Vapour Absorption Refrigeration Systems Based On Ammonia- Water Pair

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The specific objectives of this lesson are to:

1. Introduce ammonia-water based vapour absorption refrigeration systems.
2. Discuss the properties of ammonia-water mixtures and introduce pressure temperature-concentration (p-T- ξ) and enthalpy-temperature-concentration (h-T- ξ) charts.
3. Analyze some basic steady flow processes using ammonia-water mixtures such as adiabatic and non-adiabatic mixing, throttling of solution streams and the concept of rectification.

1.1. Introduction

In vapour absorption refrigeration systems based on ammonia-water pair, ammonia is the refrigerant and water is the absorbent. These systems are more adaptable than systems based on water-lithium bromide as they can be utilized for both below zero (refrigeration) too over 0 ^{0}C (cooling) applications. On the other hand, these systems are more unpredictable in outline and operation because of the littler boiling point temperature difference between the refrigerant and absorbent (around 133^{0}C). Because of the littler boiling point temperature difference the vapour produced in the generator consists of both ammonia and additionally water. If water is allowed to circulate with ammonia in the refrigerant circuit, then:

i. Heat transfer in condenser and evaporator becomes non-isothermal
ii. Evaporator temperature increases
iii. Evaporation will not be complete
iv. Water may get accumulated in the evaporator leading to malfunctioning of the plant
iv. Circulation ratio increases

Since all the above effects are detrimental to the performance of the system, it is necessary to minimize the concentration of water vapour in ammonia at the inlet to the condenser. This requires additional components, namely a rectification column and a dephlegmator between generator and absorber, which increases the design complexity and cost and also reduces the system COP compared to water-lithium bromide system.

1.2. Properties of ammonia-water solutions
1.2.1. Composition

Similar to water-lithium bromide solutions, the composition of ammonia-water solution is also expressed either in mass fraction (ξ) or mole fraction (x). However, for ammonia-water solutions, the mass and mole fractions are defined in terms of ammonia. For example the mass fraction ξ is defined as the ratio of mass of ammonia to the total mass of solution, i.e.,

$$\xi = \frac{m_A}{m_A + m_W}$$

where m_A and m_W are the mass of ammonia and water in solution, respectively.

Similarly, the mole fraction of ammonia-water solution is defined as:

$$X = \frac{n_A}{n_A + n_W}$$

where n_A and n_W are the number of moles of ammonia and water in solution, respectively. The number of moles of ammonia and water can easily be obtained from their respective masses in solution and molecular weights, thus;

$$n_A = \frac{m_A}{M_A}; \text{ and } n_W = \frac{m_W}{M_W}$$

where M_A (= 17.0 kg/kmol) and M_W (= 18.0 kg/kmol) are the molecular weights of ammonia and water respectively.

1.2.2. Vapour pressure of ammonia-water solutions

Liquid ammonia and water are totally miscible in all proportions, henceforth can frame solutions of all concentrations from 0 to 1, at normal temperatures. The impact of ammonia in water is to bring down the vapour weight of water; comparatively the impact of water in ammonia is to bring down ammonia's vapour weight. Along these lines the aggregate weight over ammonia water solutions is comprised of incomplete weight of ammonia and fractional weight of water vapour, and is always in between the saturation pressures of unadulterated ammonia and water.

If Raoult's law is applied to ammonia-water mixtures, then the total pressure at any temperature, P_{total} is given by:

$$P_{total} = xP_A + (1- x)P_W$$

where x is the liquid phase mole fraction of ammonia, P_A and P_W are the saturation pressures of pure ammonia and pure water at that temperature. However, similar to water-lithium bromide solutions, ammonia-water solutions also deviate from ideal solution behaviour predicted by Raoult's law in a negative manner, i.e., at a given temperature of the solution the actual vapour pressure will be less than that predicted by Raoult's law (activity coefficient is much smaller than 1.0). For example, at a mass fraction of 0.4 and temperature of 40^0C, Raoult's law predicts a vapour pressure of 6.47 bar, whereas the measured vapour pressure is 3.029 bar. The vapour pressure data of ammonia-water solutions is also available in the form of Dühring and other P-T-ξ plots.

1.2.3. Composition of ammonia-water vapour

Since the vapour above ammonia-water fluid consists of both ammonia and water vapour, it is crucial to recognize the composition in fluid phase and composition in vapour phase. The superscripts L and V will be utilized to recognize fluid and vapour phase

compositions. Accordingly ξ^L remains for fluid phase mass fraction and ξ^V remains for vapour phase mass fraction. In spite of the fact that the vapour phase composition can be gotten by accepting perfect solution conduct, it is watched that the genuine vapour composition goes amiss from that anticipated by perfect mixture equations.

