## Lesson 14

## Vapour Absorption Refrigeration Systems

## The objectives of this lesson are to:

1. Introduce vapour absorption refrigeration systems (Section 14.1)
2. Explain the basic principle of a vapour absorption refrigeration system (Section 14.2)
3. Compare vapour compression refrigeration systems with continuous vapour absorption refrigeration systems (Section 14.2)
4. Obtain expression for maximum COP of ideal absorption refrigeration system (Section 14.3)
5. Discuss properties of ideal and real refrigerant-absorbent mixtures (Section 14.4)
6. Describe a single stage vapour absorption refrigeration system with solution heat exchanger (Section 14.5)
7. Discuss the desirable properties of refrigerant-absorbent pairs for vapour absorption refrigeration systems and list the commonly used working fluids (Section 14.6)

At the end of the lecture, the student should be able to:

1. List salient features of vapour absorption refrigeration systems and compare them with vapour compression refrigeration systems
2. Explain the basic principle of absorption refrigeration systems and describe intermittent and continuous vapour absorption refrigeration systems
3. Find the maximum possible COP of vapour absorption refrigeration systems
4. Explain the differences between ideal and real mixtures using pressurecomposition and enthalpy-composition diagrams
5. Draw the schematic of a complete, single stage vapour absorption refrigeration system and explain the function of solution heat exchanger
6. List the desirable properties of working fluids for absorption refrigeration systems and list some commonly used fluid pairs

### 14.1. Introduction

Vapour Absorption Refrigeration Systems (VARS) belong to the class of vapour cycles similar to vapour compression refrigeration systems. However, unlike vapour compression refrigeration systems, the required input to absorption systems is in the form of heat. Hence these systems are also called as heat operated or thermal energy driven systems. Since conventional absorption systems use liquids for absorption of refrigerant, these are also sometimes called as wet absorption systems. Similar to vapour compression refrigeration systems, vapour absorption refrigeration systems have also been commercialized and are widely used in various refrigeration and air conditioning applications. Since these systems run on low-grade thermal energy, they are preferred when low-grade energy such as waste heat or solar energy is available. Since conventional absorption systems use natural refrigerants such as water or ammonia they are environment friendly.

In this lesson, the basic working principle of absorption systems, the maximum COP of ideal absorption refrigeration systems, basics of properties of mixtures and simple absorption refrigeration systems will be discussed.

### 14.2. Basic principle

When a solute such as lithium bromide salt is dissolved in a solvent such as water, the boiling point of the solvent (water) is elevated. On the other hand, if the temperature of the solution (solvent + solute) is held constant, then the effect of dissolving the solute is to reduce the vapour pressure of the solvent below that of the saturation pressure of pure solvent at that temperature. If the solute itself has some vapour pressure (i.e., volatile solute) then the total pressure exerted over the solution is the sum total of the partial pressures of solute and solvent. If the solute is nonvolatile (e.g. lithium bromide salt) or if the boiling point difference between the solution and solvent is large ( $\geq 300^{\circ} \mathrm{C}$ ), then the total pressure exerted over the solution will be almost equal to the vapour pressure of the solvent only. In the simplest absorption refrigeration system, refrigeration is obtained by connecting two vessels, with one vessel containing pure solvent and the other containing a solution. Since the pressure is almost equal in both the vessels at equilibrium, the temperature of the solution will be higher than that of the pure solvent. This means that if the solution is at ambient temperature, then the pure solvent will be at a temperature lower than the ambient. Hence refrigeration effect is produced at the vessel containing pure solvent due to this temperature difference. The solvent evaporates due to heat transfer from the surroundings, flows to the vessel containing solution and is absorbed by the solution. This process is continued as long as the composition and temperature of the solution are maintained and liquid solvent is available in the container.

For example, Fig.14.1 shows an arrangement, which consists of two vessels A and B connected to each other through a connecting pipe and a valve. Vessel A is filled with pure water, while vessel B is filled with a solution containing on mass basis 50 percent of water and 50 percent lithium bromide ( LiBr salt). Initially the valve connecting these two vessels is closed, and both vessels are at thermal equilibrium with the surroundings, which is at $30^{\circ} \mathrm{C}$. At $30^{\circ} \mathrm{C}$, the saturation pressure of water is 4.24 kPa , and the equilibrium vapour pressure of water-lithium bromide solution ( $50: 50$ by mass) at $30^{\circ} \mathrm{C}$ is 1.22 kPa .


Fig.14.1: Basic principle of vapour absorption systems
Thus at initial equilibrium condition, the pressure in vessel A is 4.24 kPa , while it is 1.22 kPa in vessel B . Now the valve between vessels A and B is opened. Initially due to pressure difference water vapour will flow from vessel A to vessel B, and this vapour will be absorbed by the solution in vessel B. Since absorption in this case is exothermic, heat will be released in vessel B. Now suppose by some means the concentration and temperature of vessel B are maintained constant at $50 \%$ and $30^{\circ} \mathrm{C}$, respectively. Then at equilibrium, the pressure in the entire system (vessels A and B) will be 1.22 kPa (equilibrium pressure of $50 \% \mathrm{LiBr}$ solution at $30^{\circ} \mathrm{C}$ ). The
temperature of water in vessel A will be the saturation temperature corresponding to 1.22 kPa , which is equal to about $10^{\circ} \mathrm{C}$, as shown in the figure. Since the water temperature in $A$ is lower than the surroundings, a refrigeration effect $\left(\mathrm{Q}_{\mathrm{e}}\right)$ can produced by transferring heat from the surroundings to water at $10^{\circ} \mathrm{C}$. Due to this heat transfer, water vaporizes in A, flows to B and is absorbed by the solution in B. The exothermic heat of absorption $\left(\mathrm{Q}_{\mathrm{a}}\right)$ is rejected to the surroundings.

