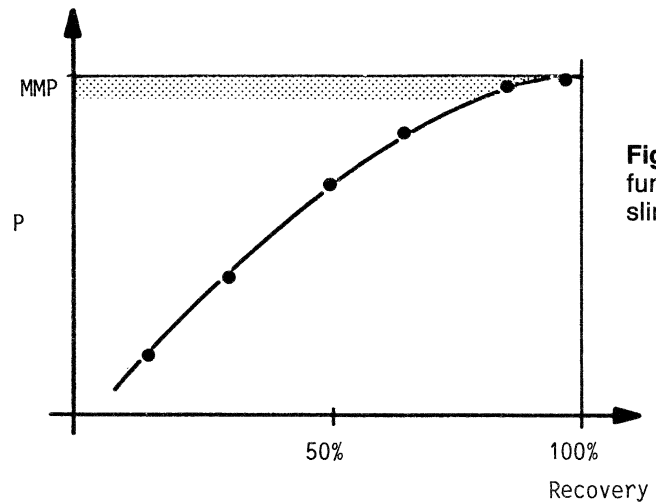

Fig. 6.16. Pressure as a function of recovery from a slim tube analysis.

The pressure at which 90-100% of the initial fluid in the sand pack is recovered is defined as the minimum miscibility pressure of the system.

Several modifications of this apparatus can be made. Online density determination of the fluids using a high-pressure densitometer, and viscosity measurements using a capillary tube viscosimeter, are examples of such modifications.

6.2. PVT analyses on Gas Condensates

At reservoir conditions, gas condensates usually exist in one single gaseous phase. Gas condensate fluids are studied in PVT cells with a construction different from those used for black oils, to improve measurement accuracy.

There are two main types of gas condensate PVT cells, phase equilibrium cell and the Sloane type of cell. A phase equilibrium cell have windows so that visual observation of the whole or the bottom part of the hydrocarbon sample can take place.

The dew point is defined as the pressure at which the first small droplet of liquid is observed in equilibrium with the gas phase. For gas condensates, normally the upper dew point is of interest, i.e., the liquid is formed ("drops out") by pressure reduction.

The separator samples, gas and liquid, are prepared as for black oil analysis. The PVT cell is charged, first with the gas, by allowing the gas to expand into the cell and displace the mercury. The volume of mercury displaced can be measured, and thus the volume of gas in the cell is known.

6.2.1. Constant Mass Expansion - Gas condensate

In order to achieve a representative reservoir fluid, separator samples (Oil and Gas) is added to the cell with the measured GOR during the sampling. With a recombined reservoir fluid sample in the PVT cell reservoir temperature, the system is compressed to above the reservoir pressure, Pres. At this pressure, the cell is left for equilibration (usually overnight). The system is checked to see if it is all in single phase (Gas), and the total system volume is then recorded. A constant mass expansion experiment can then be performed. A schematic diagram of this process is shown in Fig. 6.21.
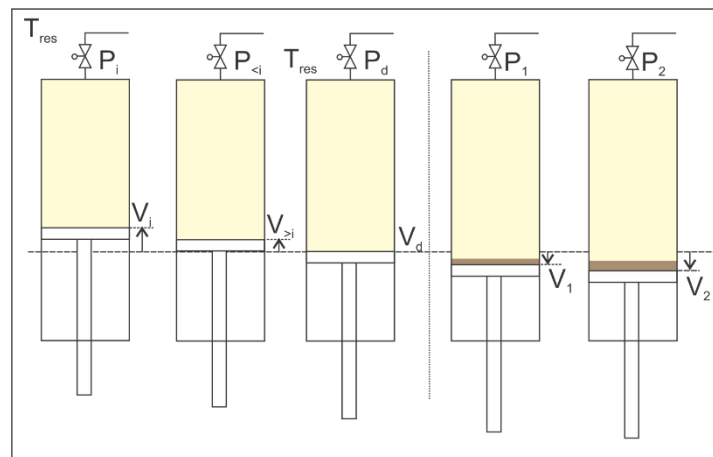

Fig. 6.21. Schematic representation of constant mass expansion (CME) experiment on a gas condensate.