Based on test estimations, graphs have been created for getting composition of ammonia-water mixture in vapour phase in harmony with a solution of ammonia and water at diverse temperatures. Figure 1.1 shows the construction of such an outline utilizing which one can get the composition of mixture in vapour phase from known estimations of fluid phase mass fraction (ξ^L) and immersed temperature of unadulterated ammonia or pressure.
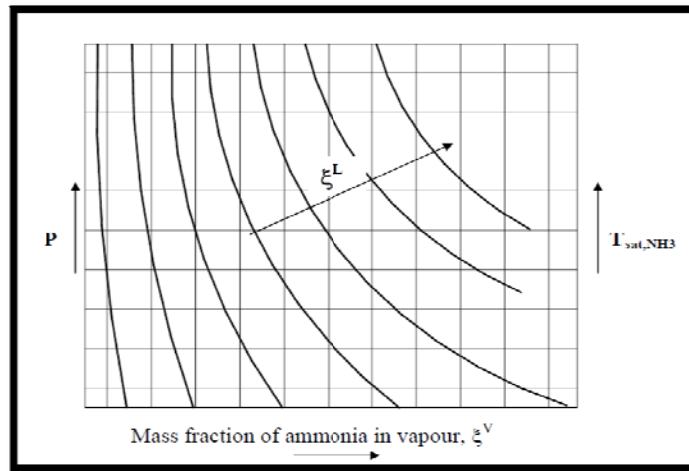

Fig.1.1. Vapour-liquid equilibrium chart for ammonia-water solution

1.2.4. Bubble point and dew point for ammonia-water mixtures

Figure 1.2 shows a barrel containing mixture of ammonia and water. The pressure on the mixture is kept up constant with the assistance of a free-gliding piston with fixed weights. At first (State 1) the barrel consists of sub cooled solution of ammonia water mixture. Presently warmth is supplied to the framework and the temperature of the solution is expanded consistently, the mass fraction of the solution stays constant at ξ^1 at first. At a certain temperature the first vapour bubble shows up. The temperature at which the first bubble shows up is called as bubble point ($=T_{bubble}$) of the solution at that concentration and pressure. Further warming results in increment in temperature and formation of more vapour as indicated in the figure (State 2).

On the off chance that warming is continued further, then the temperature increments continuously, as more fluid is converted into vapour, lastly at a specific temperature the last fluid droplet vaporizes. The temperature at which the last fluid droplet dissipates is called as dew point temperature (T_{dew}). At the point when warming is continued further the mixture goes into superheated vapour (State 3). It ought to be noticed that not at all like unadulterated liquids, the temperature of the ammonia-water mixture increments continuously as the fluid experiences vaporization. This is to say that the phase change methodology is described by a temperature coast, which is the difference between the dew point and bubble point temperatures. On the off chance that this procedure is rehashed with distinctive starting

concentrations beginning from 0 (unadulterated water) to 1 (immaculate ammonia) and at the same pressure, diverse estimations of bubble and dew points will be acquired.

Obviously when the concentration is 0 (unadulterated water) or 1 (immaculate ammonia) the bubble and dew points agree. Presently in the event that we plot the temperatures (bubble point and dew point) against concentration and join all the bubble points by a curve and all the dew points by another curve, then we would get the harmony Temperature versus concentration curve for ammonia-water mixtures at that pressure as demonstrated in Fig.1.3. The loci of all the bubble points are called as bubble point line and the loci of all the dew points are known as the dew point line. The bubble point line is the immersed fluid line and the dew point line is the soaked vapour line for the mixture at that pressure. The region between the bubble and dew point lines is the two phase region where both fluid and vapour coincide in balance. Distinctive bubble point and dew point lines will be gotten if the investigation is completed with diverse pressures.

For instance, Figure 1.4 shows the bubble and dew point lines for two separate pressures, P1 and P2. The same results can likewise be gotten if one begins the analysis at first with superheated vapour and after that begin cooling it. For this situation, the dew point is the temperature at which the first fluid droplet frames from the vapour and the bubble point is the temperature at which the last vapour bubble condenses.
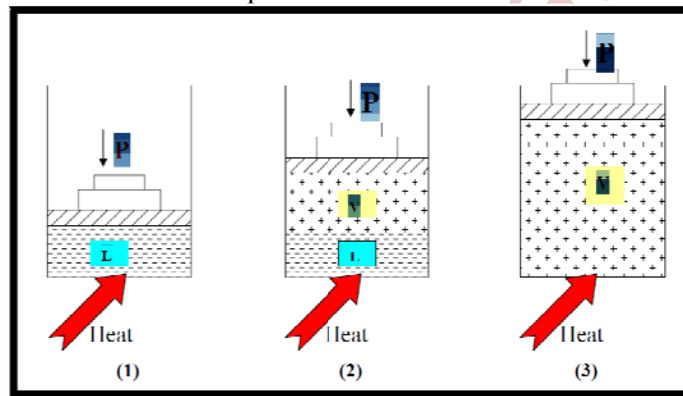