Now for the above process to continue, there should always be pure water in vessel A, and vessel B must be maintained always at 50 percent concentration and $30^{\circ} \mathrm{C}$. This is not possible in a closed system such as the one shown in Fig.14.1. In a closed system with finite sized reservoirs, gradually the amount of water in A decreases and the solution in B becomes diluted with water. As a result, the system pressure and temperature of water in A increase with time. Hence the refrigeration effect at A reduces gradually due to the reduced temperature difference between the surroundings and water. Thus refrigeration produced by systems using only two vessels is intermittent in nature. In these systems, after a period, the refrigeration process has to be stopped and both the vessels $A$ and $B$ have to be brought back to their original condition. This requires removal of water absorbed in B and adding it back to vessel A in liquid form, i.e., a process of regeneration as shown in Fig.14.1(c).

Assume that before regeneration is carried out, the valve between A and B is closed and both $A$ and $B$ are brought in thermal equilibrium with the surroundings $\left(30^{\circ} \mathrm{C}\right)$, then during the regeneration process, heat at high temperature $\mathrm{T}_{\mathrm{g}}$ is supplied to the dilute LiBr solution in B , as a result water vapour is generated in $B$. The vapour generated in B is condensed into pure water in A by rejecting heat of condensation to the surroundings. This process has to be continued till all the water absorbed during the refrigeration process (14.1(b)) is transferred back to A. Then to bring the system back to its original condition, the valve has to be closed and solution in vessel B has to be cooled to $30^{\circ} \mathrm{C}$. If we assume a steady-flow process of regeneration and neglect temperature difference for heat transfer, then the temperature of water in A will be $30^{\circ} \mathrm{C}$ and pressure inside the system will be 4.24 kPa . Then the temperature in vessel $\mathrm{B}, \mathrm{T}_{\mathrm{g}}$ depends on the concentration of solution in B . The amount of heat transferred during refrigeration and regeneration depends on the properties of solution and the operating conditions. It can be seen that the output from this system is the refrigeration obtained $\mathrm{Q}_{\mathrm{e}}$ and the input is heat supplied to vessel B during vapour regeneration process, $\mathrm{Q}_{\mathrm{g}}$.

The system described may be called as an Intermittent Absorption Refrigeration System. The solvent is the refrigerant and the solute is called as absorbent. These simple systems can be used to provide refrigeration using renewable energy such as solar energy in remote and rural areas. As already explained, these systems provided refrigeration intermittently, if solar energy is used for regenerating the refrigerant, then regeneration process can be carried out during the day and refrigeration can be produced during the night.

Though the intermittent absorption refrigeration systems discussed above are simple in design and inexpensive, they are not useful in applications that require continuous refrigeration. Continuous refrigeration can be obtained by having a modified system with two pairs of vessels A and B and additional expansion valves and a solution pump.


Figs.14.2: a) Vapour compression refrigeration system (VCRS)
b) Vapour Absorption Refrigeration System (VARS)

Figure 14.2(a) and (b) show a continuous output vapour compression refrigeration system and a continuous output vapour absorption refrigeration system. As shown in the figure in a continuous absorption system, low temperature and low pressure refrigerant with low quality enters the evaporator and vaporizes by producing useful refrigeration $\mathrm{Q}_{\mathrm{e}}$. From the evaporator, the low temperature, low pressure refrigerant vapour enters the absorber where it comes in contact with a solution that is weak in refrigerant. The weak solution absorbs the refrigerant and becomes strong in refrigerant. The heat of absorption is rejected to the external heat sink at $T_{0}$. The solution that is now rich in refrigerant is pumped to high pressure using a solution pump and fed to the generator. In the generator heat at high temperature $\mathrm{T}_{\mathrm{g}}$ is supplied, as a result refrigerant vapour is generated at high pressure. This high pressure vapour is then condensed in the condenser by rejecting heat of condensation to the external heat sink at $\mathrm{T}_{0}$. The condensed refrigerant liquid is then throttled in the expansion device and is then fed to the evaporator to complete the refrigerant cycle. On the solution side, the hot, high-pressure solution that is weak in refrigerant is throttled to the absorber pressure in the solution expansion valve and fed to the absorber where it comes in contact with the refrigerant vapour from evaporator. Thus continuous refrigeration is produced at evaporator, while heat at high temperature is continuously supplied to the generator. Heat rejection to the external heat sink takes place at absorber and condenser. A small amount of mechanical energy is required to run the solution pump. If we neglect pressure drops, then the absorption system operates between the condenser and evaporator pressures. Pressure in absorber is same as the pressure in evaporator and pressure in generator is same as the pressure in condenser.

It can be seen from Fig.14.2, that as far as the condenser, expansion valve and evaporators are concerned both compression and absorption systems are identical. However, the difference lies in the way the refrigerant is compressed to condenser pressure. In vapour compression refrigeration systems the vapour is compressed mechanically using the compressor, where as in absorption system the vapour is first
converted into a liquid and then the liquid is pumped to condenser pressure using the solution pump. Since for the same pressure difference, work input required to pump a liquid (solution) is much less than the work required for compressing a vapour due to very small specific volume of liquid ( $\mathrm{w}=-\int_{\mathrm{Pe}}^{\mathrm{Pc}} \mathrm{v}$.dP ), the mechanical energy required to operate vapour absorption refrigeration system is much less than that required to operate a compression system. However, the absorption system requires a relatively large amount of low-grade thermal energy at generator temperature to generate refrigerant vapour from the solution in generator. Thus while the energy input is in the form of mechanical energy in vapour compression refrigeration systems, it is mainly in the form of thermal energy in case of absorption systems. The solution pump work is often negligible compared to the generator heat input. Thus the COPs for compression and absorption systems are given by:

$$
\begin{align*}
& \mathrm{COP}_{\mathrm{VCRS}}=\frac{\mathrm{Q}_{\mathrm{e}}}{\mathrm{~W}_{\mathrm{c}}}  \tag{14.1}\\
& \mathrm{COP}_{\mathrm{VARS}}=\frac{\mathrm{Q}_{\mathrm{e}}}{\mathrm{Q}_{\mathrm{g}}+\mathrm{W}_{\mathrm{p}}} \approx \frac{\mathrm{Q}_{\mathrm{e}}}{\mathrm{Q}_{\mathrm{g}}} \tag{14.2}
\end{align*}
$$