A stepwise pressure reduction is performed. The system is observed visually, and the volume recorded at each pressure level by reading the mercury pump.

The dew point pressure can be difficult to observe, therefore the stepwise pressure reduction is continued below the dew point.

Below the dew point, the liquid volume at each pressure step is determined. These readings result in the liquid dropout curve. Data from the constant mass study can be plotted as shown in Fig. 6.22. It should be noted that the dew point is obtained by extrapolating the liquid dropout curve.
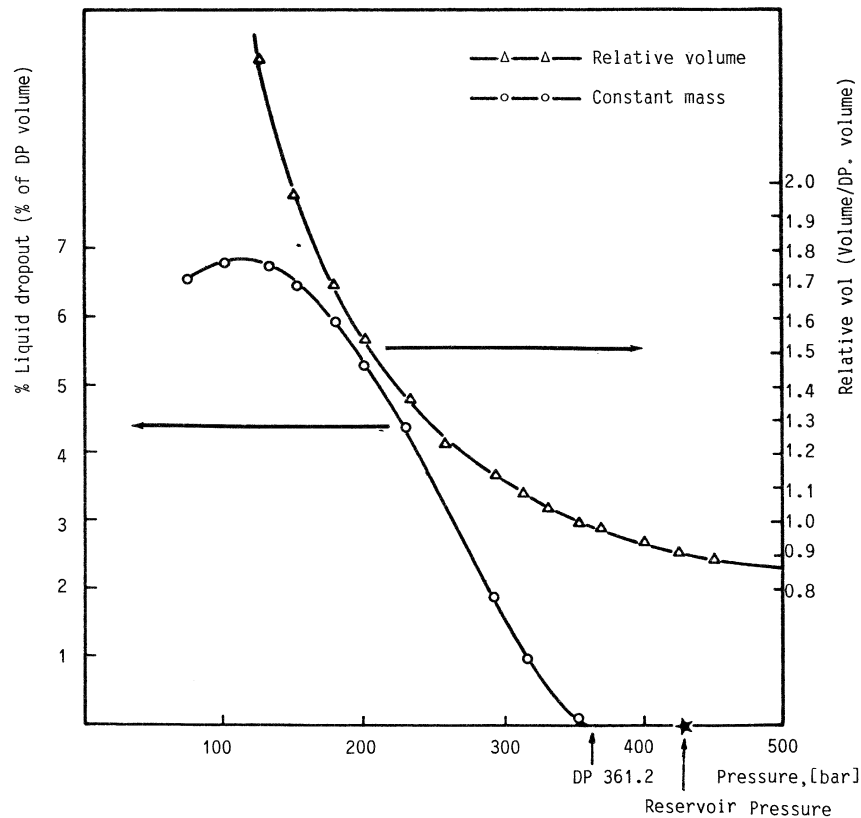
Fig. 6.22. CME liquid dropout and Pressure Volume ratio for
Gas Condensate at 121°C.

The amount of liquid formed is usually relatively small, and therefore special attention must be paid to the liquid volume determinations. The available cell designs offer different methods by which the liquid volumes can be measured. Best results are obtained in cells where charge volumes are up to 400 cm^3 at the dew point. Significant liquid volumes will then be formed, allowing relatively accurate liquid volume measurements. The amount of liquid is best determined in a cell where the window configuration allows light to shine through the system.

6.2.2. Constant Volume Depletion – Gas Condensate

In order to simulate production behavior of a reservoir condensate, a constant volume depletion experiment is performed. A schematic diagram of the process is shown in Fig. 6.23.

The system is brought to just below its dew point pressure, P_d. The dew-point volume $V_{sat} = V_d$ of the system is known from the constant mass expansion experiment.

