

33 Vapour Liquid Equilibrium

Aim

To determine the vapour-liquid equilibrium data for the given binary system. (A = more volatile component. B = less volatile component).

1. To check the thermodynamic consistency of the data.
2. To present the thermodynamic characteristics and constants of Margules equation for the given system.

Theory

Vapour-liquid equilibrium data are the basic information of the system required for the design of equilibrium stages of a vapour-liquid separation equipment like distillation. Equilibrium data represent the composition of the mixture in the vapour phase (Y) and that in the corresponding equilibrium liquid phase (X) at equilibrium. The compositions are presented in mole fractions of the more volatile component (A). Equilibrium compositions are functions of temperature and pressure. Therefore the data are reported under isothermal or isobaric conditions. However, isobaric data are required more often because industrial separations are carried out at constant pressure.

1. The vapour-liquid equilibrium data are presented as equilibrium compositions:

$$Y_A = \frac{P_A}{\pi_A} \gamma_A X_A = K_A X_A \quad (33.1)$$

2. Relative Volatility:

$$\alpha_{AB} = \frac{Y_A/(1 - Y_A)}{X_A/(1 - X_A)} \quad (33.2)$$

3. The Gibb's-Duhem equation for the binary system for checking thermodynamic consistency of the data by the integral test:

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2} dX_A = 0 \quad (33.3)$$

4. The Van Laar equations are

$$\log \gamma_A = \frac{a}{\left[1 + \frac{aX_A}{bX_B}\right]^2}; \quad \log \gamma_B = \frac{b}{\left[1 + \frac{bX_B}{aX_A}\right]^2} \quad (33.4)$$

Many systems form an azeotrope where the equilibrium vapour and liquid compositions are the same i.e. $Y_A = X_A$

Experimental setup

The apparatus shown in Figure 33.1 is known as a vapour-liquid equilibrium still and has two essential parts: (1) Vaporizer, (2) Flash chamber or Equilibrium chamber. The binary liquid mixture is vapourized by an electrical heating coil in the vaporizer at a slow rate. The vapour from this rises to the equilibrium chamber. Vapour and liquid equilibrium at the temperature and pressure