Thus absorption systems are advantageous where a large quantity of low-grade thermal energy is available freely at required temperature. However, it will be seen that for the refrigeration and heat rejection temperatures, the COP of vapour compression refrigeration system will be much higher than the COP of an absorption system as a high grade mechanical energy is used in the former, while a low-grade thermal energy is used in the latter. However, comparing these systems based on COPs is not fully justified, as mechanical energy is more expensive than thermal energy. Hence, sometimes the second law (or exergetic) efficiency is used to compare different refrigeration systems. It is seen that the second law (or exergetic) efficiency of absorption system is of the same order as that of a compression system.

### 14.3. Maximum COP of ideal absorption refrigeration system

In case of a single stage compression refrigeration system operating between constant evaporator and condenser temperatures, the maximum possible COP is given by Carnot COP:

$$
\begin{equation*}
\mathrm{COP}_{\text {Carnot }}=\frac{\mathrm{T}_{\mathrm{e}}}{\mathrm{~T}_{\mathrm{c}}-\mathrm{T}_{\mathrm{e}}} \tag{14.3}
\end{equation*}
$$

If we assume that heat rejection at the absorber and condenser takes place at same external heat sink temperature $T_{0}$, then a vapour absorption refrigeration system operates between three temperature levels, $\mathrm{T}_{\mathrm{g}}, \mathrm{T}_{\mathrm{o}}$ and $\mathrm{T}_{\mathrm{e}}$. The maximum possible COP of a refrigeration system operating between three temperature levels can be obtained by applying first and second laws of thermodynamics to the system. Figure 14.3 shows the various energy transfers and the corresponding temperatures in an absorption refrigeration system.


Fig.14.3: Various energy transfers in a vapour absorption refrigeration system

From first law of thermodynamics,

$$
\begin{equation*}
\mathrm{Q}_{\mathrm{e}}+\mathrm{Q}_{\mathrm{g}}-\mathrm{Q}_{\mathrm{c}+\mathrm{a}}+\mathrm{W}_{\mathrm{p}}=0 \tag{14.4}
\end{equation*}
$$

where $\mathrm{Q}_{\mathrm{e}}$ is the heat transferred to the absorption system at evaporator temperature $\mathrm{T}_{\mathrm{e}}$, $\mathrm{Q}_{\mathrm{g}}$ is the heat transferred to the generator of the absorption system at temperature $\mathrm{T}_{\mathrm{g}}$, $\mathrm{Q}_{\mathrm{a}+\mathrm{c}}$ is the heat transferred from the absorber and condenser of the absorption system at temperature $T_{o}$ and $W_{p}$ is the work input to the solution pump.

From second law of thermodynamics,

$$
\begin{equation*}
\Delta \mathrm{S}_{\text {total }}=\Delta \mathrm{S}_{\text {sys }}+\Delta \mathrm{S}_{\text {surr }} \geq 0 \tag{14.5}
\end{equation*}
$$

where $\Delta \mathrm{S}_{\text {total }}$ is the total entropy change which is equal to the sum of entropy change of the system $\Delta \mathrm{S}_{\text {sys }}$ and entropy change of the surroundings $\Delta \mathrm{S}_{\text {surr }}$. Since the refrigeration system operates in a closed cycle, the entropy change of the working fluid of the system undergoing the cycle is zero, i.e., $\Delta \mathrm{S}_{\text {sys }}=0$. The entropy change of the surroundings is given by:

$$
\begin{equation*}
\Delta S_{\text {surr }}=-\frac{Q_{e}}{T_{e}}-\frac{Q_{g}}{T_{g}}+\frac{Q_{a+c}}{T_{o}} \geq 0 \tag{14.6}
\end{equation*}
$$

Substituting the expression for first law of thermodynamics in the above equation

$$
\begin{equation*}
\mathrm{Q}_{\mathrm{g}}\left(\frac{\mathrm{~T}_{\mathrm{g}}-\mathrm{T}_{\mathrm{o}}}{\mathrm{~T}_{\mathrm{g}}}\right) \geq \mathrm{Q}_{\mathrm{e}}\left(\frac{\mathrm{~T}_{\mathrm{o}}-\mathrm{T}_{\mathrm{e}}}{\mathrm{~T}_{\mathrm{e}}}\right)-\mathrm{W}_{\mathrm{p}} \tag{14.7}
\end{equation*}
$$

Neglecting solution pump work, $\mathrm{W}_{\mathrm{p}}$; the COP of VARS is given by:

$$
\begin{equation*}
\mathrm{COP}_{\mathrm{VARS}}=\frac{\mathrm{Q}_{\mathrm{e}}}{\mathrm{Q}_{\mathrm{g}}} \leq\left(\frac{\mathrm{T}_{\mathrm{e}}}{\mathrm{~T}_{\mathrm{o}}-\mathrm{T}_{\mathrm{e}}}\right)\left(\frac{\mathrm{T}_{\mathrm{g}}-\mathrm{T}_{\mathrm{o}}}{\mathrm{~T}_{\mathrm{g}}}\right) \tag{14.8}
\end{equation*}
$$