When the system is equilibrated at pressure P_1 giving a cell volume $V_1 > V_{sat}$. The excess volume above the dew-point volume is displaced into a flash separation system.

The flash system are designed in such a way that it is possible to collect and measure the small amounts of liquid that are condensed out of the produced gas stream. The total gas volume can be measured using a gasometer.

From compositional analyses of the gas and the liquid phases, and by knowing the volume of each phase, a produced well stream composition can be determined.

The pressure is further reduced to P_2, and more liquid is formed in the PVT cell. The amount of liquid in this phase is measured, and the excess volume above the dew-point volume is displaced out of the cell at constant pressure. The amount of produced gas is again recorded.
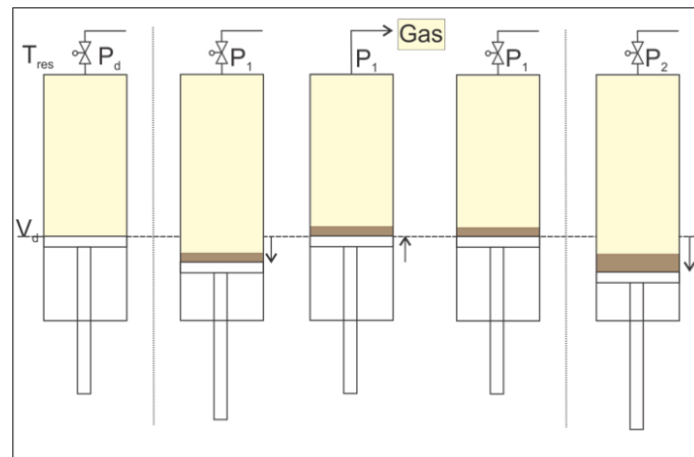

Fig. 6.23. Schematics of constant volume depletion (CVD) experiment on gas condensate.

This stepwise procedure is repeated until atmospheric pressure is reached. Typical data from a CVD experiment can be seen in Tbl. 6.4.

Tbl. 6.4. Constant Volume Depletion Data at 121°C. Hydrocarbon Analysis of Produced Wellstream

Component	Mole% at reservoir pressures (Bar)						
	362.2	307.7	274.4	222.4	171.5	20.2	71.8
Carbon dioxide	9.16	9.14	9.29	9.25	9.39	9.31	9.20
Nitrogen	0.64	0.72	0.74	0.69	0.74	0.63	0.64
Methane	68.80	70.05	70.27	70.68	71.30	71.42	69.12
Ethane	8.43	8.54	8.59	8.44	8.34	8.51	8.78
Propane	5.11	5.13	5.18	5.06	4.92	5.02	5.70
iso-Butane	0.81	0.80	0.81	0.79	0.75	0.76	0.97
n-Butane	1.45	1.42	1.45	1.39	1.33	1.35	1.79
iso-Pentane	0.52	0.49	0.50	0.49	0.46	0.46	0.68
n-Pentane	0.53	0.50	0.51	0.49	0.46	0.46	0.72
Hexanes	0.63	0.54	0.55	0.55	0.51	0.53	0.80
Heptanes	0.83	0.62	0.64	0.66	0.62	0.68	0.81
Octanes	0.95	0.55	0.52	0.59	0.59	0.59	0.54
Nonanes	0.52	0.27	0.21	0.26	0.24	0.19	0.16
Decanes+	1.62	1.23	0.74	0.66	0.35	0.09	0.09
Σ	100.00	100.00	100.00	100.00	100.00	100.00	100.00
M_{C10+}	200	180	168	157	151	157	147
ρ_{C10+} (g/cm^3)	0.856	0.828	0.827	0.821	0.819	0.817	0.817
Gas compr., Z	1.003	0.946	0.922	0.882	0.882	0.903	0.934
Mole% prod	0	9.6	7.6	13.4	14.8	16.3	15.5
Σmole% prod.	0	9.6	17.2	30.6	45.4	61.7	77.2
M_g	28.31	26.47	25.60	25.42	24.81	24.49	25.44
Two-phase Z	1.003	0.943	0.918	0.887	0.870	0.869	0.872
μ_g (cP)	0.0332	0.0271	0.0246	0.0215	0.0187	0.0164	0.0147

