

CHAPTER 5

EXPERIMENTAL APPARATUS

5.1 Introduction

Several classes of equipment have been developed for and used over the last decades in order to measure VLE data experimentally. This chapter starts by providing brief general background information. The specific instrument used in this study will then be covered in more detail.

5.2 General overview

According to Hala et al (1967:280) the methods for the direct determination of equilibrium data can be classified for the most part into the following groups:

- (1) Distillation method.
- (2) Circulation method.
- (3) Static method.
- (4) Dew and Bubble point method.
- (5) Flow method.

5.2.1 Distillation Method

This is the oldest method known. In one variation, a small amount of liquid is distilled off from a boiling flask which contains a large charge. Due to various drawbacks (large liquid sample, small vapour sample etc.) this method is rarely used (see Hala et al, 1967:281).

In another variation a small column is operated under total reflux. Gerster (1969:46) makes the following comment regarding such columns:

"Because of uncertainties in tray efficiency and foaming, development of a new solvent system for extractive distillation is often carried out in small scale tray columns rather than in equilibrium stills. ... On the other hand, for large, important, and unusual solvent distillations, complete relative volatility data obtained from equilibrium stills may be required."

In this case the reader should keep in mind that the price of the pure chemicals required for the tests implies that maximum use of experimental equipment be made. Although the potential benefits of a column can not be questioned, the amounts of chemicals required can be restrictive.

5.2.2 Circulation Method

(see Hala, 1967:281)

This method is probably the most widely used. It is convenient to use for both medium and low pressures. While many variations exist, all are based on a simple principle shown in figure 5.1.

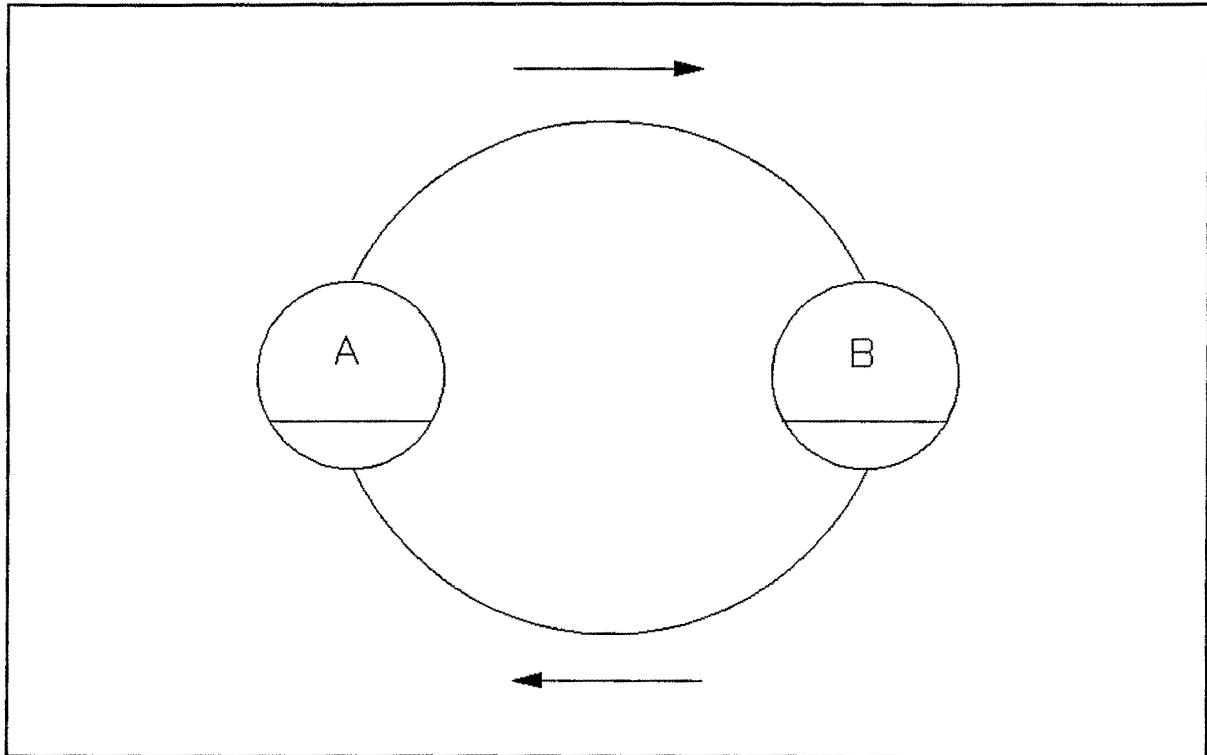


Figure 5.1: Circulation principle.