An ideal vapour absorption refrigeration system is totally reversible (i.e., both internally and externally reversible). For a completely reversible system the total entropy change (system+surroundings) is zero according to second law, hence for an ideal VARS $\Delta \mathrm{S}_{\text {total, rev }}=0 \Rightarrow \Delta \mathrm{~S}_{\text {surr, rev }}=0$. Hence:

$$
\begin{equation*}
\Delta S_{\text {surr, rev }}=-\frac{Q_{e}}{T_{e}}-\frac{Q_{g}}{T_{g}}+\frac{Q_{a+c}}{T_{o}}=0 \tag{14.9}
\end{equation*}
$$

Hence combining first and second laws and neglecting pump work, the maximum possible COP of an ideal VARS system is given by:

$$
\begin{equation*}
\mathrm{COP}_{\text {ideal VARS }}=\frac{\mathrm{Q}_{\mathrm{e}}}{\mathrm{Q}_{\mathrm{g}}}=\left(\frac{\mathrm{T}_{\mathrm{e}}}{\mathrm{~T}_{\mathrm{o}}-\mathrm{T}_{\mathrm{e}}}\right)\left(\frac{\mathrm{T}_{\mathrm{g}}-\mathrm{T}_{\mathrm{o}}}{\mathrm{~T}_{\mathrm{g}}}\right) \tag{14.10}
\end{equation*}
$$

Thus the ideal COP is only a function of operating temperatures similar to Carnot system. It can be seen from the above expression that the ideal COP of VARS system is equal to the product of efficiency of a Carnot heat engine operating between $T_{g}$ and $\mathrm{T}_{\mathrm{o}}$ and COP of a Carnot refrigeration system operating between $\mathrm{T}_{\mathrm{o}}$ and $\mathrm{T}_{\mathrm{e}}$, i.e.,

$$
\begin{equation*}
\mathrm{COP}_{\text {ideal VARS }}=\frac{\mathrm{Q}_{\mathrm{e}}}{\mathrm{Q}_{\mathrm{g}}}=\left(\frac{\mathrm{T}_{\mathrm{e}}}{\mathrm{~T}_{\mathrm{o}}-\mathrm{T}_{\mathrm{e}}}\right)\left(\frac{\mathrm{T}_{\mathrm{g}}-\mathrm{T}_{\mathrm{o}}}{\mathrm{~T}_{\mathrm{g}}}\right)=\mathrm{COP}_{\text {Carnot }} \cdot \eta_{\text {Carnot }} \tag{14.11}
\end{equation*}
$$

Thus an ideal vapour absorption refrigeration system can be considered to be a combined system consisting of a Carnot heat engine and a Carnot refrigerator as shown in Fig.14.4. Thus the COP of an ideal VARS increases as generator temperature ( $\mathrm{T}_{\mathrm{g}}$ ) and evaporator temperature ( $\mathrm{T}_{\mathrm{e}}$ ) increase and heat rejection temperature $\left(\mathrm{T}_{\mathrm{o}}\right)$ decreases. However, the COP of actual VARS will be much less than that of an ideal VARS due to various internal and external irreversibilities present in actual systems.


Fig.14.4: Vapour absorption refrigeration system as a combination of a heat engine and a refrigerator

### 14.4. Properties of refrigerant-absorbent mixtures

The solution used in absorption refrigeration systems may be considered as a homogeneous binary mixture of refrigerant and absorbent. Depending upon the boiling point difference between refrigerant and absorbent and the operating temperatures, one may encounter a pure refrigerant vapour or a mixture of refrigerant and absorbent vapour in generator of the absorption system. Unlike pure substances, the thermodynamic state of a binary mixture (in liquid or vapour phase) cannot be fixed by pressure and temperature alone. According to Gibbs’ phase rule, one more parameter in addition to temperature and pressure is required to completely fix the thermodynamic state. Generally, the composition of the mixture is taken as the third independent parameter. The composition of a mixture can be expressed either in mass fraction or in mole fraction. The mass fraction of components 1 and 2 in a binary mixture are given by:

$$
\begin{equation*}
\xi_{1}=\frac{\mathrm{m}_{1}}{\mathrm{~m}_{1}+\mathrm{m}_{2}} ; \quad \xi_{2}=\frac{\mathrm{m}_{2}}{\mathrm{~m}_{1}+\mathrm{m}_{2}} \tag{14.12}
\end{equation*}
$$

where $m_{1}$ and $m_{2}$ are the mass of components 1 and 2 , respectively
The mole fraction of components 1 and 2 in a binary mixture are given by:

$$
\begin{equation*}
\mathrm{x}_{1}=\frac{\mathrm{n}_{1}}{\mathrm{n}_{1}+\mathrm{n}_{2}} ; \quad \mathrm{x}_{2}=\frac{\mathrm{n}_{2}}{\mathrm{n}_{1}+\mathrm{n}_{2}} \tag{14.13}
\end{equation*}
$$

where $\mathrm{n}_{1}$ and $\mathrm{n}_{2}$ are the number of moles of components 1 and 2 , respectively
An important property of a mixture is its miscibility. A mixture is said to be completely miscible if a homogeneous mixture can be formed through any arbitrary range of concentration values. Miscibility of mixtures is influenced by the temperature at which they are mixed. Some mixtures are miscible under certain conditions and immiscible at other conditions. The refrigerant-absorbent mixtures used in absorption refrigeration systems must be completely miscible under all conditions both in liquid and vapour phases.

### 14.4.1. Ideal, homogeneous binary mixtures

A binary mixture of components 1 and 2 is called as an ideal mixture, when it satisfies the following conditions.