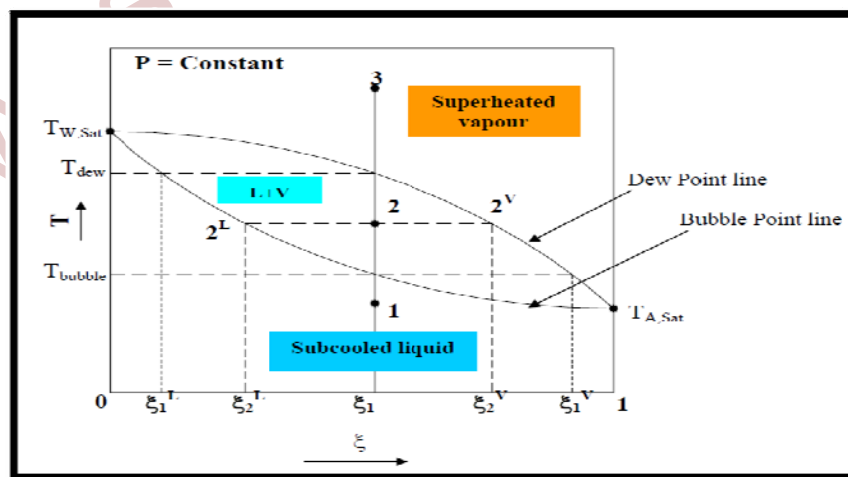**Fig.1.2**: A simple experiment illustrating the principle of bubble and dew points

Fig.1.3: Equilibrium temperature-concentration curve for NH_3-H_2O at a constant pressure
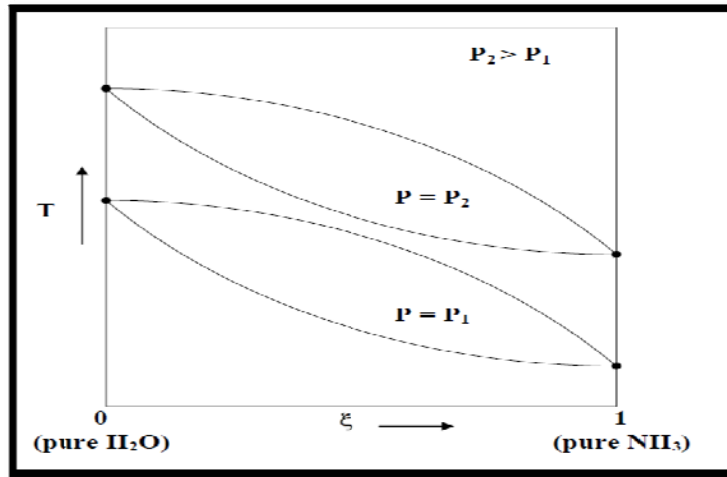
Fig.1.4: Bubble point and dew point curves at two different pressures

Now since the process is carried out in a closed system, the mass of both ammonia and water will be conserved. The concentration of sub cooled liquid will be same as the concentration of superheated vapour. However, in the two-phase region in which the saturated liquid exists in equilibrium with saturated vapour, the concentration of liquid and vapour will be different. For example, at point 2 in Fig.1.3, the temperature of saturated liquid and vapour will be same as they are in equilibrium, hence, the concentration of liquid will be ξ_2^L **(intersection of constant temperature line with bubble point line)** and that of vapour will be ξ_2^V **(intersection of constant temperature line with dew point line)** as shown in the figure.

Obviously the vapour formed initially will be richer in the low boiling point substance (ammonia) and the liquid remaining will be rich in high boiling point substance (water). For example, as shown in Fig.1.3, the concentration of the first vapour bubble will be ξ_1^V and the concentration of the last liquid droplet will be ξ_1^L. Since the total mass as well as mass of individual components is always conserved, we can write mass balance for total mass (m_{total}) and ammonia (m_A) mass at state 2 as:

$$m_{total} = m_2^L + m_2^V$$
$$m_A = \xi_2^L m_2^L + \xi_2^V m_2^V = \xi_1 m_{total}$$

where m_2^L and m_2^V are the mass of liquid and vapour at state 2, respectively.
From the above equations it can be easily shown that:

$$\frac{m_2^L}{m_2^V} = \left(\frac{\xi_2^V - \xi_1}{\xi_1 - \xi_2^L} \right), \text{ or}$$

$$m_2^L (\xi_1 - \xi_2^L) = m_2^V (\xi_2^V - \xi_1)$$

The above equation is called as the *mixing rule or lever rule* for the binary mixtures such as ammonia and water. It implies that the fraction of liquid and vapour in the two-phase mixture is inversely proportional to the distance between the mixture condition 2 and the saturated liquid and vapour states 2^L and 2^V, respectively.