The vapours evolved from the boiling mixture in the distilling flask A pass through the vapour conduit (\rightarrow) and after complete condensation collect in receiver B. After filling the receiver the condensate returns to the distilling flask through liquid conduit (\leftarrow), in which there is usually inserted a trap or cock to prevent the flow of liquid from the distilling flask back into the receiver. Initially the contents of receiver B (when it first fills) are richer in the more volatile constituent than is the vapour phase over the boiling mixture in the distilling flask. With further operation of the still, the contents of the distillation flask become richer in the more volatile component and the receiver becomes poorer. This process continues until the steady state is attained.

The first equilibrium still which functioned satisfactorily was constructed by Othmer. Many improvements have since been suggested and a large number of variations are in operation today (see Hala, p. 287 ff).

5.2.3 Static method

(see Hala, 1967: 312)

"In this method the solution is charged into a closed and evacuated cylinder, which is placed in a thermostat. The cylinder is rotated until equilibrium is established between the liquid and its vapour, when both samples are taken for analysis."

Although tedious, this method can yield exceptionally accurate results.

At low pressures the amount of vapour required for analysis is of the same order as the total amount of vapour phase in the cell, so that removal can lead to disturbances. For this reason the static method is not often used at medium and low pressures.

5.2.4 Dew and Bubble Point Method

(p. 316)

This method measures the dew and bubble points of a mixture of specific composition by manipulating the pressure. It has been used for a long time for the study of mixtures which are gases or low boiling liquids at normal conditions.

5.2.5 Flow Method

(p. 319)

The dynamic flow method was developed in an effort to attain the steady state as quickly as possible. In this method the equilibrium chamber is fed with a steady stream of constant composition.

The simple Colburn flow still is probably the best known in this category. From the consistency of measured data it appears to work very well.

5.3 Equipment used in previous studies

When planning to test azeotropic or extractive agents experimentally, it is a good idea to consider the types of equipment used in other studies:

- Raal et al (1972 and 1992) used a modified Othmer-type still to study vapour-liquid equilibria of highly non-ideal alcohol-hydrocarbon systems.
- Prabhu & Van Winkle (1963) used a Colburn-type still to study the effects of polar components on the n-octane-ethylcyclohexane system.
- Updike & Langdon (1945) used three equilibrium stills to study the effect of added components on the relative volatility of binary mixtures. One was a simple (Raleigh) batch still and the other two were Othmer-type stills.
- Stephenson & Van Winkle (1962) used a Colburn type recirculation still to study the modification of relative volatilities by addition of solvent.
- Prabhu & Van Winkle (1963) used a modified Colburn still to test the effect of polar components on the octane-ethylcyclohexane system.
- Wu et al (1991) used a Stage-Muller dynamic still to measure VLE of hydrocarbons and fuel oxygenates.
- Gerster (1969) used a small column to study potential extractive agents.

- Berg et al (1969) used a small rectification column to test the effect of various entrainers on hydrocarbon pairs.

It does not appear as if any specific type of still has found favour among researchers. Colburn and Othmer-type stills appear to be used most times.

5.4 Equipment for this study

5.4.1 Description

The Othmer type stills used in this study are virtual copies of the one developed by Prof. JD Raal from the University of Natal. The initial design is described in a journal article in which the systems ethanol-n-heptane and methanol-n-hexane were studied (Raal et al, 1972:211). The following important paragraphs deserve to be quoted:

"Among the more serious difficulties encountered with many of the equilibrium stills presented in the literature are partial condensation of the equilibrium vapour (which may lead to considerable error), inadequate mixing and vapour-liquid contact in the equilibrium chamber, complete evaporation of liquid droplets, and imprecise temperature measurement.

An attractive feature of stills with vapour-phase circulation ... is the excellent mixing and intimate contact of vapour bubbles with surrounding liquid in the equilibrium chamber. Drawbacks ... are the imprecise measurement of boiling temperature and the difficulties encountered in exactly balancing heat losses to maintain adiabatic operation of the equilibrium chamber. Also, vertical temperature gradients, such as may arise from uneven heating, may produce erroneous results.