Condition 1: The volume of the mixture is equal to the sum of the volumes of its constituents, i.e., upon mixing there is neither contraction nor expansion. Thus the specific volume of the mixture, $v$ is given by:

$$
\begin{equation*}
\mathrm{v}=\xi_{1} \cdot \mathrm{v}_{1}+\xi_{2} \cdot \mathrm{v}_{2} \tag{14.14}
\end{equation*}
$$

where $\xi_{1}$ and $\xi_{2}$ are the mass fractions of components 1 and 2 . For a binary mixture, $\xi_{1}$ and $\xi_{2}$ are related by:

$$
\begin{equation*}
\xi_{1}+\xi_{2}=1 \Rightarrow \xi_{2}=1-\xi_{1} \tag{14.15}
\end{equation*}
$$

Condition 2: Neither heat is generated nor absorbed upon mixing, i.e., the heat of solution is zero. Then the specific enthalpy of the mixture, $h$ is given by:

$$
\begin{equation*}
\mathrm{h}=\xi_{1} \cdot \mathrm{~h}_{1}+\xi_{2} \cdot \mathrm{~h}_{2}=\xi_{1} \cdot \mathrm{~h}_{1}+\left(1-\xi_{1}\right) \mathrm{h}_{2} \tag{14.16}
\end{equation*}
$$

Condition 3: The mixture obeys Raoult's law in liquid phase, i.e., the vapour pressure exerted by components 1 and $2\left(\mathrm{P}_{\mathrm{v}, 1}\right.$ and $\left.\mathrm{P}_{\mathrm{v}, 2}\right)$ at a temperature T are given by:

$$
\begin{align*}
& P_{v, 1}=x_{1} \cdot P_{1, \text { sat }}  \tag{14.17}\\
& P_{v, 2}=x_{2} \cdot P_{2, \text { sat }} \tag{14.18}
\end{align*}
$$

where $\mathrm{x}_{1}$ and $\mathrm{x}_{2}$ are the mole fractions of components 1 and 2 in solution, and $\mathrm{P}_{1, \text { sat }}$ and $P_{2 \text {, sat }}$ are the saturation pressures of pure components 1 and 2 at temperature $T$. The mole fractions $\mathrm{x}_{1}$ and $\mathrm{x}_{2}$ are related by:

$$
\begin{equation*}
\mathrm{x}_{1}+\mathrm{x}_{2}=1 \Rightarrow \mathrm{x}_{2}=1-\mathrm{x}_{1} \tag{14.19}
\end{equation*}
$$

Condition 4: The mixture obeys Dalton's law in vapour phase; i.e., the vapour pressure exerted by components 1 and $2\left(\mathrm{P}_{\mathrm{v}, 1}\right.$ and $\left.\mathrm{P}_{\mathrm{v}, 2}\right)$ in vapour phase at a temperature T are given by:

$$
\begin{align*}
& \mathrm{P}_{\mathrm{v}, 1}=\mathrm{y}_{1} \cdot \mathrm{P}_{\text {total }}  \tag{14.20}\\
& \mathrm{P}_{\mathrm{v}, 2}=\mathrm{y}_{2} \cdot \mathrm{P}_{\text {total }} \tag{14.21}
\end{align*}
$$

where $\mathrm{y}_{1}$ and $\mathrm{y}_{2}$ are the vapour phase mole fractions of components 1 and 2 and $\mathrm{P}_{\text {total }}$ is the total pressure exerted at temperature T . The vapour phase mole fractions $\mathrm{y}_{1}$ and $\mathrm{y}_{2}$ are related by:

$$
\begin{equation*}
\mathrm{y}_{1}+\mathrm{y}_{2}=1 \Rightarrow \mathrm{y}_{2}=1-\mathrm{y}_{1} \tag{14.22}
\end{equation*}
$$

and the total pressure $\mathrm{P}_{\text {total }}$ is given by:

$$
\begin{equation*}
P_{\text {total }}=P_{v, 1}+P_{v, 2} \tag{14.23}
\end{equation*}
$$

If one of the components, say component 2 is non-volatile compared to component 1 (e.g. component 1 is water and component 2 is lithium bromide salt), then $\mathrm{y}_{1} \approx 1$ and $\mathrm{y}_{2} \approx 0, \mathrm{P}_{\mathrm{v}, 2} \approx 0$, then from Raoult's and to Dalton's laws:

$$
\begin{equation*}
\mathrm{P}_{\text {total }} \approx \mathrm{P}_{\mathrm{v}, 1}=\mathrm{x}_{1} \cdot \mathrm{P}_{1, \text { sat }} \tag{14.24}
\end{equation*}
$$

14.4.2. Real mixtures

Real mixtures deviate from ideal mixtures since:

1. A real solution either contracts or expands upon mixing, i.e.,

$$
\begin{equation*}
\mathrm{v} \neq \xi_{1} \cdot \mathrm{v}_{1}+\xi_{2} \cdot \mathrm{v}_{2} \tag{14.25}
\end{equation*}
$$

2. Either heat is evolved (exothermic) or heat is absorbed upon mixing;

$$
\begin{equation*}
\mathrm{h}=\xi_{1} \cdot \mathrm{~h}_{1}+\left(1-\xi_{1}\right) \mathrm{h}_{2}+\Delta \mathrm{h}_{\text {mix }} \tag{14.26}
\end{equation*}
$$

where $\Delta \mathrm{h}_{\text {mix }}$ is the heat of mixing, which is taken as negative when heat is evolved and positive when heat is absorbed.

The above two differences between ideal and real mixtures can be attributed to the deviation of real mixtures from Raoult's law. Real mixtures approach ideal mixtures as the mole fraction of the component contributing to vapour pressure approaches unity, i.e., for very dilute solutions. Figure 14.5 shows the equilibrium pressure variation with liquid phase mole fraction (x) of ideal and real binary mixtures with positive (+ve) and negative deviations (-ve) from Raoult's law at a constant temperature. It can be seen that when the deviation from Raoult's law is positive (+ve), the equilibrium vapour pressure will be higher than that predicted by Raoult's law, consequently at a given pressure and composition, the equilibrium temperature of solution will be lower than that predicted by Raoult's law. The converse is true for solutions with -ve deviation from Raoult's law, i.e., the equilibrium temperature at a given pressure and composition will be higher than that predicted by Raoult's law for solution with negative deviation. This behaviour can also be shown on specific enthalpy-composition diagram as shown in Fig. 14.6 for a solution with negative deviation from Raoult's law. Refrigerant-absorbent mixtures used in vapour absorption refrigeration systems exhibit a negative deviation from Raoult's law, i.e., the process of absorption is exothermic with a negative heat of mixing.