1.2.5. Enthalpy of ammonia-water mixtures

Liquid phase:

The enthalpy of ammonia-water solution in liquid phase, h_L is calculated in a manner similar to that of water-lithium bromide solutions, i.e., by the equation:

$$h^L = \xi^L h_A^L + (1 - \xi^L) h_W^L + \Delta h_{mix}$$

Where ξ^L is the liquid phase mass fraction of ammonia, h_{AL} and h_{WL} are liquid phase enthalpies of pure ammonia and water respectively. Δh_{mix} is the heat of mixing, which is negative (exothermic) similar to water-lithium bromide mixtures. Using the above equation one can calculate the specific enthalpy of ammonia water solutions at any concentration and temperature provided the heat of mixing is known from measurements.

Thus enthalpy charts for solution are plotted as a field of isotherms against mass fraction by taking suitable reference values for enthalpy of ammonia and water. Since pressure does not have a significant effect on liquid enthalpy (except at critical point), normally pressure lines are not shown on typical solution enthalpy charts. Also **enthalpy of sub cooled liquid is generally assumed to be equal to the saturated enthalpy at that temperature without loss of much accuracy**.

Vapour phase:

Evaluation of enthalpy of a mixture of vapours of ammonia and water is more complicated compared to liquid phase enthalpy. This is due to the dependence of vapour enthalpy on both temperature and pressure. However, to simplify the problem, it is generally assumed that ammonia and water vapour mix without any heat of mixing. Then the enthalpy of the vapour mixture, h^V is given by:

$$h^V = \xi^V h_A^V + (1 - \xi^V) h_W^V$$

Where ξ^V is the vapour phase mass fraction of ammonia and the specific enthalpies of ammonia vapour and water vapour respectively at the temperature of the mixture. However, since vapour enthalpies depend on temperature as well as pressure, one has to evaluate the vapour enthalpy at suitable pressure, which is not equal to the total pressure. An approximate, but practically useful method is to evaluate the vapour enthalpies of ammonia and water at pressures, P_A and P_W given by

$$P_A = y P_{total}$$

$$P_W = (1 - y) P_{total}$$

where y is the vapour phase mole fraction of ammonia and P_{total} is the total pressure. It should be noted that P_A and P_W are equal to the partial pressures of ammonia and water only if they behave as ideal gases. However since ammonia and water vapour may not approach the ideal gas behaviour at all temperatures and pressures, in general P_A and P_W are not equal to the

partial pressures. Using these method enthalpies of ammonia-water mixtures in vapour phase have been obtained as functions of temperature and mass fraction.

1.2.6. The complete enthalpy-composition diagram for ammonia-water mixtures:

Normally, charts of enthalpy-temperature-mass fraction are available which give both liquid phase as well as vapour enthalpy of mixtures. Figure 1.5 shows one such chart. Figure 1.6 shows the enthalpy-synthesis diagram at a constant weight P. In the figure point **a** represents to the state of saturated liquid mixture at a temperature T with a liquid phase mass fraction of ξ^L. The liquid phase enthalpy corresponding to this condition is given by h L. The organization and enthalpy of vapour mixture in harmony with the liquid mixture at temperature T and weight P are obtained by drawing a vertical line from an up to the auxiliary line and then drawing a horizontal line to one side from the convergence of the vertical line with the auxiliary line.

The crossing point of this horizontal line with the dew point line a' gives the vapour phase mass fraction ξ^V and the vapour phase enthalpy h V as demonstrated in the figure. The isotherm T in the two-phase district is obtained by joining focuses on and an' as indicated in the figure. Point b in the figure lies in the two-phase district. The particular enthalpy of this point h b is given by:

$$h_b = (1 - \psi_b)h^L + \psi_b h^V$$

where ϕ_b is the quality or dryness fraction of the two-phase mixture at b. Since points a, a' and b are co-linear, the dryness fraction ϕ_b is given by:

$$\psi_b = \frac{\xi_b - \xi^L}{\xi^V - \xi^L}$$

In actual enthalpy-composition diagrams the isotherms are not shown in two-phase region as a different set of them exist for each pressure. It is important to note that it is not possible to fix the state of the mixture (sub cooled, saturated, two-phase or superheated) just from temperature and mass fraction alone, though one can calculate enthalpy of the mixture from temperature and mass fraction. This is due to the reason that at a given mass fraction and temperature, depending upon the pressure the point can be sub cooled or saturated or superheated. For example, a liquid mixture with a mass fraction of 0.4 and temperature of 80_oC has an enthalpy of 210 kJ/kg, and it will be in sub cooled condition if the pressure is 4.29 bar and saturated if the pressure is 8.75 bar.
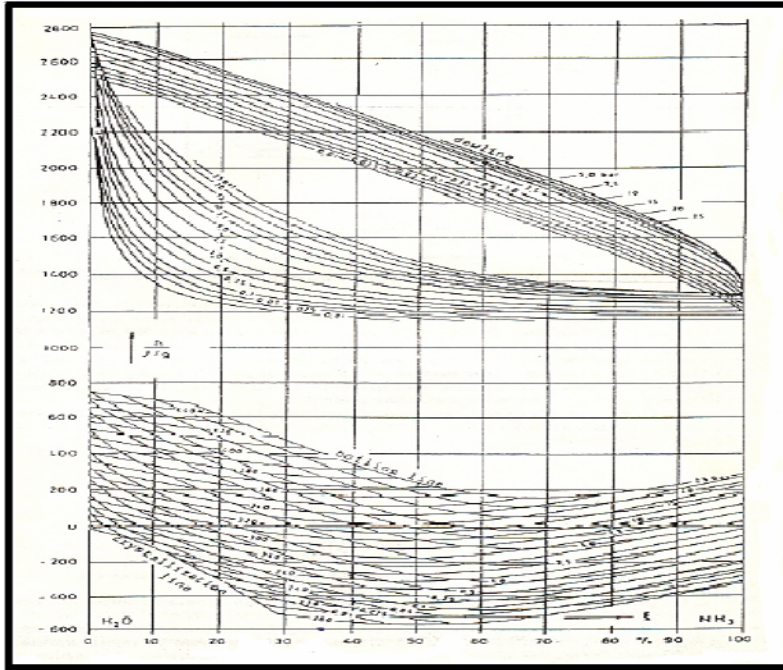
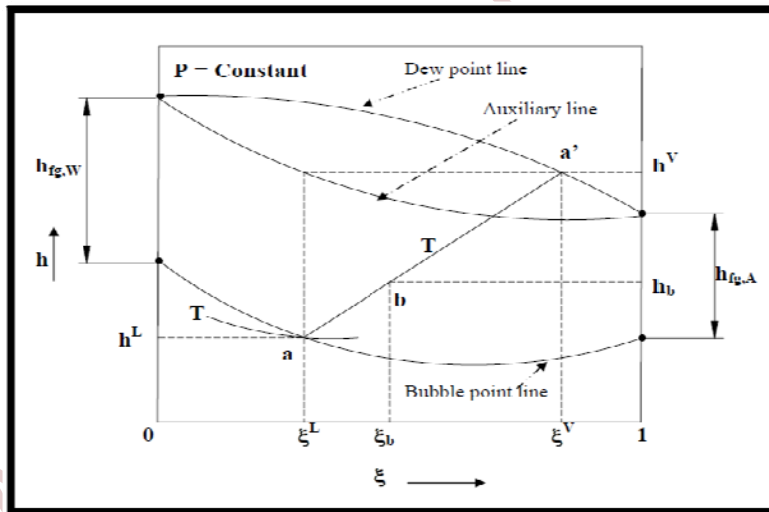**Fig.1.5**: h-T- ξ chart for ammonia-water solution

Fig.1.6: Enthalpy-composition diagram of NH₃-H₂O at a constant pressure P

Determination of temperature of mixture in two-phase region:

A trial-and-error system has to be utilized to focus the temperature of a point in two-phase district in the event that its enthalpy, liquid phase mass fraction and weight are known. The trial-and-error strategy can be graphical or numerical. Figure 1.7 shows a graphical system for finding the temperature of point x in the two-phase region which is at a known weight Px, liquid phase mass fraction ξx and enthalpy hx. To start with, point an' is obtained as demonstrated in the figure by drawing a vertical line from point x up to the auxiliary line and then drawing a horizontal line from the convergence point an" up to the dew point line,

the convergence of which gives a'. Then a straight line a'-x-an is drawn as demonstrated. Next point b' is obtained by drawing a vertical line up to the auxiliary line and then drawing a horizontal line from b'' up to the dew point line to get b'. Then line b'-x-b is drawn passing through x. This procedure is repeated until meeting is obtained. Numerically the temperature can be obtained from the equation, which needs to be satisfied for each end of the isotherm passing through x, i.e.,