The above drawbacks are largely eliminated in stills with circulation of both liquid and vapour phases... The Cottrell pump feature of these stills permits very precise temperature

measurement but provides less satisfactory mixing and vapour-liquid contact than the bubbling chamber of the Jones still. Partial condensation of equilibrium vapour is not completely eliminated... The rather long times required to reach steady state is somewhat unsatisfactory.

In the still used the efficient mixing characteristics of the Jones-Colburn design are combined with a novel adaptation of the Cottrell pump to provide accurate temperature measurement and to ensure adiabatic operation of the equilibrium chamber at all operating temperatures."

Measurements taken with said still were reported to be accurate to $\pm 0.1^{\circ}\text{C}$ and ± 0.4 mm mercury, with equilibrium times of $1\frac{1}{2}$ - $2\frac{1}{2}$ hr depending on composition.

Accurate data could not be measured in the very dilute region where the relative volatility is very large. This was considered to be due to incomplete mixing in the outer chamber. An additional stirring device in the lower outer chamber region was suggested. All in all, accurate data could be produced for very demanding non-ideal systems.

The extra stirring mechanism was indeed added in later versions of the still, as described by Raal et al., 1992:253. Capillary tubes were also introduced in the condensate return line and in the liquid return line from the vapour-liquid disengagement chamber. A split downcomer was also added (The latter modification is not present in the stills used for this study).

The heater in the boiler chamber produces a rapid two-phase flow in the annular space surrounding the inner equilibrium chamber. At equilibrium the vapour passes unchanged through the liquid in the inner equilibrium chamber and is conveyed through a superheated take-off to the condensate receiver. Liquid in the inner chamber is effectively agitated and adiabacity is ensured by the rapid exterior fluid flow and by insulating vapour flow

in the inner downcomer. Best results were obtained when the cell was well insulated.

Temperatures were measured with an accuracy of ± 0.02 °C, pressures to ± 0.1 kPa and compositions analysis to 0.005 mole fraction.

As stated by Hala et al (1967:324), Othmer stills are for homogeneous solutions only. In a 1992 study published by Raal, an unstable emulsion formed in the condensate receiver and sample compositions were not reproducible.

The vapour cooler is normally open to the atmosphere, so that the temperature measured is the boiling point of the liquid in the equilibrium chamber at ambient pressure.

5.4.2 Verification of the equipment

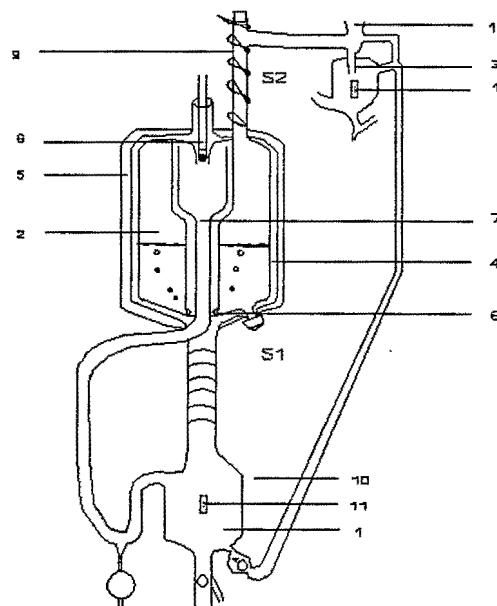
5.4.2.1 Introduction

In the execution of any experimental work the researcher must always initially establish the accuracy of his work. This will not only indicate the reliability of new work to potential future users, but also ensure him that he has mastered the equipment and no systematic errors are present.

In order to determine the integrity of the Othmer stills, a known system was measured. The ethanol / benzene system was chosen for the following reasons:

- i) These chemicals are inexpensive and readily available in pure form.
- ii) The system temperatures are in a comfortable range.

EQUILIBRIUM STILL



- | | | |
|------------------------|------------------|---------------|
| 1. Evaporator | 6. Thermometer | 11. Magnetic |
| 2. Equilibrium chamber | 7. Downflow tube | stirrers |
| 3. Condensate chamber | 8. Openings | 12. Connector |
| 4. Cottrel tube | 9. Vapour arm | for |
| 5. Isolation material | 10. Heater | water cooler |

Figure 5.2: The Othmer type still used, as modified by JD Rall.

- iii) The system has been studied by reputable researchers and data at several pressures is available.

Equilibrium data for said system has been published in DECHEMA (Gmehling, 1977, Vol.I, Part 2c, Supplement 1: 382) at constant pressure of 93.3 kPa. Given that the activity coefficient is insensitive to slight changes in pressure, the Wilson constants at this pressure were used to describe the system at 84 kPa³¹. These, shown in Table 4.1, were used with PROCESS to predict temperature-composition data at the desired pressure.

³¹ Keep in mind that activity coefficients are virtually insensitive to small pressure changes, especially at near atmospheric conditions.

Table 4.1: Wilson constants

A12	A21	Pressure
1136.075	302.9235	93.3 kPa

(The average error reported for the Wilson equation in DECHEMA for this case is 0.0122 for the composition in the vapour phase and 0.49 °C in temperature.)

The program and values generated are listed in appendix A.

5.4.2.2 GC Calibration

A GC analysis typically produces area percentages. These can be converted to mass or mol percentages using response factors³². Published response factors for ethanol and benzene are shown in table 4.2. One should keep in mind that these factors depend on the specific GC being used and the amounts injected. Where accuracies in excess of one or two digits are required, response factors must be measured.

Table 4.2

Published response factors	
Ethanol	0.46
Benzene	1.12

Mixtures containing 20.0 ml ethanol and 10.0 ml benzene were carefully made up and analyzed. (Absolute ethanol and 99.8%+ benzene were used). The average percentage ethanol was 43.490 % with an STD of 0.123.

³² Response factors are used to correct lower area percentages reported for non hydrocarbon components.

The response factors here are used in the following manner: Divide the areas (or area percentages) of the components by their respective factors. Normalize these values up to 1 or 100 to obtain mass fractions or percentages.

To determine better response factors, one factor was kept fixed at an arbitrary value (near a published one) while the other was modified so that the computed composition is equal to the actual one. The computed response factors are listed in table 4.3.

Table 4.3: Computed Response Factors

Ethanol	0.4740 (fixed)
Benzene	1.1057

The published factors result in a composition error of 1.5 %. Response factors should always be determined experimentally when accurate results are desired. One can even increase the accuracy further by determining factors at various ratios of the components.

5.4.2.3 Measurements

The run was initiated by using pure ethanol, just to verify temperature measurements. For every new point a small amount of benzene was added and the equipment given ample (4 hours+) time to reach equilibrium³³.

The measured values are presented in table 4.6 along with predicted values from the Wilson equation using the constants from DECHEMA (see appendix A).

³³ Ideally one would monitor the temperature and compositions continually and wait for them to stabilize. This is not always possible if the GC is used for other tasks as well.

Table 4.6: Measured versus DECHEMA interpolated data

Temperature (°C)		Liquid mass %	Vapour mass %	
DECHEMA	Measured		DECHEMA	Measured
66.5	65.1	0.0588	0.1863	0.1804
63.9	63.3	0.1492	0.2691	0.2578
63.2	62.7	0.2884	0.3197	0.3060
63.2	62.8	0.3641	0.3397	0.3211
63.2	63.1	0.3834	0.3448	0.3321
63.3	63.1	0.4223	0.3552	0.3442
63.5	63.1	0.4953	0.3765	0.3716
63.7	63.4	0.5298	0.3878	0.4122
63.8	63.6	0.5566	0.3974	0.4046
64.1	63.7	0.5919	0.4114	0.4088
67.2	67.3	0.8177	0.5690	0.5880
70.1	70.1	0.9186	0.7351	0.7592
71.0	71.7	0.9417	0.7928	0.8168
73.7	73.5	Absolute ethanol (1.0)		

5.4.2.4 Statistical comparison

The two figures below compare the measured values with ones from DECHEMA. Please note that the solid lines are constructed from the data in appendix A (representing "true" values) and are not regressed.

Comparison of compositions.

Measured versus calculated.

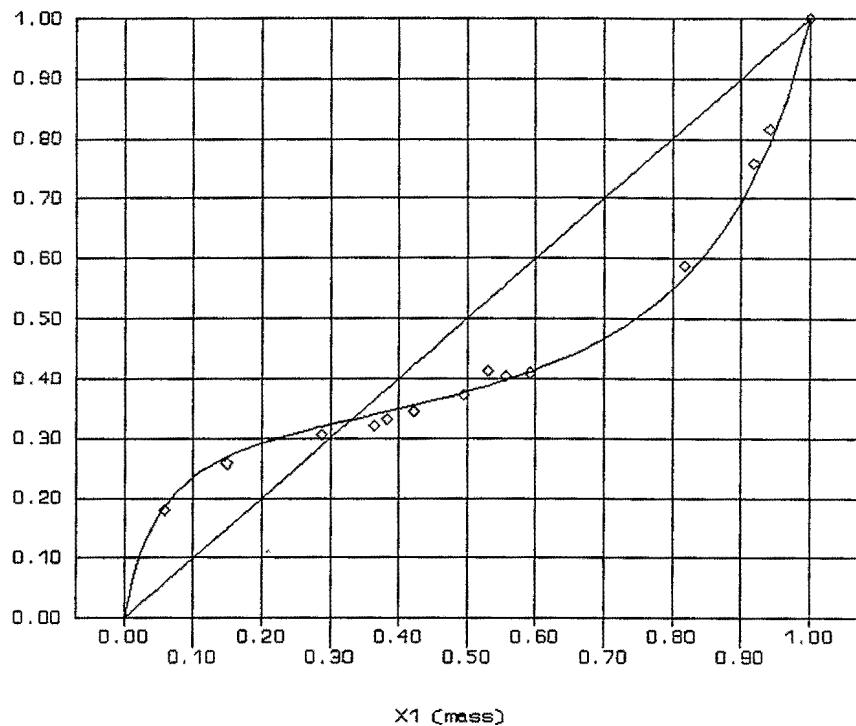


Figure 5.3: Ethanol - benzene XY (liquid and vapour mole fraction) diagram.

The average difference in vapour composition was 0.014^{34} with a standard deviation of 0.007. The average temperature error was 0.41°C with a standard deviation of 0.34.

One should now answer: How do these values compare?

To resolve this, a paired sample t test is used (see Miller, 1985:223,190).

Composition analysis

Null hypothesis:

³⁴ The average difference between the Wilson equation and the values used to determine the interaction parameters is 0.0122.

Comparison of temperatures.

Measured versus calculated.

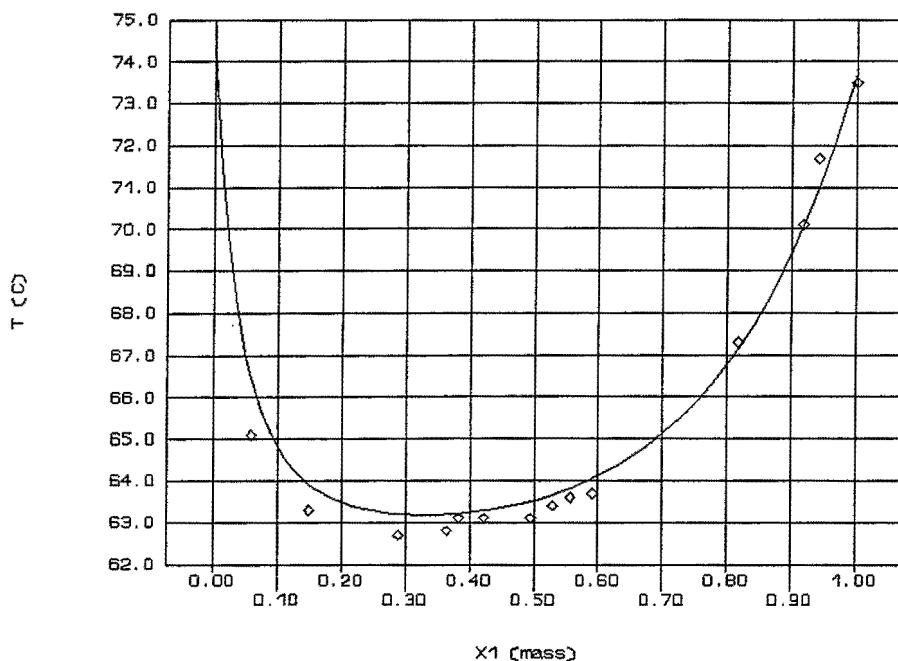


Figure 5.4: Ethanol benzene TX diagram.

The mean of the differences is zero: $\mu=0$ (ie the measured composition data is the same of that obtained from DECHEMA).

Alternative hypothesis:

$\mu>0$ (ie the measured data does not agree with DECHEMA).

Level of significance:

$$\alpha=0.005$$

Criterion:

Reject the null hypothesis if $t>3.055$, the value of $t(0.005)$ for $13-1=12$ degrees of freedom.

Calculations:

For the differences in compositions, the mean x is 0.00139 and the standard deviation s is 0.0156. Using the formula

$$t = \frac{\frac{x-\mu}{s}}{\sqrt{n}} \quad (5.65)$$

t can be computed to be 0.3227.

Decision:

It can be safely assumed that the compositions are the same. In fact, it is 99% sure that the difference is less than 0.0132 in mass fraction. This maximum error of estimate was computed from

$$E = t_{\frac{\alpha}{2}} \cdot \frac{s}{\sqrt{n}} \quad (5.66)$$

Temperature analysis

This analysis proceeds in a similar manner to the previous one except for numeric changes:

The mean for the differences in temperatures is $x=0.274^{35}$ and the standard deviation $s=0.455$. This gives $t=2.17$, which is below 3.055.

³⁵ The average difference between the Wilson equation and the values used to determine the interaction parameters is 0.49 °C.

It can thus be concluded with a 99.5% certainty that the temperatures are the same and with a 99% certainty that the errors obtained will be less than $E=0.372\text{ }^{\circ}\text{C}$ ³⁶.

Conclusion

The above comparison in actual fact compares the measured values to those predicted by Wilson. It must be noted that this model also contains errors. However, the values measured here agree well with those predicted from DECHEMA. The differences between these experimental values and the reproduced ones are about the same as the differences reported for the Wilson equation in DECHEMA. A closer look at the DECHEMA results indicate that the Wilson model tends to over predict the vapour composition slightly. The vapour compositions measured here are also slightly lower than the predicted values. This indicates that the values determined in this study probably agree better with the original values than the values above indicate.

The reproducibility is estimated to be around 99.8 %.

The statistical maximum errors reported may appear to indicate that the data contains larger errors than is actually the case. The values presented above also depend on the level of statistical certainty being used (99.5%). As the t values indicate, a higher level of certainty could surely have been proved, which would give considerably lower maximum errors.

Improvements in the temperature measurements could possibly be achieved by using a more robust instrument. As was noted by Prof. Raal (in conversation), the practice of putting a thermocouple tip into a glycol pit has been known to lead to small errors.

³⁶ The digital thermometer used during this series did start to give increasingly fluctuating readings and was replaced later on. The new instrument gives more stable readings and the temperature measurements given later on this work should be more accurate.

5.4.3 Operating recommendations

During the experimental work, the following notes were made:

- 1) The water pressure changes during the day. Adequate cooling water flow early in the morning may thus be insufficient later in the day.
- 2) The heating element must be properly sealed with the correct o rings otherwise leaks develop in a few hours.
- 3) Continuous stirring can be ensured by adjusting the rotation rate of the motors. If stirring stops in the condenser chamber, compositions may be negatively affected.
- 4) The digital thermometer must be calibrated and monitored to ensure accurate temperature readings.
- 5) Response factors must always be determined. The assumption that area % values are equal to mass % values is totally unacceptable.
- 6) In cases with large relative volatilities or heavier components, longer time is required for the still to reach equilibrium. The author feels that an absolute minimum of three hours after circulation started is required.³⁷
- 7) It was always found that if the still is allowed to operate for a long time it will stabilize with correct compositions and temperatures being analyzed irrespective of starting conditions or any upsets. This is not noted as a recommendation, but just as an interesting observation.

³⁷ Late note: This author has found that if the stills are given more time to circulate, the results are much smoother. In the experimental work which was later performed on the stills for this project, much longer times were used.

- 8) It does happen that the liquid chamber may reach a state of containing only a small fraction of the mixture initially deposited. Accurate values were found in all of these cases despite the liquid level being so low that the vapour no longer bubbles through it. Working under this condition is not advised.
- 9) It was found that, if the vapour flowing towards the condenser is heated to high, it will have a negative affect on the values measured. Temperatures in the vapour arm should not be higher than 10 degrees above the equilibrium temperature.