Fig.14.5: Pressure-concentration behaviour of ideal and real mixtures at a constant temperature


Fig.14.6: Enthalpy-concentration behaviour of an ideal mixture and a real mixture with negative deviation from Raoult's law

### 14.5. Basic Vapour Absorption Refrigeration System

Figure 14.7 shows a basic vapour absorption refrigeration system with a solution heat exchanger on a pressure vs temperature diagram. As shown in the figure, low temperature and low pressure refrigerant vapour from evaporator at state 1 enters the absorber and is absorbed by solution weak in refrigerant (state 8). The heat of absorption $\left(\mathrm{Q}_{\mathrm{a}}\right)$ is rejected to an external heat sink at $\mathrm{T}_{\infty}$. The solution, rich in refrigerant (state 2) is pumped to the generator pressure $\left(\mathrm{P}_{\mathrm{g}}\right)$ by the solution pump (state 3). The pressurized solution gets heated up sensibly as it flows through the solution heat exchanger by extracting heat from hot solution coming from generator (state 4). Heat is supplied to this solution from an external heat source in the generator ( $\mathrm{Q}_{\mathrm{g}}$ at $\mathrm{T}_{\mathrm{g}}$ ), as a result refrigerant vapour is generated (absorbent may also boil to give off vapour in case of ammonia-water systems) at state 5 . This high-pressure refrigerant vapour condenses in the condenser by rejecting heat of condensation to the external heat sink ( $\mathrm{Q}_{\mathrm{c}}$ at $\mathrm{T}_{\infty}$ ) and leaves the condenser as a high pressure liquid (state 9). This high pressure refrigerant liquid is throttled in the expansion device to evaporator pressure $\mathrm{P}_{\mathrm{e}}$ (state 10) from where it enters the evaporator, extracts heat from low temperature heat source ( $\mathrm{Q}_{\mathrm{e}}$ at $\mathrm{T}_{\mathrm{e}}$ ) and leaves the evaporator as vapour at state 1, completing a cycle. The hot solution that is weak in refrigerant (state 6) leaves the generator at high temperature and is cooled sensibly by rejecting heat to the solution going to the generator in the solution heat exchanger (state 7). Then it is throttled to the evaporator pressure in the throttle valve (state 8), from where it enters the absorber to complete the cycle. It can be seen that though not an essential component, the solution heat exchanger is used in practical systems to improve the COP by reducing the heat input in the generator. A solution heat exchanger as shown in Fig. 14.7 is a counterflow heat exchanger in which the hot solution coming from the generator comes in thermal contact with the cold solution going to the generator. As a
result of this heat exchange, less heat input is required in the generator and less heat is rejected in the absorber, thus improving the system performance significantly.


Fig.14.7: Basic vapour absorption refrigeration system with a solution heat exchanger on a pressure vs temperature diagram

The thermodynamic performance of the above system can be evaluated by applying mass and energy balance to each component assuming a steady flow process. In simple theoretical analyses, internal irreversibilities such as pressure drops between the components are generally neglected. To find the performance from the mass and energy balance equations one needs to know inputs such as the type of refrigerant-absorbent mixtures used in the system, operating temperatures, composition of solution at the entry and exit of absorber, effectiveness of solution heat exchanger etc. A simple steady flow analysis of the system will be presented in later sections.

### 14.6. Refrigerant-absorbent combinations for VARS

The desirable properties of refrigerant-absorbent mixtures for VARS are:
i. The refrigerant should exhibit high solubility with solution in the absorber. This is to say that it should exhibit negative deviation from Raoult's law at absorber.
ii. There should be large difference in the boiling points of refrigerant and absorbent (greater than $200^{\circ} \mathrm{C}$ ), so that only refrigerant is boiled-off in the generator. This ensures that only pure refrigerant circulates through refrigerant circuit (condenser-expansion valve-evaporator) leading to isothermal heat transfer in evaporator and condenser.
iii. It should exhibit small heat of mixing so that a high COP can be achieved. However, this requirement contradicts the first requirement. Hence, in practice a trade-off is required between solubility and heat of mixing.
iv. The refrigerant-absorbent mixture should have high thermal conductivity and low viscosity for high performance.
v. It should not undergo crystallization or solidification inside the system.
vi. The mixture should be safe, chemically stable, non-corrosive, inexpensive and should be available easily.

The most commonly used refrigerant-absorbent pairs in commercial systems are:

1. Water-Lithium Bromide $\left(\mathrm{H}_{2} \mathrm{O}-\mathrm{LiBr}\right)$ system for above $0^{\circ} \mathrm{C}$ applications such as air conditioning. Here water is the refrigerant and lithium bromide is the absorbent.
2. Ammonia-Water $\left(\mathrm{NH}_{3}-\mathrm{H}_{2} \mathrm{O}\right)$ system for refrigeration applications with ammonia as refrigerant and water as absorbent.

Of late efforts are being made to develop other refrigerant-absorbent systems using both natural and synthetic refrigerants to overcome some of the limitations of $\left(\mathrm{H}_{2} \mathrm{O}-\mathrm{LiBr}\right)$ and $\left(\mathrm{NH}_{3}-\mathrm{H}_{2} \mathrm{O}\right)$ systems.

Currently, large water-lithium bromide $\left(\mathrm{H}_{2} \mathrm{O}-\mathrm{LiBr}\right)$ systems are extensively used in air conditioning applications, where as large ammonia-water $\left(\mathrm{NH}_{3}-\mathrm{H}_{2} \mathrm{O}\right)$ systems are used in refrigeration applications, while small ammonia-water systems with a third inert gas are used in a pumpless form in small domestic refrigerators (triple fluid vapour absorption systems).