$$\frac{h^V - h_x}{\xi^V - \xi_x} = \frac{h_x - h^L}{\xi_x - \xi^L}$$

To start with guess values of h^L and ξ^L are assumed by taking some point on the bubble point line. Then saturated vapour properties h^V and ξ^V are obtained from the enthalpy composition charts using the guess values of h^L and ξ^L. Then using the above equation, new values of h^L and ξ^L are obtained. Then these new values are used to obtain next set of h^V and ξ^V. This procedure is repeated till the values converge. Once the converged values of h^L and ξ^L are obtained then the temperature is read from the enthalpy composition chart.
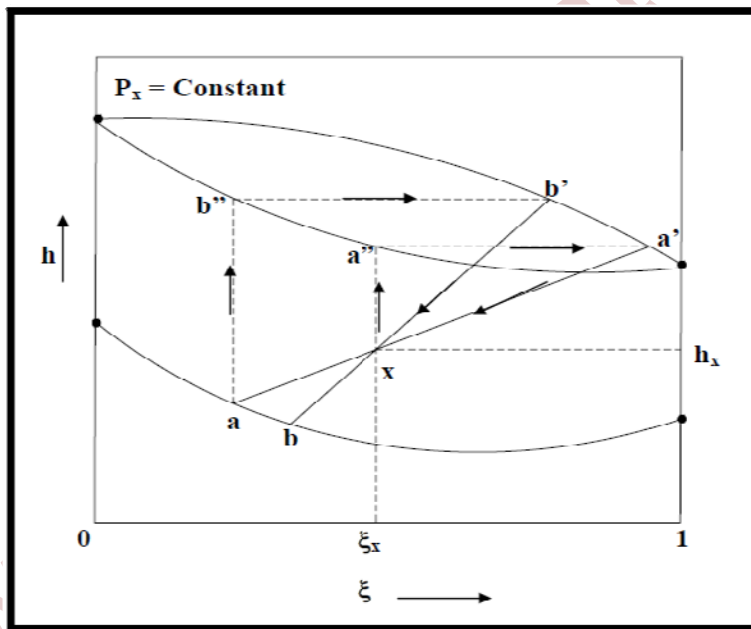

Fig.1.7: A graphical method for finding temperature of liquid-vapour mixture

1.3 Basic steady-flow processes with binary mixtures

a)Adiabatic mixing of two streams: When two streams of ammonia-water solutions are mixed adiabatically as shown in Fig.1.8, one can write mass and energy balance equations as:

$$m_1 + m_2 = m_3$$
$$m_1\xi_1 + m_2\xi_2 = m_3\xi_3$$
$$m_1h_1 + m_2h_2 = m_3h_3$$

From the above equations, the mass fraction and enthalpy of the mixture at 3 are given by:

$$\xi_3 = \xi_1 + \frac{m_2}{m_3}(\xi_2 - \xi_1)$$
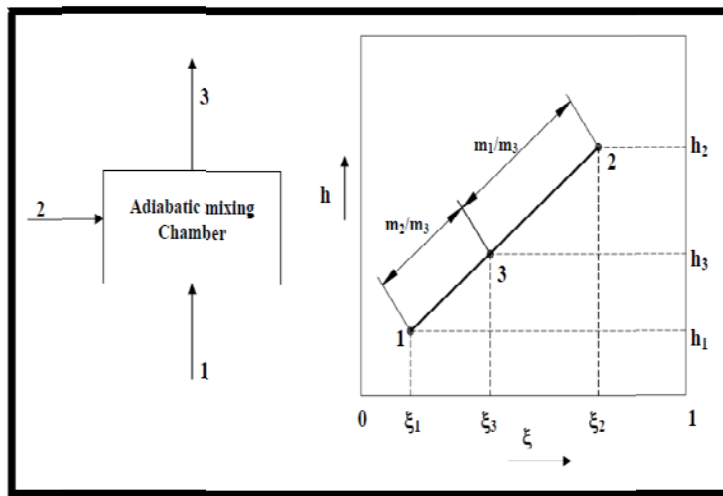
$$h_3 = h_1 + \frac{m_2}{m_3}(h_2 - h_1)$$

Fig.1.8: Adiabatic mixing of two solution streams

Figure 1.9 shows the adiabatic mixing process with the mixture state 3 lying in two phase region on the enthalpy-composition diagram. The mixture state in two-phase region implies that some vaporization has occurred during adiabatic mixing of the two inlet streams 1 and 2. The enthalpy and composition of the two-phase mixture at 3 can be obtained by using the equations given above. However, since this is in two-phase region, the mixture consists of saturated liquid and vapour. The dryness fraction and temperature of the mixture (T_3) have to be obtained by trial-and-error method by applying mixing rules. The fraction of the vapour in the mixture at 3 is then given by:

$$\frac{m_3^V}{m_3} = \frac{\xi_3 - \xi_3^L}{\xi_3^V - \xi_3^L} = \frac{\overline{3\,3L}}{\overline{3V\,3L}}$$

b) Mixing of two streams with heat transfer: The process of mixing of two streams with heat transfer takes place in absorber and generator of absorption refrigeration systems. For example, Fig.1.10 shows the mixing of saturated refrigerant vapour (state 1) with saturated solution of refrigerant-absorbent (state 2) in the absorber. The resulting mixture is a solution that is rich in refrigerant (state 3). Since the process is exothermic, heat (Q) is

released during this process. Mass and energy balance equations for this process can be written as:
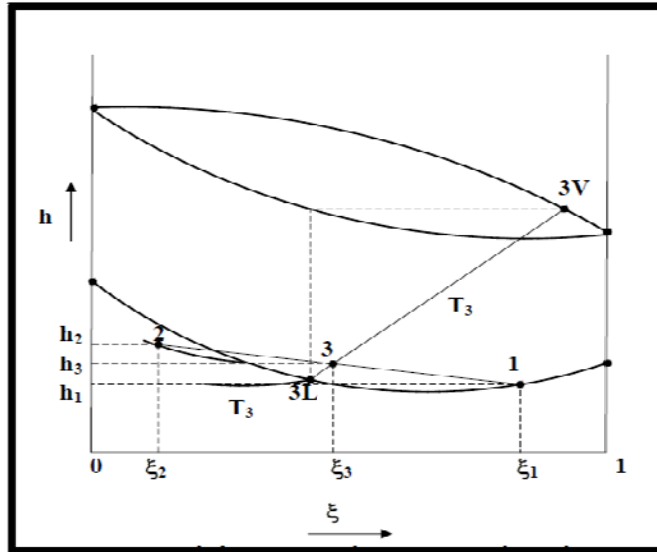

Fig.1.9: Adiabatic mixing of two streams on h-T-ξ diagram

$$m_1 + m_2 = m_3$$
$$m_1\xi_1 + m_2\xi_2 = m_3\xi_3$$
$$m_1h_1 + m_2h_2 = m_3h_3 + Q$$

From the above equations, the enthalpy of the mixture at 3 is given by:

$$h_3 = h_1 + \frac{m_2}{m_3}(h_2 - h_1) - \frac{Q}{m_3}$$

Thus with heat transfer from the mixing chamber, the exit state lies at a vertical distance of (Q/m_3) below the state which would result without heat transfer (point 3').The exit point would lie above the state without heat transfer if heat is transferred to the mixing chamber.

c) Throttling process: Throttling or isenthalpic expansion of ammonia-water solution takes place in the solution expansion valve of the absorption refrigeration system. Figure 1.11 shows the throttling process on enthalpy-composition diagram. Since both mass and energy are conserved during this process, and there is neither work nor heat transfer, we obtain:

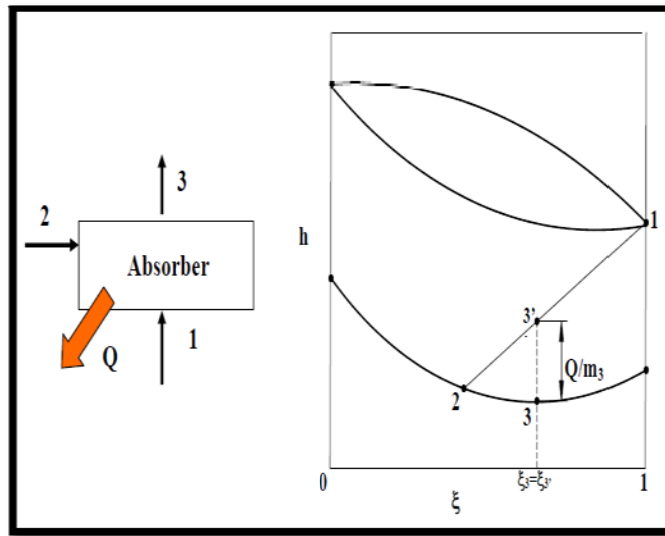$$\xi_1 = \xi_2$$
$$h_1 = h_2$$

Fig.1.10: Mixing of two streams with heat transfer

Hence the inlet and outlet states, points 1 and 2 are identical on enthalpy-composition diagram as shown in the figure. However, as there is possibility of vapour generation due to flashing, the exit condition may be a mixture of saturated liquid and vapour at the outlet pressure P_2 then the exit temperature T_2 will be much lower than the inlet temperature T_1. Taking point 2 as in the two-phase region corresponding to the outlet pressure P_2, one can get the vapour fraction and exit temperature T_2 by trial-and-error method as discussed earlier.
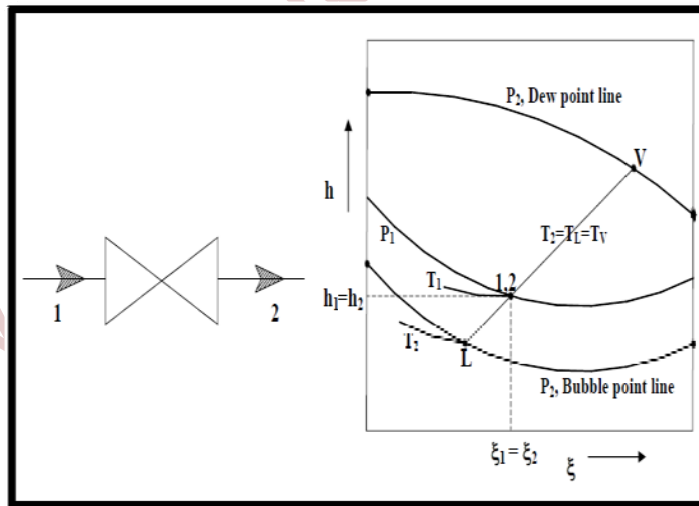

Fig.1.11: Throttling of ammonia-water solution

d) Heating and cooling process–Concept of rectification: Figure 1.12 shows an arrangement wherein an initially sub cooled solution (state 1) is heated in a heat exchanger A (HX A) in such a way that the exit condition 2 lies in the two-phase region. This two-phase mixture then flows into an adiabatic separator (SEP A) where the saturated liquid (state 3)

and saturated vapour (state 4) are separated. The saturated vapour at state 4 is then cooled to state 5 in another heat exchanger B (HX B) by rejecting heat $_4Q_5$. The resulting two-phase mixture is then fed to another adiabatic separator B (SEP B), where again the saturated liquid (state 6) and saturated vapour (state 7) are separated. It is assumed that the entire process takes place at a constant pressure and is a steady-flow process.
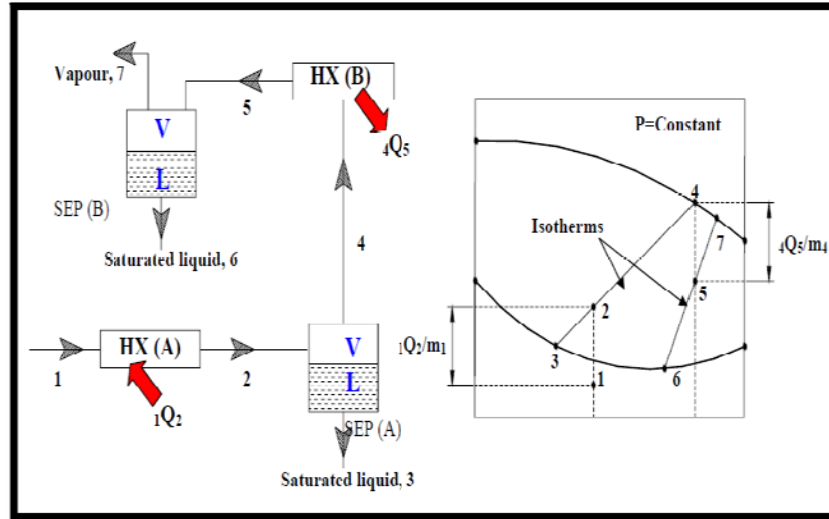

Fig.1.12: Heating and cooling of NH₃-H₂O solution – concept of rectification

Now mass and energy balances are applied to each of the components as shown below:

Heat exchanger A:

Mass balance:

$$m_1 = m_2$$
$$\xi_1 = \xi_2$$

Energy balance:

$$_1Q_2 = m_1(h_2 - h_1)$$

Separator A:

Mass balance:

$$m_2 = m_3 + m_4$$

$$m_2\xi_2 = m_3\xi_3 + m_4\xi_4$$

Energy balance:

$$m_2 h_2 = m_3 h_3 + m_4 h_4$$

from the above equations:

$$\frac{m_3}{m_2} = \frac{\xi_4 - \xi_2}{\xi_4 - \xi_3} = \frac{h_4 - h_2}{h_4 - h_3} = \frac{\text{length } 4 - 2}{\text{length } 4 - 3}$$

$$\frac{m_4}{m_2} = \frac{\xi_2 - \xi_3}{\xi_4 - \xi_3} = \frac{h_2 - h_3}{h_4 - h_3} = \frac{\text{length } 2 - 3}{\text{length } 4 - 3}$$

Similar equations can be obtained for heat exchanger B and separator B. The entire process is also shown on enthalpy-composition diagram in Fig.1.12.

It may be noticed that from the above arrangement comprising of heating, cooling and separation, one finally obtains a vapour at state 7 that is rich in ammonia. That is the combination of heat exchangers with separators is equivalent to the methodology of rectification. Heat exchanger A plays the part of generator, while heat exchanger B plays the part of dephlegmator. To enhance the procedure of rectification in actual vapour absorption refrigeration frameworks, a rectifying column is presented between the generator and dephlegmator. In the rectifying column, the vapour from the separator an interacts with the saturated liquid originating from separator B.

Therefore, there will be heat and mass transfer between the vapour and liquid and finally the vapour turns out at a much higher concentration of ammonia. The practical ammonia-water based vapour absorption refrigeration framework incorporating rectifying column.