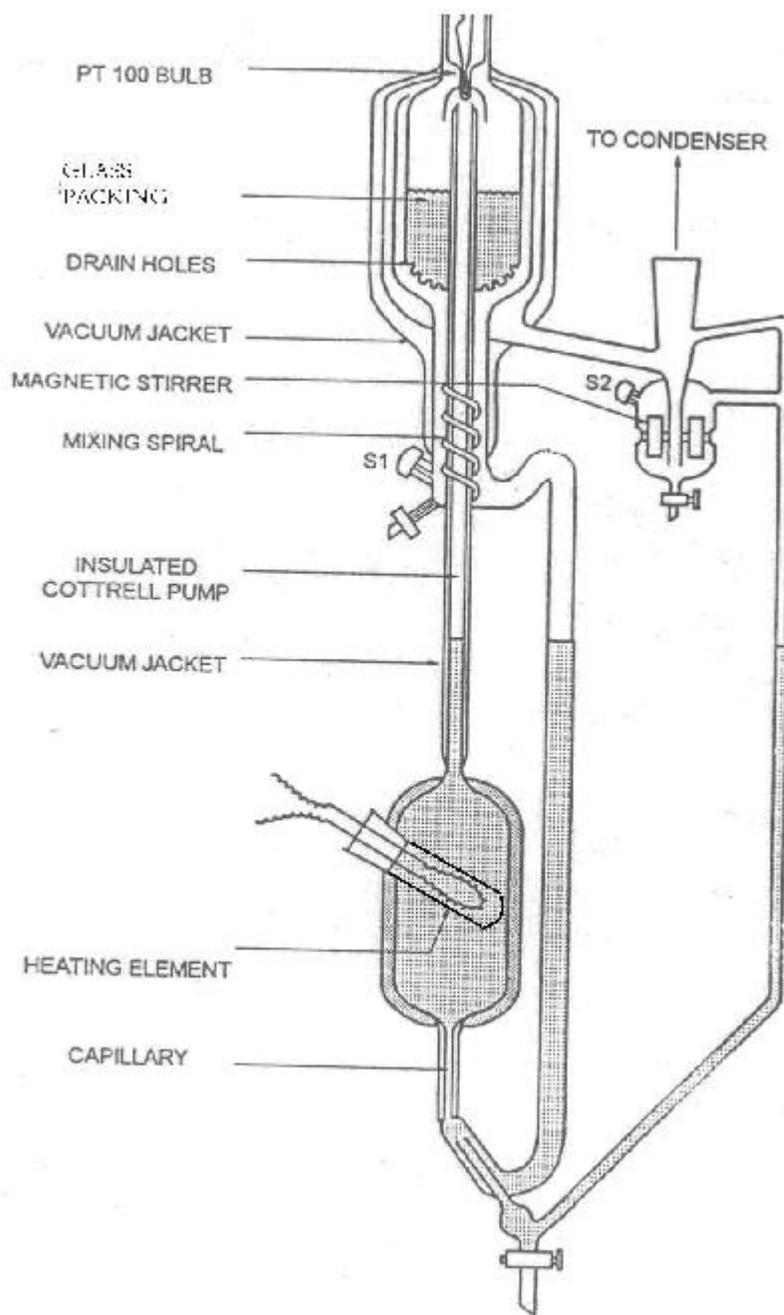


Figure 33.1: Schematic diagram of VLE setup

of the chamber is established. The temperature of the chamber is recorded by the thermometer which extends well inside the equilibrium chamber. The pressure of the chamber may be regulated by connecting the vapour line to vacuum or pressure header. The vapour and liquid phases separate from each other in the flash chamber. The liquid flows down the liquid line through a water cooled joint to the feeder line, through which the mixture again goes back to the vaporizer. The still may be drained through the feeder line and may be charged through either the vapour or the liquid line.

Procedure

1. Prepare a calibration chart of composition vs. refractive index (R.I.) or density, for the two pure components A and B and their mixtures with X_A varying from 0 to 1. Prepare the mixture of various compositions and determine the R.I. or density.
2. Prepare about 200 ml of mixture of A and B. The experiment should be started with the mixture richer in more volatile component (say 160 ml of A and 40 ml of B) so that in subsequent readings temperature increases. This mixture should be filled in the still through either of the limbs.
3. Check carefully that the electrical coil is completely submerged in the liquid (to avoid ignition) and the mixture is more than 2/3rd level in the vaporizer. Switch on the power and slowly increase the power input in slow steps. Heating should be regulated so that there is no entrainment or foaming of the mixture from vaporizer to the flash chamber.
4. The circulation of the vapour and liquid will soon get established. Allow the system to approach equilibrium. This will be indicated by constant temperature of the thermometer at least for five minutes.
5. Take the liquid and vapour samples and determine the refractive index (or density). Also record the temperature and from R.I. (or density), determine X_A and Y_A .
6. Drain out about 40 ml of mixture from the still and add about 40 ml of less volatile component. Repeat steps (1) to (5) and record the composition and temperature readings. Take at least six samples, covering whole range of compositions.

Observations & Results

1. More Volatile Component (A):
2. Less Volatile Component (B):
3. Properties of components (from literature/experimental)

Component	Density at 30°C	Molecular Weight	Boiling Point	R.I at 30°C
A				
B				

4. Report X_A and $R.I$ for the whole range as follows:

X_A									
$R.I.$									

5. Report $t - X - Y$ as follows:

$t, ^\circ\text{C}$									
X_A									
Y									

- Calculate K_A , γ_A and γ_B . Report in a data table the following: t , X , Y , γ_A , γ_B , $\ln(\gamma_A/\gamma_B)$, K_A .
- Plot $\ln \gamma_A$, $\ln \gamma_B$ (on the same graph) and $\ln(\gamma_A/\gamma_B)$ vs X_A (as another graph) and check for thermodynamic consistency. Find the difference in the positive and negative areas of $\ln(\gamma_A/\gamma_B)$ vs. X_A (should be less than 20% due to experimental error).
- Calculate the Van Laar constants a and b from

$$a = \log \gamma_A \left[1 + \frac{X_B \log \gamma_B}{X_A \log \gamma_A} \right]^2$$

$$b = \log \gamma_B \left[1 + \frac{X_A \log \gamma_A}{X_B \log \gamma_B} \right]^2$$

Comments