## Questions:

1. Compared to compression systems, absorption systems offer the benefits of:
a) Higher COPs
b) Lower refrigeration temperatures
c) Possibility of using low-grade energy sources
d) All of the above

## Ans.: c)

2. Absorption of the refrigerant by the absorbent in a vapour absorption refrigeration system is accompanied by:
a) Absorption of heat
b) Release of heat
c) No thermal effects
d) Reduction in volume

Ans. b)
3. An absorption system consisting of only two closed vessels:
a) Can provide continuous refrigeration
b) Provides refrigeration intermittently
c) Can work on solar energy alone
d) Has no practical application

## Ans. b) and c)

4. The conventional, continuously operating single stage vapour absorption refrigeration system:
a) Requires only thermal energy as input
b) Uses a thermal compressor in place of a mechanical compressor
c) Does not require a condenser
d) Consists of two expansion valves

## Ans. b) and d)

5. For an ideal refrigerant-absorbent mixture:
a) There is neither expansion nor contraction upon mixing
b) The mixing process is exothermic
c) The mixing process is endothermic
d) Obeys Raoult's law in liquid phase and Dalton's law in vapour phase

## Ans. a) and d)

6. For a refrigerant-absorbent mixture with a negative deviation from Raoult's law:
a) The mixing process is exothermic
b) The mixing process is endothermic
c) The actual equilibrium temperature will be less than that predicted by Raoult's law
d) The actual equilibrium temperature will be less more that predicted by Raoult's law

## Ans. a) and d)

7. Refrigerant-absorbent pairs used in vapour absorption refrigeration systems should:
a) Exhibit negative deviation from Raoult's law at absorber
b) Exhibit positive deviation from Raoult's law at absorber
c) Have large heat of mixing
d) Have large boiling point difference between refrigerant and absorbent

## Ans. a) and d)

8. Which of the following statements are true:
a) Water-lithium bromide systems are used for refrigeration applications above $0^{\circ} \mathrm{C}$ only
b) Ammonia-water systems can be used for refrigeration applications below $0^{\circ} \mathrm{C}$ only
c) Small ammonia-water systems are used in domestic refrigerators
d) Small water-lithium bromide systems are used in room air conditioners

## Ans. a) and c)

9. The operating temperatures of a single stage vapour absorption refrigeration system are: generator: $\mathbf{9 0} \mathbf{0}^{\circ} \mathrm{C}$; condenser and absorber: $\mathbf{4 0 ^ { \circ }} \mathrm{C}$; evaporator: $\mathbf{0}^{\mathbf{0}} \mathrm{C}$. The system has a refrigeration capacity of $\mathbf{1 0 0} \mathbf{~ k W}$ and the heat input to the system is $\mathbf{1 6 0} \mathbf{~ k W}$. The solution pump work is negligible.
a) Find the COP of the system and the total heat rejection rate from the system.
b) An inventor claims that by improving the design of all the components of the system he could reduce the heat input to the system to $\mathbf{8 0} \mathbf{~ k W}$ while keeping the refrigeration capacity and operating temperatures same as before. Examine the validity of the claim.

Ans.:
a)

$$
\mathrm{COP}=\mathrm{Q}_{\mathrm{e}} / \mathrm{Q}_{\mathrm{g}}=100 / 160=\mathbf{0 . 6 2 5}
$$

$$
\text { Total heat rejection rate }=\mathrm{Q}_{\mathrm{a}}+\mathrm{Q}_{\mathrm{c}}=\mathrm{Q}_{\mathrm{e}}+\mathrm{Q}_{\mathrm{g}}=100+160=\mathbf{2 6 0} \mathbf{~ k W} \text { (Ans.) }
$$

b) According to the inventor's claim, the $\mathrm{COP}_{\text {claim }}$ is given by:

$$
\mathrm{COP}_{\text {claim }}=\mathrm{Q}_{\mathrm{e}} / \mathrm{Q}_{\mathrm{g}}=100 / 80=\mathbf{1 . 2 5}
$$

However, for the given temperatures, the maximum possible COP is given by:

$$
\operatorname{COP}_{\text {ideal }} \text { VARS }=\left(\frac{Q_{e}}{Q_{g}}\right)_{\max }=\left(\frac{T_{e}}{T_{o}-T_{e}}\right)\left(\frac{T_{g}-T_{o}}{T_{g}}\right)
$$

Substituting the values of operating temperatures, we find that:

$$
\mathrm{COP}_{\max }=\left(\frac{T_{e}}{T_{0}-T_{e}}\right)\left(\frac{T_{g}-T_{o}}{T_{g}}\right)=\left(\frac{273}{313-273}\right)\left(\frac{50}{363}\right)=0.94
$$

$$
\text { Since } \mathbf{C O P}_{\text {claim }}>\mathbf{C O P}_{\text {max }} \Rightarrow \text { Inventor's claim is FALSE }
$$

(Ans.)