At the end of the analyses a molar balance (n) is performed to check if some fluid has been lost during the experiment. The balance may be written as:

$$n_{charged} = n_{produced} \qquad (6.12)$$

The agreement should be within ± 1 % in order to avoid errors in the subsequent calculations from the analysis.

Fig. 6.24 shows the difference in the two liquid dropout curves from constant mass expansion (CME) and constant volume depletion (CVD), respectively.
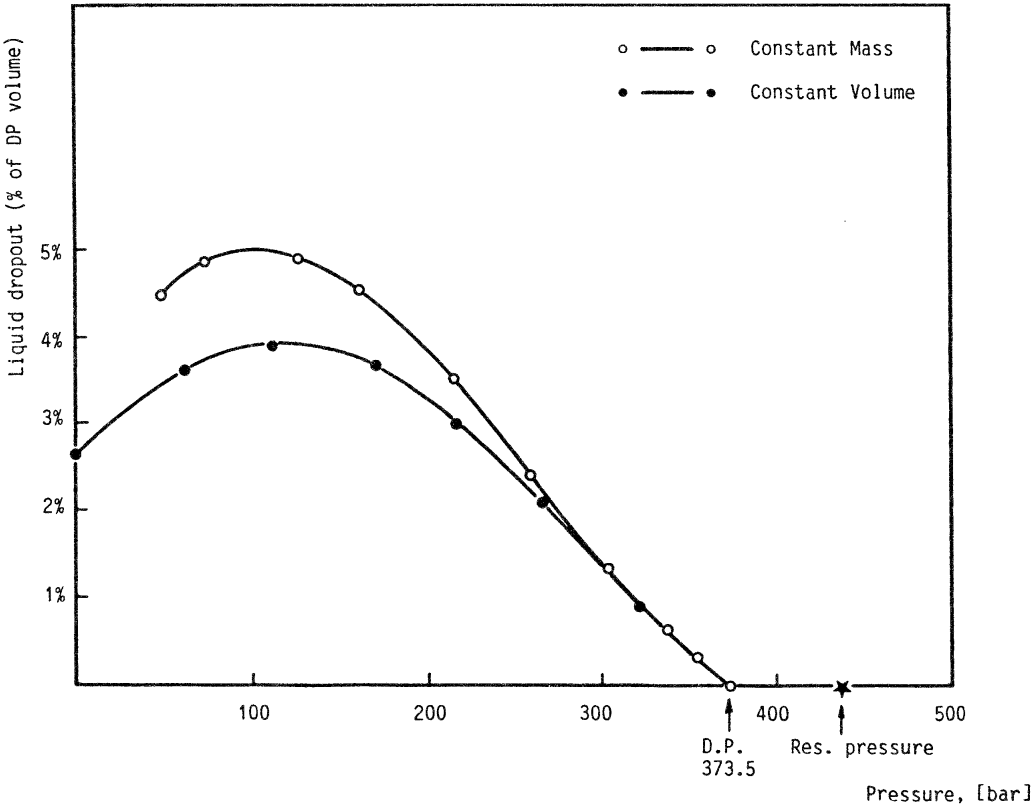

Fig. 6.25. Comparison of Liquid dropout from CME and CVD experiment for a gas condensate.

6.3 VOLATILE FLUIDS

Some naturally occurring hydrocarbon mixtures can be classified as volatile fluids or near-critical fluids.

The PVT behavior of these systems is difficult to analyze, because there are virtually impossible at reservoir conditions to distinguish between the gas and liquid phase.

Normally these fluids are treated as for gas condensates in the PVT laboratory. A long windowed PVT cell is often used. This cell allows visual inspection of the whole sample at any stage of the laboratory analysis.

The cell is charged with the fluid sample (recombined or reservoir fluid). The pressure in the cell is then increased far above saturation Pressure (P_{sat}) raised by means of a Hg-pump. The sample is left at reservoir temperature to equilibrate.

The pressure is then reduced stepwise in the cell, and observations are made to determine the saturation pressure. In the case of a volatile fluid it may be difficult to see whether a phase transition is a dew or a bubble point, because the two phases are nearly identical.

Phase changes are rapid, and a near critical system exhibits large changes in its PVT and phase behavior for relatively small temperature and pressure changes. Fig. 6.27 shows the typical, large, liquid dropout curve changes over a temperature range of only 20°C.

Once the saturation pressure of the system has been found, and the constant mass study has been performed, the work program of the analysis follows that of a gas condensate system.
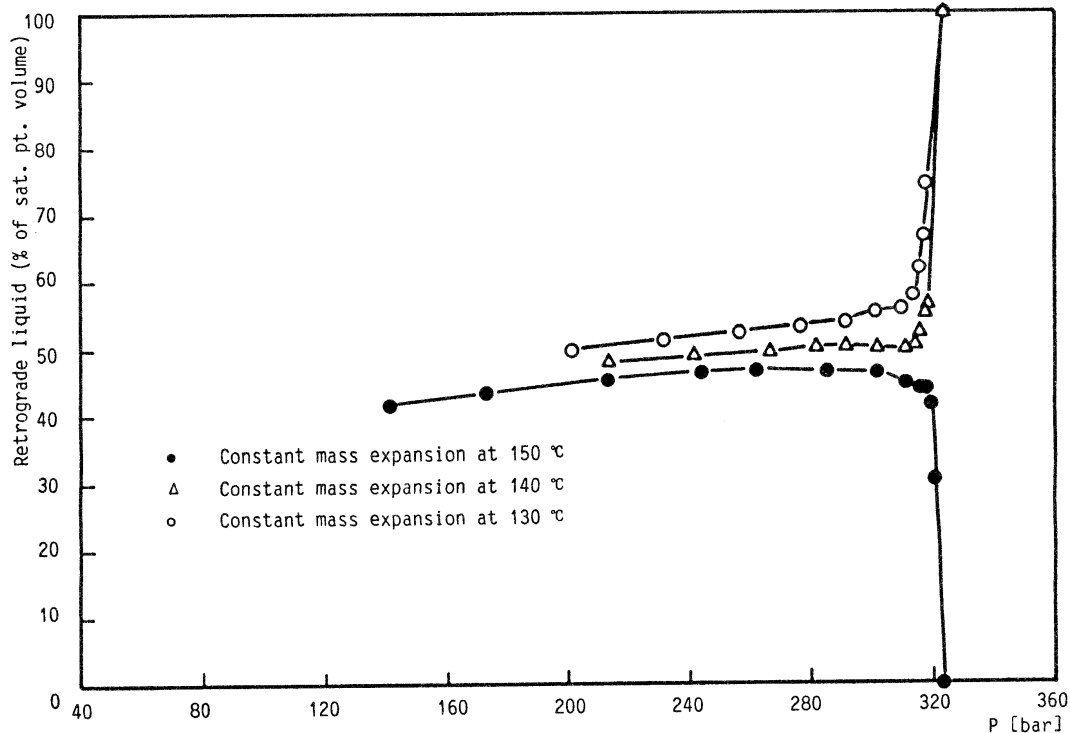

Fig. 6.27. Liquid dropout curves for a volatile fluid. Note that a dew point is obtained at 130°C, whereas bubble points are obtained at 140 and 150°C.

6.4. VISCOSITY MEASUREMENTS

An important property of a hydrocarbon system is its viscosity at relevant pressures and temperatures.

A few methods have been developed for these measurements at reservoir pressure and temperature. The most commonly used methods are:

1. Rolling ball viscosimeter

2. Capillary tube viscosimeter

6.4.1. Falling Ball Viscosimeter

Fig. 6.28 shows a schematic diagram of a rolling ball viscometer. It consists of the fall tube, an expansion chamber, and a steel ball of known dimensions.

A hydrocarbon fluid is transferred into the evacuated viscosimeter at constant pressure. The system must be equilibrated at above reservoir pressure for several hours before the analysis can start.

Prior to charging, the viscosimeter must be calibrated with known calibration fluids. The ball size should be chosen so that the calibration curve is linear in the range of operations, normally 0.2-3 cP. Calibrations are made at each of the three angular positions in which the viscosimeter can be placed.

To start the viscosity determination, the top valve is closed in order to seal the upper end of the ball tube. The apparatus is turned upside down, allowing the steel ball to roll to the top. The valve stem of

the top valve is made magnetic by a coil, so that the ball will stay at the top when the apparatus is turned back to measurement position.

Using a switch, the magnet is deactivated, and the ball starts to fall. The time it takes to reach the bottom of the tube is recorded.
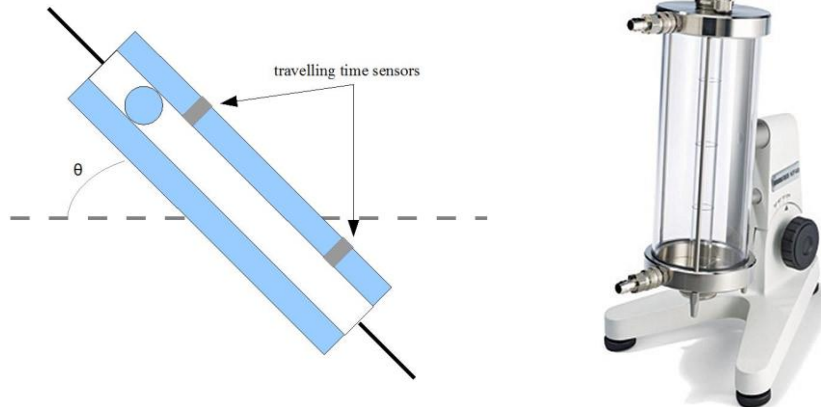

Fig. 6.28. Falling ball viscometer (a) principle, and (b) Broookfield type
with 0.5 - 2.0% accuracy depending on ball being used.

With this time and the known density of the fluid, its viscosity can be determined from the calibration curves.

This method is generally found to be reliable; it is, however, rather cumbersome to operate.

6.4.2. Capillary Tube Viscosimeter

With the capillary tube viscosimeter the viscosity (η) of flowing fluid could be measured on single phase fluids at high pressure and temperature. η is calculated using the flow equation:

$$\eta = \frac{d^2\,\Delta P}{32\,L\,v} \tag{6.13}$$

Where:
   d = internal diameter of the capillary tube
   L = length of the capillary tube
   ΔP = pressure drop
   v = velocity of the fluid flowing through the capillary tube.

The equipment used is shown schematically in Fig. 6.30.

Reservoir fluid is charged to the adjoining PVT cell and equilibrated at reservoir conditions or above.

To measure viscosity, the fluid is charged to the coiled capillary tube, and equilibrated. Flow of fluid through the capillary is established using a motorized pump. The pressure drop across the coil is monitored at constant flow rate. The temperature and pressure are kept constant.

The process can be repeated at different pressures above the saturation pressure, and the viscosity calculated from Eq.6.13.

Since the coiled capillary tube does not have a perfectly homogenous inner-diameter, it must be calibrated with calibration fluids of known viscosity.
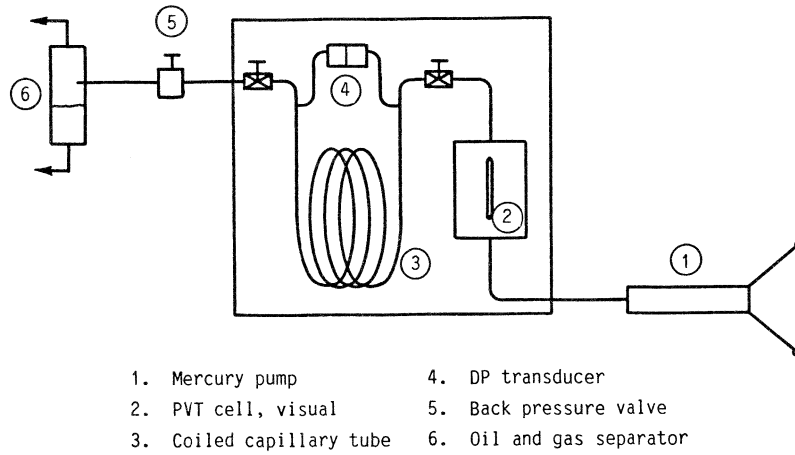
1. Mercury pump   4. DP transducer
2. PVT cell, visual   5. Back pressure valve
3. Coiled capillary tube 6. Oil and gas separator

Fig. 6.30. Schematic diagram of a capillary tube viscosimeter.

6.5. Interfacial tension

The interfacial tension between two fluids is an important fluid property in the evaluation of reservoir fluid flow. Interfacial tension exists between a water phase and an oil phase, between a water phase and a gas phase, and between an oil phase and a gas phase. The interfacial tension can, with some difficulty, be measured at reservoir conditions using either a pendant drop or a spinning drop apparatus. Both methods are optical, in the sense that the measurements are made on images of bubbles of one fluid suspended in the other.

6.5.1. Pendant Drop Tensiometer

The basic apparatus, consisting of a high-pressure sight glass or PVT-cell, is shown in Fig. 6.31.
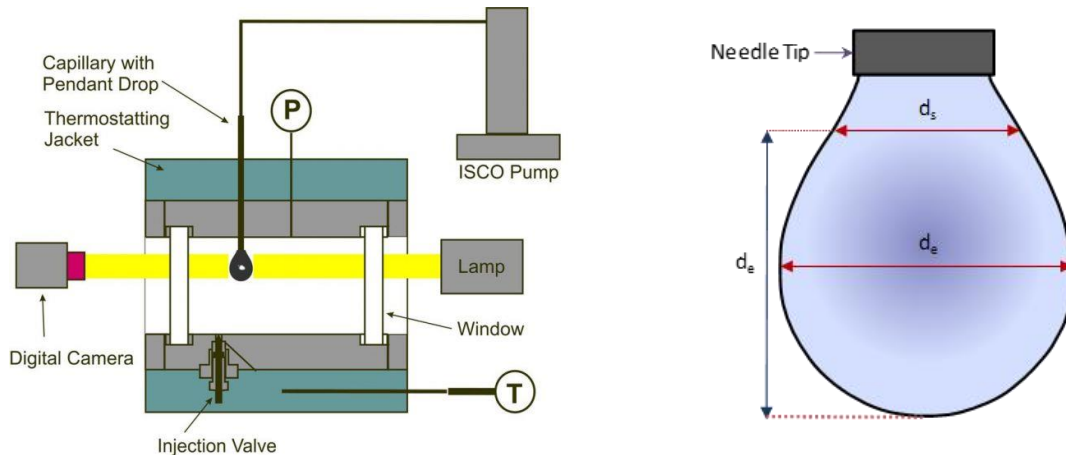

Fig. 6.31. Pendant drop cell. (left) experimental set up and (right) drop shape measurements.

This can be charged with brine at reservoir conditions P and T. Through a capillary tube extending into the cell, an oil droplet is seen suspended from the tip of the needle/capillary tube. The shape of the droplet will depend on the interfacial tension between the fluids, and the interfacial tension (σ) can be calculated from the droplet's geometry [1, 2] using the following expression:

$$\sigma = \frac{\Delta\rho \; g \; d_e}{H} \qquad (6.14)$$

where:

σ = interfacial tension, normally reported in mPa s

$\Delta\rho$ = difference in the density of the two fluids at T and P

g = gravitational acceleration

d_e = equatorial diameter (Fig. 6.31)

d_s = distance shown in Fig. 6.31

1/H = tabulated function of d_e/d_s [2].

6.5.2. Spinning Drop Tensiometer

The spinning drop method (rotating drop method) is one of the methods used to measure interfacial tension. Measurements are carried out in a rotating horizontal tube which contains a dense fluid (Ex. Brine). A drop of a less dense liquid (Oil) bubble is placed inside the fluid. Since the rotation of the horizontal tube creates a centrifugal force towards the tube walls, the liquid drop will start to deform into an elongated shape; this elongation stops when the interfacial tension and centrifugal forces are balanced. The surface tension between the two liquids can then be derived from the shape of the drop at this equilibrium point. A device used for such measurements is called a "spinning drop tensiometer", Fig. 6.32.
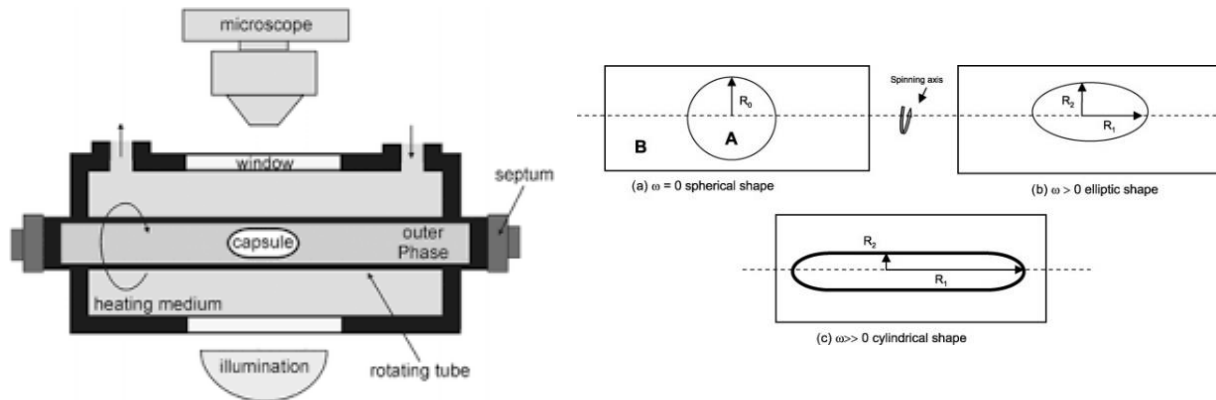

Fig. 6.32. Spinning drop tensiometer

The spinning drop method are recommended for surface tensions below 10 mN/m, and is usually preferred for the accurate measurements of surface tensions below 10^{-2} mN/m. It refers to either using the fluids with low interfacial tension or working at very high angular velocities. This method is widely used in many different applications such as measuring the interfacial tension of surfactant systems.

The interfacial tension (σ) could be calculated by :

$$\sigma = \frac{\Delta\rho \ \omega^2}{4} R_2^3 \qquad (6.15)$$

This equation is known as Vonnegut's expression [3]. Interfacial tension of any liquid that gives a shape very close to a cylinder at steady state, can be estimated using this equation. The straight cylindrical shape will always develop for sufficiently high ω; this typically happens for $R_1/R_2 > 4$. Once this shape has developed, further increasing ω will decrease R_2 while increasing L keeping LR_2 fixed to meet conservation of volume. The interfacial tension is calculated as described by [4].

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