1. The following figure shows a pair of containers A \& B. Container B contains an aqueous solution of $\left(\mathrm{LiBr}+\mathrm{H}_{2} \mathrm{O}\right)$ at a mass fraction $\left(\mathrm{x}_{\mathrm{i}}\right)$ of 0.6 . Container A and connecting pipe are filled with pure water vapor. Initially the system $(A+B)$ is at an equilibrium temperature of $90^{\circ} \mathrm{C}$, at which the pressure is found to be 9.0 kPa . Now water vapour starts condensing in A as cooling water starts flowing through the coil kept in A.

a) What is the temperature of the coil at which steam starts condensing in A?
b) Does the System pressure remain constant during condensation? If not, how to maintain the pressure constant at 9.0 kPa ? What happens to the temperature of solution in B?
c) As water vapour condenses in A there will be transfer of water vapour from $B$ to A resulting in change of mass fraction of solution ( $\Delta x$ ) in B. Find a relation between $\Delta \mathrm{x}$ and $f$, where $f$ is the ratio of initial mass of solution in B to the mass of water vapour transferred from B to A.
d) What is the amount of solution required initially in B so that a mass of 1 kg of water is transferred from B to A with a corresponding change of mass fraction( $\Delta x$ ) by 0.05 ?
e) Neglecting the contribution of temperature changes, what is the amount of heat transferred at $A$ and $B$ during the transfer of 1 kg of water from $B$ to $A$ ? Is energy balanced?
f) What is required to reverse the process so that initial conditions are restored?
g) Show the forward and reverse process on D ring plot.

## Use the following data:

Initial enthalpy of solution $=220 \mathrm{~kJ} / \mathrm{kg}$; Final enthalpy of solution $=270 \mathrm{~kJ} / \mathrm{kg}$ Assume that the average latent heat of vaporization of water and enthalpy of water vapour $=2500 \mathrm{~kJ} / \mathrm{kg}$
Saturation pressure of water vapour (in kPa ) is given by the Antoine's equation:
$\ln \left(\mathrm{p}_{\text {sat }}\right)=\mathrm{C}_{\mathrm{o}}-\frac{\mathrm{C}_{1}}{\mathrm{~T}+\mathrm{C}_{2}}$; where T is temperature in $\mathrm{K}, \mathrm{c}_{0}=16.54, \mathrm{c}_{1}=3985, \mathrm{c}_{2}=-39.0$
Ans.:
a) Steam in vessel A starts condensing when the surface temperature of the coil falls below the saturation temperature of water at 9.0 kPa . Using Antoine's equation:

$$
\operatorname{In}(9)=16.54-\frac{3985}{\mathrm{~T}-39} \Rightarrow \mathrm{~T}=316.84 \mathrm{~K}=43.7^{\circ} \mathrm{C}
$$

b) System pressure falls as condensation of water vapour takes place in A. To keep the system pressure constant, vapour has to be generated in $B$ by supplying heat to solution in B. Since the solution in B becomes richer in LiBr (i.e., concentration increases), at the same pressure of 9.0 kPa , the solution temperature in $\mathbf{B}$ increases.

## (Ans.)

c) From the definition of concentration for $\mathrm{H}_{2} \mathrm{O}-\mathrm{LiBr}$ solution;

$$
\Delta x=x_{f}-x_{i}=\left(\frac{M_{L}}{M_{L}+M_{W, f}}\right)-\left(\frac{M_{L}}{M_{L}+M_{W, i}}\right)=M_{L}\left[\frac{\left(M_{W, i}-M_{W, f}\right)}{\left(M_{L}+M_{W, i}\right) \cdot\left(M_{L}+M_{W, i}\right)}\right]
$$

Amount of water transferred from B to $\mathrm{A}=\left(\mathbf{M}_{\mathbf{W}, \mathbf{i}}-\mathbf{M}_{\mathbf{W}, \mathbf{f}}\right)$
The factor f is defined as:

$$
\mathbf{f}=\left(\frac{\mathbf{M}_{\mathbf{L}}+\mathbf{M}_{\mathbf{W}, \mathrm{i}}}{\mathbf{M}_{\mathbf{W}, \mathbf{i}}-\mathbf{M}_{\mathbf{W}, \mathbf{f}}}\right)
$$

Substituting the above in the expression for $\Delta \mathrm{x}$ and using the definition of concentration, we find that:

$$
\begin{equation*}
\Delta x=\mathbf{x}_{\mathrm{f}}-\mathbf{x}_{\mathbf{i}}=\left(\frac{\mathbf{x}_{\mathbf{f}}}{\mathbf{f}}\right) \tag{Ans.}
\end{equation*}
$$

d) Mass of water transferred is 1.0 kg and change in concentration is 0.05 . Hence the final concentration is:

$$
x_{f}=x_{i}+0.05=0.60+0.05=0.65
$$

Substituting this value in the expression for $\Delta \mathrm{x}$, we find that

$$
f=\left(\frac{x_{f}}{\Delta x}\right)=\left(\frac{0.65}{0.05}\right)=13
$$

Hence the initial mass of solution is given by:

$$
\left.\left(M_{L}+M_{W, i}\right)=\mathrm{f} . \text { (mass of water transferred }\right)=13 \times 1.0=13 \mathrm{kgs}
$$

e) From energy balance of vessel B, the amount of energy transferred to B is given by:

$$
Q_{B, i n}=\left(M_{B, f} \cdot h_{f}-M_{B, i} \cdot h_{i}\right)+\left(M_{W, i}-M_{W, f}\right) h_{w}
$$

Substituting the values of enthalpies and initial and final mass of solution (13 kg and 12 kg , respectively), we find that the heat transferred to B is:

$$
\mathrm{Q}_{\mathrm{B}, \mathrm{in}}=2880 \mathrm{~kJ}
$$

(Ans.)
Neglecting the heat transferred during initial sensible cooling of vapour, the total heat transferred at Vessel A is:
$\mathrm{Q}_{\mathrm{A}, \text { out }}=$ Amount of water vapour condensed X latent heat of vapourization $=\mathbf{2 5 0 0} \mathbf{~ k J}$

## (Ans.)

The difference in energy transferred at A and B is stored in the form of heat of solution.
(Ans.)
f) To reverse the process and arrive at initial condition, the condensed water in vessel A has to be vapourized by supplying heat to vessel $A$. The vapour generated is absorbed by strong solution in B. Since this is an exothermic process, heat has to be rejected from B.
(Ans.)
g) $\mathrm{D}^{\wedge}$ hring plot of forward and reverse processese is shown below:


