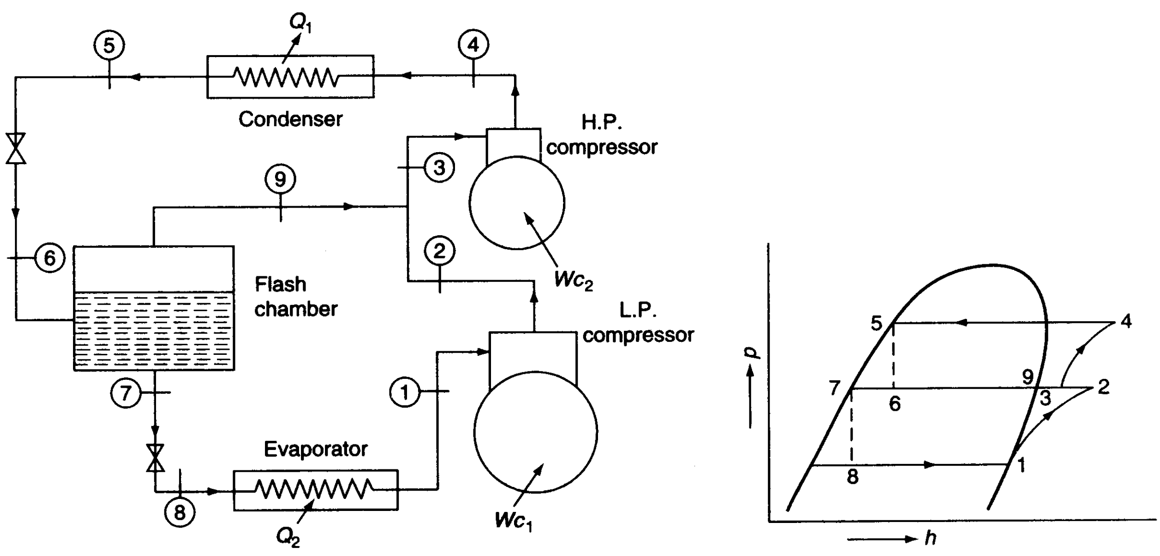


(a) (b)

Fig. 14.21 *Two-stage vapour compression system with a flash intercooler*

Figure 14.21 shows a two-stage vapour compression system with a flash chamber intercooler, where the vapour from the flash chamber (state 9) mixes with the vapour from the LP compressor (state 2) to form vapour at state 3, which enters the HP compressor.

14.3.7 Multi-Evaporator Systems

A situation often arises when varied types of cooling loads are connected to the same refrigeration system. Each load may need an evaporator working at a different refrigeration temperature. A two-evaporator single-compressor system with individual expansion valves for each evaporator and one compressor is shown in Fig. 14.22(a) and the corresponding *p-h* diagram is shown is Fig. 14.22(b) The mass flow rates through evaporators 1 and 2 are

$$m_1 = \frac{Q_{e1}}{h_7 - h_5} \quad \text{and} \quad m_2 = \frac{Q_{e2}}{h_6 - h_4}$$

The enthalpy of liquid–vapour mixture entering the compressor is

$$h_1 = \frac{m_1 h_7 + m_2 h_6}{m_1 + m_2}$$

and the work input is

$$W = (m_1 + m_2)(h_2 - h_1)$$

14.3.8 Cascade Systems

Two important parameters that need to be considered in the selection of a refrigerant are the temperatures of the two media (the refrigerated space and the environment) with which the refrigerant exchanges heat. To have reasonable heat transfer rate, a temperature difference of 5°C to 10°C should be maintained between the refrigerant and the medium. If a space is to be maintained at –10°C e.g., the refrigerant should evaporate at –20°C (Fig. 14. 23), the saturation pressure at which must be above the atmospheric pres-

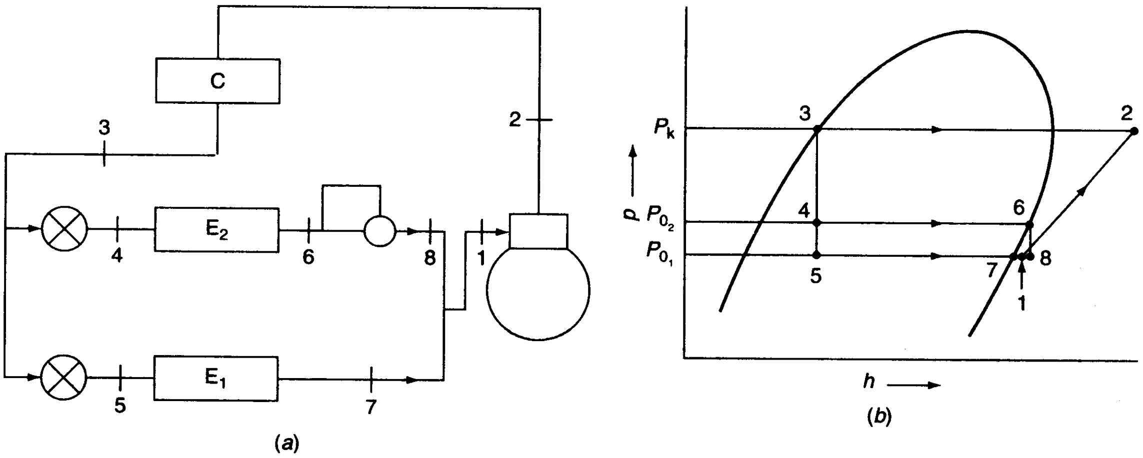


Fig. 14.22 (*a*) *System with two evaporators and single compressor, with indivdual expansion valves* (*b*) *Thermodynamic cycle for the system of Fig.* 14.22(*a*)

sure to prevent any air leakage into the system. Again, the temperature of the refrigerant in the condenser should be above the cooling medium by about 10°C, as shown in the figure, the saturation pressure at which must be below the critical pressure of the refrigerant. If a single refrigerant cannot meet the temperature requirements in the range from −20°C to 50°C, two cycles with two different refrigerants can be used in series, as shown in Fig. 14.24. Such a coupled cycle makes a *cascade refrigeration system*. Two independent vapour compression systems combine together in such a way that the evaporator of the high-temperature system becomes the condenser of the low-temperature system. But the working media of the two systems are separated from each other. The intermediate heat exchanger is also called a *cascade heat exchanger or condenser*. There are many industrial and medical applications where very low temperatures are required such as liquefaction of petroleum vapours, liquefaction of gases, dry ice manufacture etc. The blood storage needs as low as −80°C and precipitation hardening of special alloy steels needs around −90°C. At such low temperatures, the saturation pressures are very low prompting air leakage and the piston displacements become very large. For low-temperature side, R-13 can be used for which at atmospheric pressure the saturation temperature is below −80°C and for the high temperature side, R-12 or R-22 can be used.

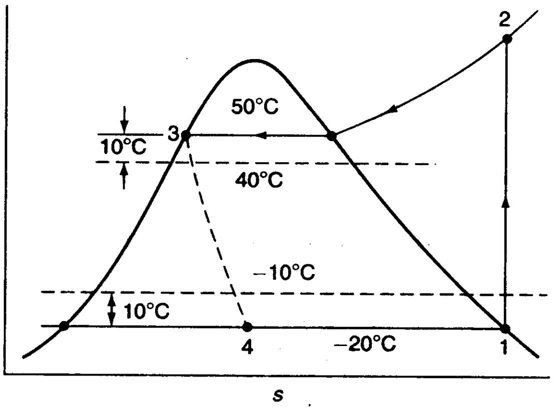
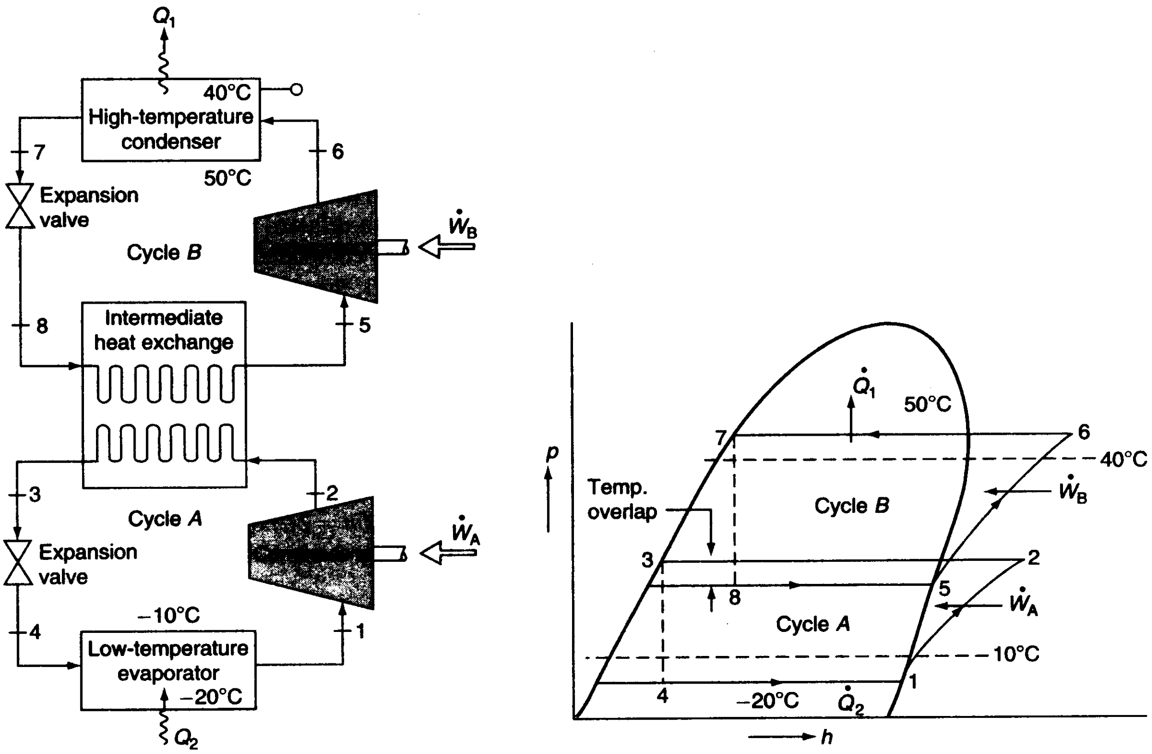


Fig. 14.24

14.3.9 Refrigerants

In the earlier days, ethyl chloride (C_2H_5Cl), sulphur dioxide (SO_2), methylchloride (CH_3Cl), and carbon dioxide (CO_2), etc., were used as refrigerants. A great breakthrough occurred with the development of freons (a



(a) (b)

[illegible] *Cascade refrigeration cycle*

trade name) in 1930s by E.I. du Pont de Nemours and Co, USA. Freons are a series of fluorinated hydrocarbons, generally known as *fluorocarbons*, derived from methane and ethane as bases. With fluorine, chlorine and sometimes bromine in their molecule, these form a series of refrigerants with a wide range of *normal boiling points* (NBP) (saturation temperature at atmospheric pressure), which satisfy the varied requirements of different refrigerators.

Among the most common inorganic refrigerants are ammonia (NH_3), water (H_2O), and carbon dioxide (CO_2). Presently, the most commonly used organic refrigerants are the chloro-fluoro derivatives of CH_4 and C_2H_6, as given below:

1. *CFCs*: Fully halogenated ones with chlorine in their molecule are *chloro-fluoro carbons*, referred to as CFCs.
2. *HCFCs*: These contain H atoms in the molecule along with Cl and F, called *hydro-chloro-fluoro carbons*.
3. *HCs*: These have no chlorine atoms in the molecule, called *hydrocarbons*. Thus, we have HCs, HFCs, HCFCs and CFCs.

The *F-atom* in the molecule of these substances makes the substances physically more favourable. The *Cl-atom* in the molecule is considered responsible for the depletion of the ozone layer in the upper atmosphere (stratosphere), thus allowing harmful ultra-violet radiation to penetrate through the atmosphere and reach the earth's surface. The *H-atoms* in the molecule impart a degree of flammability to the substance depending upon the number of these atoms.

Freons are either methane-based or ethane-based, where the hydrogen atoms are replaced by chlorine or fluorine atoms. Methane-based compounds are denoted by a number of two digits, where the first digit minus one is the number of hydrogen atoms and the second digit indicates the number of fluorine atoms, while the other atoms are chlorine. For Refrigerant-12 or R-12, e.g., the number of hydrogen atoms is zero, the number of fluorine atoms is two, and hence the other two atoms must be chlorine. Therefore, the compound is CCl_2F_2, dichloro-difluoro methane. Similarly, for R-22, it is $CHClF_2$, monochloro-difluoro methane. For R-50, it is methane, CH_4. For R-10, it is CCl_4, carbon tetrachloride, and so on. If the compound is ethane-based, a three digit number is assigned to the refrigerant, where the first digit is always 1, the second digit minus one is the number of hydrogen atoms, and the third digit indicates the number of fluorine atoms, all other atoms in the hydrocarbon being chlorine. For example, R 110 is C_2Cl_6, R-113 is $C_2Cl_3F_3$, R142 is $C_2H_3Cl\,F_2$, and so on.

Alternatively, for a compound derived from a saturated hydrocarbon denoted by the chemical formula

$$C_mH_nF_pCl_g$$

in which $(n + p + q) = 2m + 2$, the complete designation is

$$R - (m - 1)(n + 1)(p)$$

Hence, for dichloro-tetrafluoro-ethane in which there are two carbon atoms ($m = 2$), no hydrogen atom ($n = 0$), and four fluorine atoms ($p = 4$) is R-114. Similary, CCl_3F is R11, CCl_2F_2 is R-12, $CHClF_2$ is R22, $C_2Cl_3F_3$ is R113, CH_4 is R-50, C_2H_6 is R170, C_3H_8 is R-290, and so on.

The brominated refrigerants are denoted by putting an additional B and a number to denote the number of chlorine atoms replaced by bromine atoms. Thus, R13 B1 is derived from R13 with one chlorine atom replaced by a bromine atom and its formula is CF_3Br.

In case of *isomers*, compounds having the same chemical formula but different molecular structure, subscripts a, b, etc., are used.

In addition, there are *azeotropes*, which are mixtures of refrigerants, but which behave like pure substances. They are given arbitrary designations, e.g., R502 for a mixture of 48.8% R-22, an HCFC, and 51.2% R-115, a CFC.

In the case of common inorganic refrigerants, numerical designations are given according to their molecular weight added to 700. Thus ammonia is noted by 717, water by 718 and carbon dioxide by 744.

14.4 SELECTION OF A REFRIGERANT

Refrigerants have to be physiologically nontoxic and nonflammable. There is no ideal refrigerant as such. A refrigerant which is suitable in a certain application may not suit at all in other applications. The selection of a refrigerant depends on certain thermodynamic, chemical and physical properties:

14.4.1 Thermodynamic Properties

(i) Evaporation and Condensing Pressure The pressure in the evaporator should be positive and a little above the ambient pressure so that the atmospheric air and moisture do not leak into the system. The pressure in the condenser should not be high so as to necessitate heavy construction of equipment and high cost.

(ii) Critical Pressure and Temperature Fluids have a better heat-transfer rate at temperatures below critical temperature. So the critical temperature should be as high as possible. This would give a high COP. The critical pressure should be low so as to give lower condensing pressure.

(iii) Freezing Point The freezing-point temperature should be as low as possible so that the refrigerant can operate freely at higher temperatures in the cycle.

(iv) Latent Heat and Specific Heat A higher latent heat of vaporization at the working pressure would permit a greater amount of heat extraction in the evaporator. The specific heat of the liquid should be small so that less liquid flashes into vapour during expansion and there is higher refrigerating effect.

(v) Liquid and Vapour Density Refrigerants must not have a high specific volume at evaporator pressure so as to have smaller suction and discharge lines and the displacement volumes.

(vi) COP and kW per TR The refrigerant should have a high COP and low power input to compressor per ton of refrigeration.

14.4.2 Chemical Properties

(i) Inflammability The refrigerant should not be inflammable and explosive as far as possible.

(ii) Toxicity Toxic refrigerants should not be used in domestic refrigerating systems and comfort air conditioning.

(iii) Solubility in Water Refrigerants should have poor affinity for water, since the presence of moisture would lead to formation of ice and choking of the capillary tube.

(iv) Action on Material of Construction Refrigerants must not react chemically or carrode materials of construction. If a refrigerant, e.g., attacks copper and copper alloys, then pipes, fittings, valves, etc. are to be made with ferrous materials.

14.4.3 Physical Properties

(i) Thermal Conductivity For better heat-transfer rate, the refrigerant should have a high value of thermal conductivity.

(ii) Viscosity A low viscosity is desirable for low pumping power and high heat-transfer rate.

(iii) Leak Tendency The tendency for leakage of the refrigerant should be low and the detection of leak should be easy.

Besides these, the refrigerant should be cheap in cost and readily available. It should be chemically stable at all conditions of operating pressures and temperatures. It should not allow the lubricating oil to be carried over into the evaporator and condenser to casue fouling and reduce the rate of heat transfer.

14.4.4 Ozone Depletion Potential of CFC Refrigerants

The earth's *ozone layer* in the upper atmosphere or stratosphere absorbs harmful ultraviolet rays from the sun and protects us from skin cancer. Scientists were shocked to find in 1985 a gaping hole in the ozone layer above the Antartic through which ultraviolet rays directly reach the earth. CFCs are linked to the depletion of this ozone layer. They have varying degrees of *ozone depletion potential* (ODP). In addition, they also act as *greenhouse gases*, and hence they have *global warming potential* (GWP). According to an international agreement, called the Montreal Protocol, the use of fully halogenated CFCs (no hydrogen in the molecule), that are considered to have high ODP, viz., R-11, R-12, R-113 and R-114, have to be phased out by the year 2000. HCFCs like R-22 have ODP of 5% of that of R-12. However, because of their GWP, they will be phased out by 2030.

CFCs being heavier than N_2 and O_2 migrate to the upper atmosphere by molecular diffusion due to partial pressure difference. Chlorine atoms from the CFC molecule would be split off by the action of sunlight and the free chlorine atoms react with ozone in the stratosphere as follows:

$$CCl_2F_2 \xrightarrow{\text{sunlight}} CClF_2 + Cl$$

$$O_3 + Cl \xrightarrow{\text{sunlight}} ClO + O_2$$

Thus, O_3 will be depleted to O_2. Because of chain reaction, a single atom of Cl reacts taking out 100,000 O_3 molecules. Therefore, even a small concentration of CFC becomes very significant.

HCs and HFCs substitute for CFCs, since they do not contain any Cl atom and have zero ODP. Even HCFCs do contain Cl atoms, but in association with H-atoms have much reduced ODP. The two most common refrigerants having very high ODP are being replaced by R-134a (Tetra fluoro ethane), the most preferred substitute.

14.5 ABSORPTION REFRIGERATION CYCLE

The absorption refrigeration system is a *heat operated unit* which uses a refrigerant that is *alternately absorbed and liberated from the absorbent.* In the basic absorption system, the compressor in the vapour compression cycle is *replaced by an absorber-generator assembly* involving less mechanical work. Figure 14.25 gives the basic absorption refrigeration cycle, in which *ammonia is the refrigerant and water is the absorbent.* This is known as the *aqua-ammonia absorption* system.

Ammonia vapour is vigorously absorbed in water. So when low-pressure ammonia vapour from the evaporator comes in contact in the absorber with the weak solution (the concentration of ammonia in water is low) coming from the generator, it is readily absorbed, releasing the latent heat of condensation. The temperature of the solution tends to rise, while the absorber is cooled by the circulating water, absorbing the *heat of solution* (Q_A), and maintaining a constant temperature. Strong solution, rich in ammonia, is pumped to the generator where heat (Q_G) is supplied from an external source (steam, electricity, gas flame, etc.). Since the boiling point of ammonia is less than that of water, the ammonia vapour is given off from the aqua-ammonia solution at high pressure, and the weak solution returns to the absorber through a pressure reducing valve.

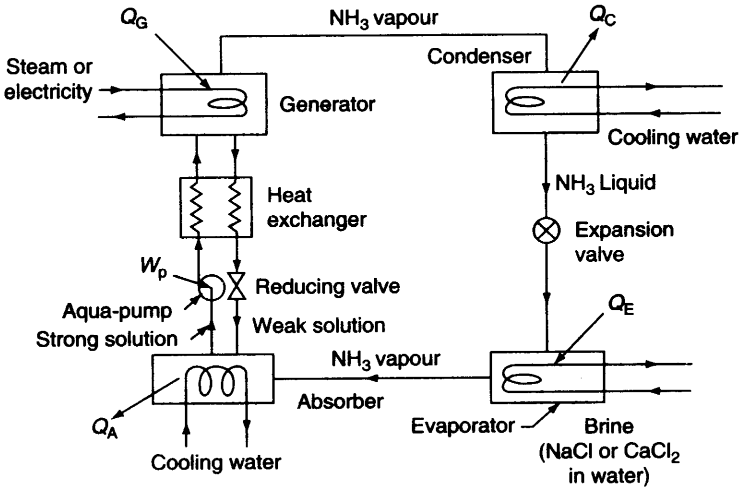


Fig. 14.25 *Vapour absorption refrigeration plant-flow diagram*

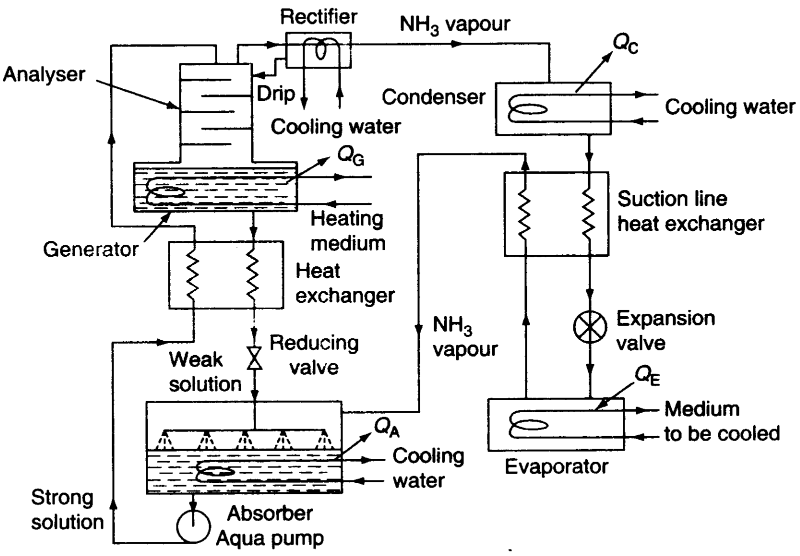


Fig. 14.26 *Actual vapour absorption refrigeration plant with analyzer and rectifier*

The heat exchanger preheats the strong solution and precools the weak solution, reducing both Q_G and Q_A, the heat to be supplied in the generator and the heat to be removed in the absorber respectively. The ammonia vapour then condenses in the condenser, is throttled by the expansion valve, and then evaporates, absorbing the heat of evaporation from the surroundings or the brine to be chilled.

In driving the ammonia vapour out of the solution in the generator, it is impossible to avoid evaporating some of the water. This water vapour going to the condenser along with the ammonia vapour, after condensation, may get frozen to ice and block the expansion valve. So an *analyzer-rectifier combination* (Fig. 14.26) is used to eliminate water vapour from the ammonia vapour going into the condenser.

The analyzer is a direct-contact heat exchanger consisting of a series of trays mounted above the generator. The strong solution from the absorber flows downward over the trays to cool the outgoing vapours. Since the saturation temperature of water is higher than that of ammonia at a given pressure, it is the water vapour which condenses first. As the vapour passes upward through the analyzer, it is cooled and enriched by ammonia, and the liquid is heated. Thus the vapour going to the condenser is lower in temperature and richer in ammonia, and the heat input to the generator is decreased.

The final reduction in the percentage of water vapour in the ammonia going to the condenser occurs in the rectifier which is a water-cooled heat exchanger which condenses water vapour and returns it to the generator through the drip line, as shown in Fig. 14.26. The use of a suction-line heat exchanger is to reduce Q_A and increase Q_E, thus achieving a double benefit. In the absorber the weak solution is sprayed to expose a larger surface area so as to accelerate the rate of absorption of ammonia vapour.

There is another absorption refrigeration system, namely, lithium bromide-water vapour absorption (Fig. 14.27). Here the refrigerant is water and the absorbent is the solution of lithium bromide salt in water. Since water cannot be cooled below 0°C, it can be used as a refrigerant in air conditioning units. Lithium bromide solution has a strong affinity for water vapour because of its very low vapour pressure. It absorbs water vapour as fast as it is released in the evaporator.

While the vapour compression refrigeration system requires the expenditure of 'high-grade' energy in the form of shaft work to drive the compressor with the concommitant disadvantage of vibration and noise, the

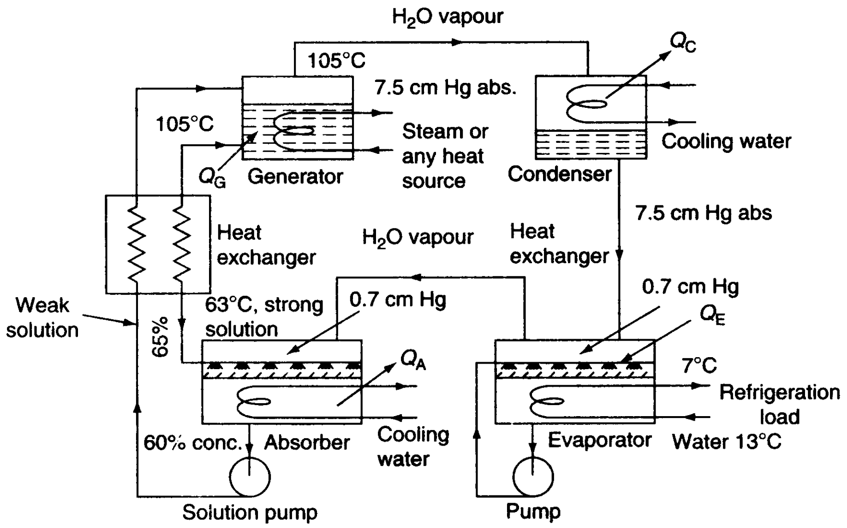


Fig. 14.27 *Lithium bromide-water absorption refrigeration plant*

absorption refrigeration system requires only 'low-grade' energy in the form of heat to drive it, and it is relatively silent in operation and subject to little wear. Although the COP = Q_E/Q_G is low, the absorption units are usually built when waste heat is available, and they are built in relatively bigger sizes. One current application of the absorption system that may grow in importance is the *utilization of solar energy* for the generator heat source of a refrigerator for food preservation and perhaps for comfort cooling.

14.5.1 Theoretical COP of an Absorption System

Let us assume that an absorption refrigeration plant uses heat Q_G from a source at T_1, provides refrigeration Q_E for a region at T_R, and rejects heat (Q_A+Q_C) to a sink (atmosphere) at T_2, as shown in Fig 14.28.

By the first law

$$Q_E + Q_G = Q_C + Q_A \tag{14.3}$$

By the second law

$$(\Delta S)_{\text{source}} + (\Delta S)_{\text{sink}} + (\Delta S)_{\text{region}} \geq 0$$

$$\therefore \quad -\frac{Q_G}{T_1} + \frac{Q_E + Q_G}{T_2} - \frac{Q_E}{T_R} \geq 0$$

From Eq. (14.3)

$$-\frac{Q_G}{T_1} + \frac{Q_E + Q_G}{T_2} - \frac{Q_E}{T_R} \geq 0$$

$$\therefore \quad \frac{T_1 - T_2}{T_1 T_2} Q_G + \frac{T_R - T_2}{T_2 T_R} Q_E \geq 0$$

$$\therefore \quad \frac{T_2 - T_R}{T_2 T_R} Q_E \leq \frac{T_1 - T_2}{T_1 T_2} Q_G$$

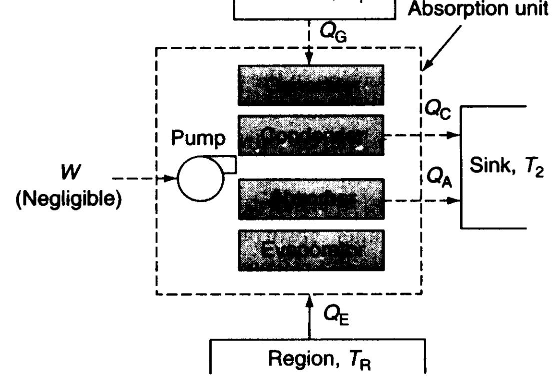


Fig. 14.28 *Energy fluxes in vapour absorption plant*

$$\therefore \quad \frac{Q_E}{Q_G} \le \frac{(T_1 - T_2)T_R}{(T_2 - T_R)T_1}$$

or

$$\text{COP} \le \frac{(T_1 - T_2)T_R}{(T_2 - T_R)T_1}$$

$$\therefore \quad (\text{COP})_{\max} = \frac{(T_1 - T_2)T_R}{(T_2 - T_R)T_1} \qquad (14.4)$$

or

$$(\text{COP})_{\max} = \frac{T_R}{T_2 - T_R} \times \frac{T_1 - T_2}{T_1}$$

Therefore, the maximum possible COP is the product of the ideal COP of a refrigerator working between T_R and T_2, and the ideal thermal efficiency of an engine working between T_1 and T_2. The cyclic heat engine and the refrigerator together, as shown in Fig. 14.29, is equivalent to the absorption cycle.

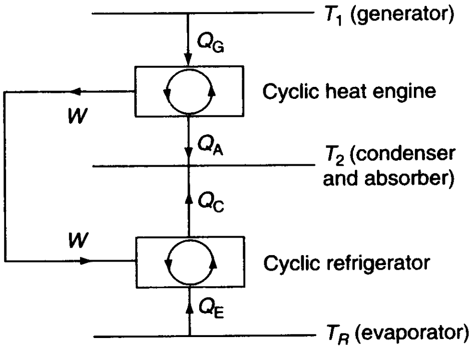


Fig. 14.29 An absorption cycle as equivalent to a cyclic heat engine and a cyclic refrigerator

14.6 ELECTROLUX REFRIGERATOR

An electrolux refrigerator works on three-fluid system. There is no circulation pump. The total pressure is the same throughout the system. The third fluid remains mainly in the evaporator, which reduces the partial pressure of refrigerant to enable it to evaporate at low pressure and hence low temperature.

The schematic diagram of an electrolux refrigerator working on $NH_3 - H_2O$ system with H_2 as the third fluid is shown in Fig. 14.30. Liquid NH_3 evaporates in the evaporator in the presence of H_2. Hydrogen is chosen because it is non-corrosive and insoluble in water. Thus a complete leakproof silent system is achieved.

A thermosiphon bubble pump is used to lift the weak aqua solution from the generator to the separator. The discharge tube from the generator is extended down below the liquid level in the generator. The bubbles rise and carry slugs of weak $NH_3 - H_2O$ solution into the separator. Two U-bend constrictions are provided as *vapour-locks* or *liquid-seal* to prevent H_2 from getting into the high side of the condenser.

The partial pressure of H_2 provides the pressure difference of NH_3 between the condenser and evaporator.

Accordingly, we have the following:

In the *condenser*, there is the pure NH_3 vapour pressure which is the total pressure.

In the *evaporator*, NH_3 vapour pressure = total pressure minus the partial pressure of H_2.

For example, let us consider the condenser temperature as 50°C, and evaporator temperature as −15°C. The corresponding vapour pressure of NH_3 are

Condenser, $p_c = 20.33$ bar
Evaporator exit, $p_e = 2.36$ bar

The approximate pressures in various parts of the system are given below:

The vapours leaving the generator top are assumed to be in equilibrium with the rich solution entering at 40°C, at which the saturation pressure of NH_3 is 15.54 bar. The temperature at the evaporator inlet is assumed to be at −25°C at which the saturation pressure of NH_3 is 1.516 bar.

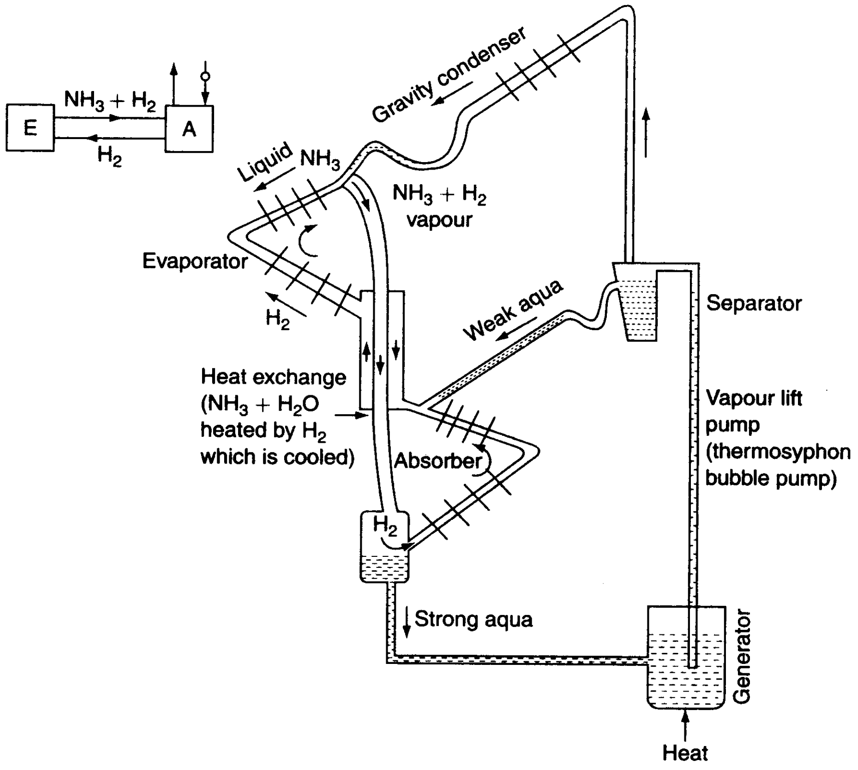


Fig. 14.30 *Electrolux refrigerator*

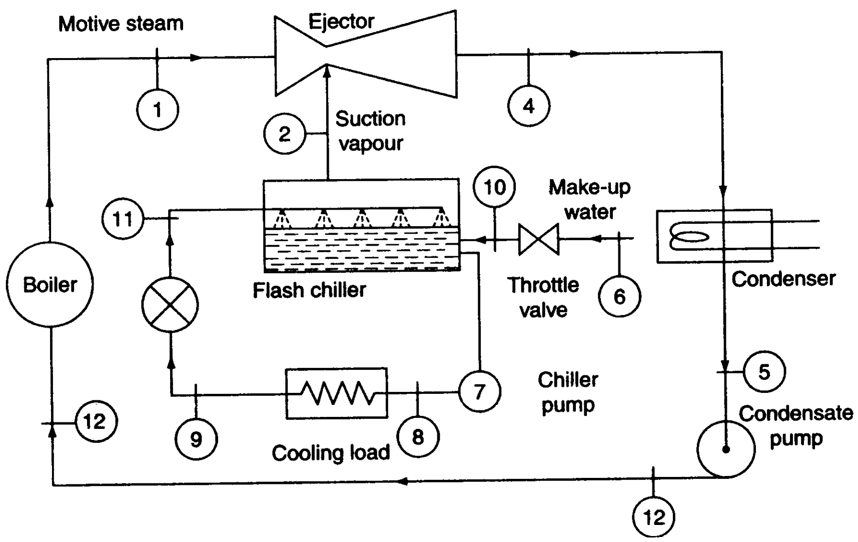
Table 14.1

Partial pressures in bar in the electrolux refrigerator

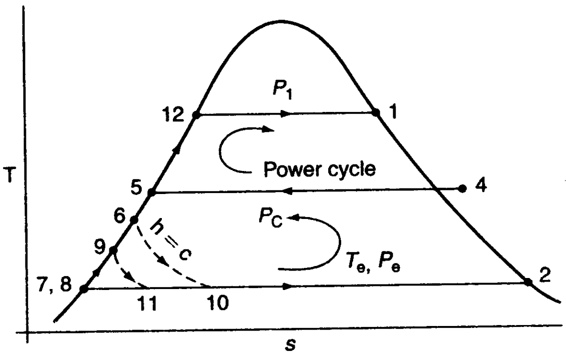
Component	NH_3	H_2O	H_2	*Total*
Condenser	20.33	0	0	20.33
Evaporator inlet	1.516	0	18.814	20.33
Evaporator exit	2.36	0	17.97	20.33
Generator top	15.54	4.79	0	20.33

14.7 STEAM JET REFRIGERATION SYSTEM

A simple steam-jet refrigeration system and its thermodynamic cycle is shown in Figs.14.31 and 14.32. Water at state 9 expands to 11 through the throttle valve into the flash chiller. Due to flashing (evaporation) of some liquid, the remaining water gets chilled to the desired temperature T_e. The pressure in the flash chamber is maintained at the corresponding saturation temperature T_e. The chilled water at 7 is recirculated after taking up the load in the cooling coil. The amount of water vaporized is compensated by make-up water at 6 entering through a throttle valve. Water vapour at 2 is compressed to 4 by the ejector driven by motive steam at 1. The compressed water vapour at 4 is then condensed to 5 and pumped back to the boiler.



Water-vapour refrigeration system



Thermodynamic cycle of water-vapour refrigeration system

Though the overall COP of the system is low, the steam-jet refrigeration finds application in air conditioning for comfort where steam is available and safety is the prime concern. It is also suitably used for the concentration or drying of heat-sensitive foods and chemicals. It has certain limitations like

(i) Enormous volume to be handled, e.g., at 8°C, 665 $m^3/(hr) \times (TR)$ are required, whereas for R-12, it is only 7 $m^3/h \times TR$. Centrifugal compressors can be used, but they are expensive. Ejector compression is the most economical to use with water as refrigerant.

(ii) High operating vacuum, e.g., at 8°C evaporator, the pressure is 0.01072 bar and the same at 35°C condenser, it is 0.0595 bar.

(iii) High freezing point, which can be used for refrigeration above 0°C only, such as is required for air conditioning

14.8 HEAT PUMP SYSTEMS

The heat pump is a cyclic device which is able to extract energy at a low temperature heat source and upgrade it to a high temperature heat source, enabling it to be used more effectively. Low grade reject heat available at a low temperature may be upgraded to a high temperature heat source by a heat pump. While a refrigerator is meant for the removal of heat and to achieve cooling, a heat pump is used to supply heat at a high temperature.

Heat pump systems have many features in common with the refrigeration systems and may be of the vapour-compression or the absorption type. A typical vapour-compression heat pump for space heating

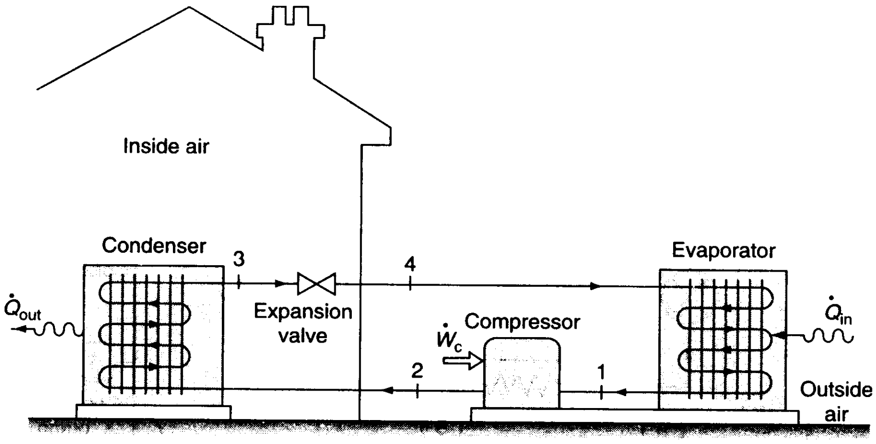


Fig. 14.33 Vapour-compression heat pump system for space heating

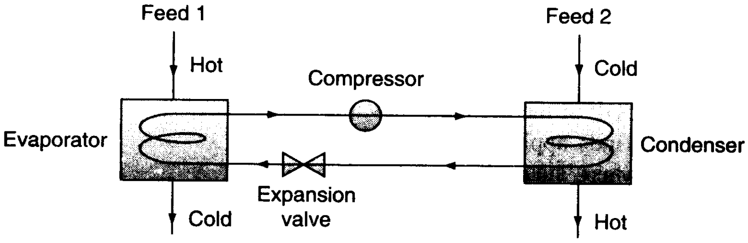


Fig. 14.34 Heating and cooling of two process streams

(Fig. 14.33) has the same basic components as the vapour-compression refrigeration system: compressor, condenser, expansion valve, and evaporator. The heat $\dot{Q}_{in}$ comes from the surroundings (cold air), and $\dot{Q}_{out}$ is directed to the dwelling as the desired effect, with the COP given by:

$$\mathrm{COP} = \frac{\dot{Q}_{out}}{W_C} = \frac{h_2 - h_3}{h_2 - h_1}$$

Many possible sources are available for heat transfer $\left(\dot{Q}_{in}\right)$ to the refrigerant passing through the evaporator. These include the outside air, the ground, and water from lakes, rivers, or wells. Liquid circulated through a solar collector and stored in an insulated tank also can be used as a source for a heat pump. Industrial heat pumps employ waste heat or warm liquid or gas streams as the low temperature heat source and upgrade it.

An air-air heat pump can be used for year-round air conditioning, to achieve heating during winter and cooling during summer, by using a reversing valve with the evaporator and condenser executing opposite duties. A heat pump in industry will be very effective if both condenser and evaporator are utilized for heating and cooling respectively, e.g., for cooling a process stream and heating another (Fig. 14.34).

14.9 GAS CYCLE REFRIGERATION

Refrigeration can also be accomplished by means of a gas cycle. In the gas cycle, an expander replaces the throttle valve of a vapour compression system, because the drop in temperature by throttling a real gas is very

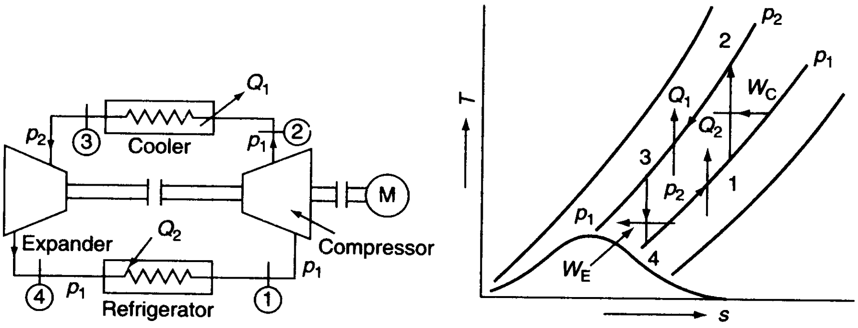


Fig. 14.35 Gas refrigeration cycle

small. For an ideal gas, enthalpy is a function of temperature only, and since in throttling enthalpy remains unchanged, there would not be any change in temperature also. Work output obtained from the expander is used as an aid in compression, thus decreasing the net work input. The ideal gas-refrigeration cycle is the same as the *reversed Brayton cycle*. The flow and *T-s* diagrams of the cycle are shown in Fig. 14.35. *Since there is no* phase change, the condenser and evaporator in a vapour compression system are here called the cooler and refrigerator respectively. At 1, the air is isentropically compressed from (1 to 2) from p_1 to p_2 after which it is cooled at constant pressure p_2 to p_3. The air, since it is presently used only in aircraft, is finally expanded isentropically to cool to 4. The COP of the refrigeration cycle, assuming the gas to be ideal, is given by

$$\text{COP} = \frac{Q_2}{W_{\text{net}}} = \frac{h_1 - h_4}{(h_2 - h_1) - (h_3 - h_4)}$$

$$= \frac{T_1 - T_4}{(T_2 - T_1) - (T_3 - T_4)} = \frac{T_1 - T_4}{T_1\left[\frac{T_2}{T_1} - 1\right] - T_4\left[\frac{T_3}{T_4} - 1\right]}$$

For isentropic compression and expansion

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}} = \frac{T_3}{T_4}$$

$\therefore$

$$\text{COP} = \frac{T_1 - T_4}{(T_1 - T_4)\left[\frac{T_3}{T_4} - 1\right]} = \frac{T_4}{T_3 - T_4}$$

Also

$$\text{COP} = \frac{1}{\left[\frac{p_2}{p_1}\right]^{(\gamma-1)/\gamma} - 1} \tag{14.5}$$

where p_2 is the pressure after compression and p_1 is the pressure before compression.

The COP of a gas-cycle refrigeration system is low. The power requirement per unit capacity is high. Its prominent application is in aircraft and missiles, where the vapour compression refrigeration system becomes heavy and bulky. Figure 14.36 shows the open cycle aircraft cabin cooling.

The compressed air is available and is a small percentage of the amount handled by the compressor of a turbo-jet or a supercharged aircraft engine. Large amounts of cool ambient air are available for cooling the compressed

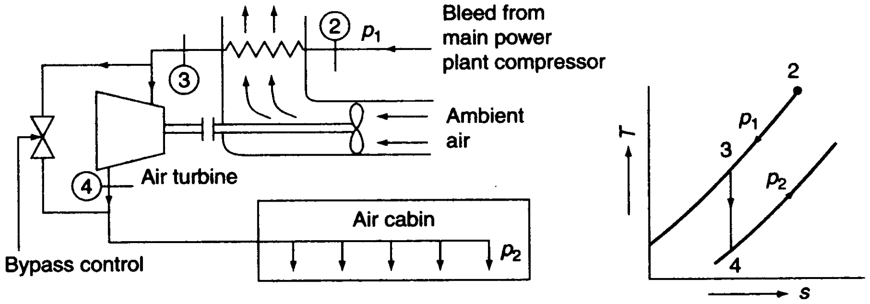


Fig. 14.36 *Open cycle aircraft cabin cooling*

air. In addition to cooling, the replacement of stale air in the cabin is possible. At high altitudes the pressurization of cabin air is also possible. Because of these considerations, air cycle refrigeration is favoured in aircrafts.

The flow and T-s diagrams of gas cycle refrigeration are shown in Fig. 14.37.

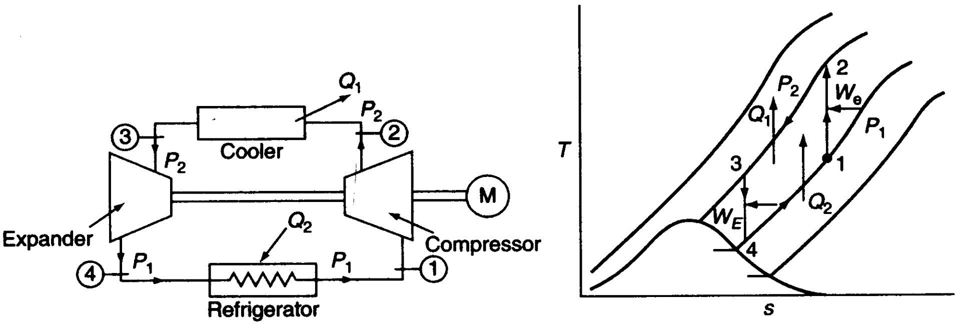


Fig. 14.37 *Gas refrigeration cycle*

14.9.1 Polytropic and Multistage Compression

Polytropic compression with cooling would reduce the net work input with the compression index being n instead of γ. The expression for compressor work becomes

$$W_c = \frac{n}{n-1}(p_2 v_2 - p_1 v_1) = \frac{n}{n-1}\frac{\gamma-1}{\gamma}c_p(T_2 - T_1)$$

Net work is

$$W_{net} = W_c - W_e = c_p\left[\frac{n}{n-1}\frac{\gamma-1}{\gamma}(T_2 - T_1) - (T_3 - T_4)\right]$$

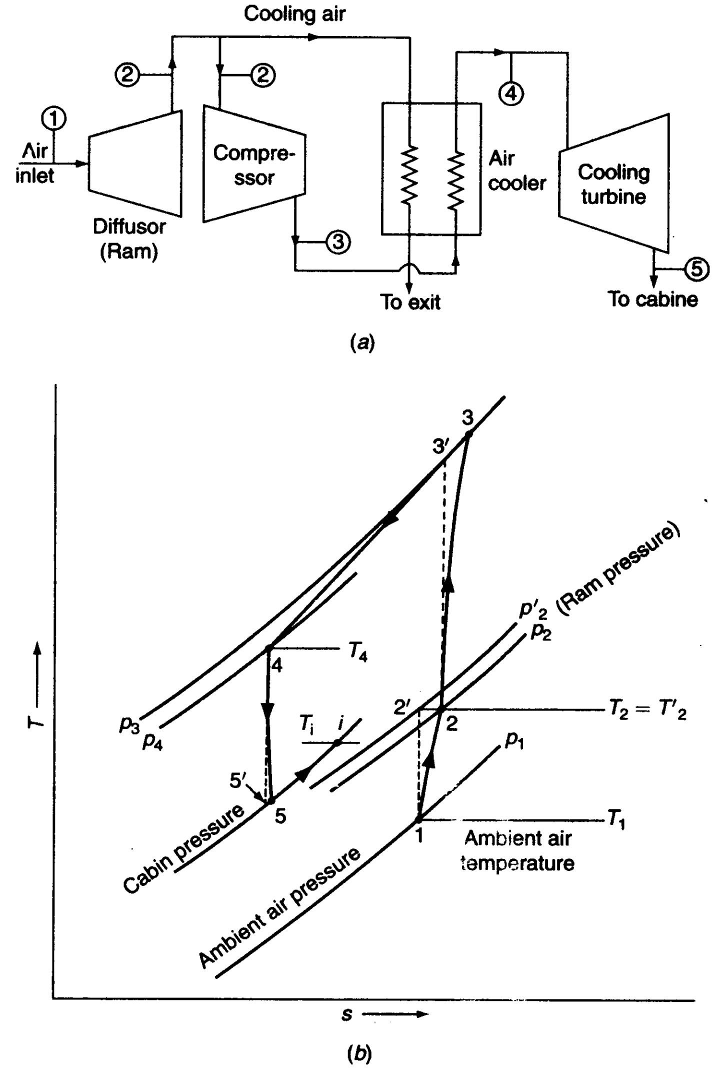
$$\therefore \qquad COP = \frac{T_1 - T_4}{\frac{n}{n-1}\frac{\gamma-1}{\gamma}(T_2 - T_1) - (T_3 - T_4)}$$

14.10 APPLICATION TO AIRCRAFT REFRIGERATION

The gas cycle is exclusively used in air conditioning systems of military and commercial aircrafts, though refrigerated cargo aircrafts generally use dry ice. It is appropriate to call it *air-cycle refrigeration*, since only air is the working substance in this cycle. The air cycle can work as an open cycle or a closed cycle. The main considerations for using air-cycle refrigeration in aircrafts are weight, space and operating power. Other advantages are the following:

(i) Small amounts of leakages are tolerable with air as the refrigerant.
(ii) In its simplest form as an open cycle it requires only one heat exchanger.
(iii) Availability of the refrigerant in mid air is of no concern.
(iv) Cabin pressurization and air conditioning can be combined into one operation.
(v) Initial compression of the air can be obtained by ram effect.

A simple aircraft refrigeration cycle is shown in Fig. 14.38(a) and 14.38(b). The ram effect is shown by the line 1–2. Point 2′ denotes the state after isentropic compression to pressure p_2' and temperature T_2'. The energy equation for the diffusion process:



(a)

(b)

[redacted] (a) *Flow diagram for aircraft refrigeration* (b) *Simple aircraft refrigeration cycle*

$$h_2 = h_2' = h_1 + \frac{v^2}{2}$$

where v is the velocity of the aircraft.

$$c_p T_2 = c_p T_2' = c_p T_1 + \frac{v^2}{2}$$

$$T_2 = T_2' = T_1 + \frac{v^2}{2c_p}$$

$$\frac{T_2'}{T_1} = 1 + \frac{v^2}{\frac{2\gamma R}{\gamma - 1} T_1} = 1 + \frac{\gamma - 1}{2}\frac{v^2}{c^2} = 1 + \frac{\gamma - 1}{2} M^2$$

where c = sonic velocity = $\sqrt{\gamma R T_1}$ and M = Mach number of the flight.

The temperature $T_2 = T_2'$ is the stagnation temperature of the ambient air. The stagnation pressure after isentropic diffusion, p_2' is given from

$$\frac{p_2'}{p_1} = \left(\frac{T_2'}{T_1}\right)^{\frac{\gamma}{\gamma - 1}}$$

The irreversible compression in the ram results in air reaching the point 2 instead of the point 2′, i.e., at the same stagnation temperature but at a reduced stagnation pressure p_2, which is obtained from the knowledge of ram efficiency η_R defined by

$$\eta_R = \frac{\text{Actual pressure recovery}}{\text{Ideal pressure recovery}} = \frac{p_2 - p_1}{p_2' - p_1}$$

The rest of the cycle is shown in Fig. 14.38. The pressure after expansion p_5 is slightly above the cabin pressure. It is also higher than the ambient air static pressure at that altitude. The refrigerating effect produced is

$$Q_2 = c_p (T_i - T_5)$$

where T_i is the room temperature maintained inside the cabin. The net work of the cycle is the difference of work for process 2–3 of the compressor and process 4–5 of the expander plus the ram air work, $c_p(T_2 - T_1)$, which is derived directly from the engine.

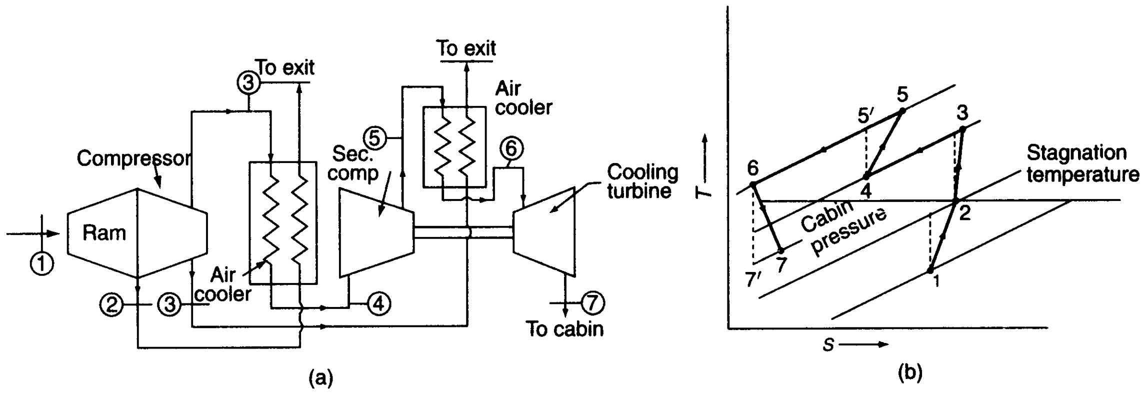
The ambient air temperature varies with the altitude of the flight of the aircraft. Generally, the temperature drops by 0.64°C per 100 m of height from the sea-level temperature.

14.10.1 Bootstrap System

The bootstrap system (Fig. 14.39) has two heat exchangers to provide additional cooling capacity whenever required. The expansion turbine drives a second compressor to raise the pressure of air before it enters the cooling turbine via the air cooler.

14.11 LIQUEFACTION OF GASES

An important application of gas refrigeration processes is in the liquefaction of gases. A gas may be cooled either by making it expand isentropically in an expander, thus performing work (sometimes known as *external-work method*), or making the gas undergo Joule-Kelvin expansion through a throttle valve (sometimes called the *internal-work method*). While the former method always brings about a temperature decrease, the



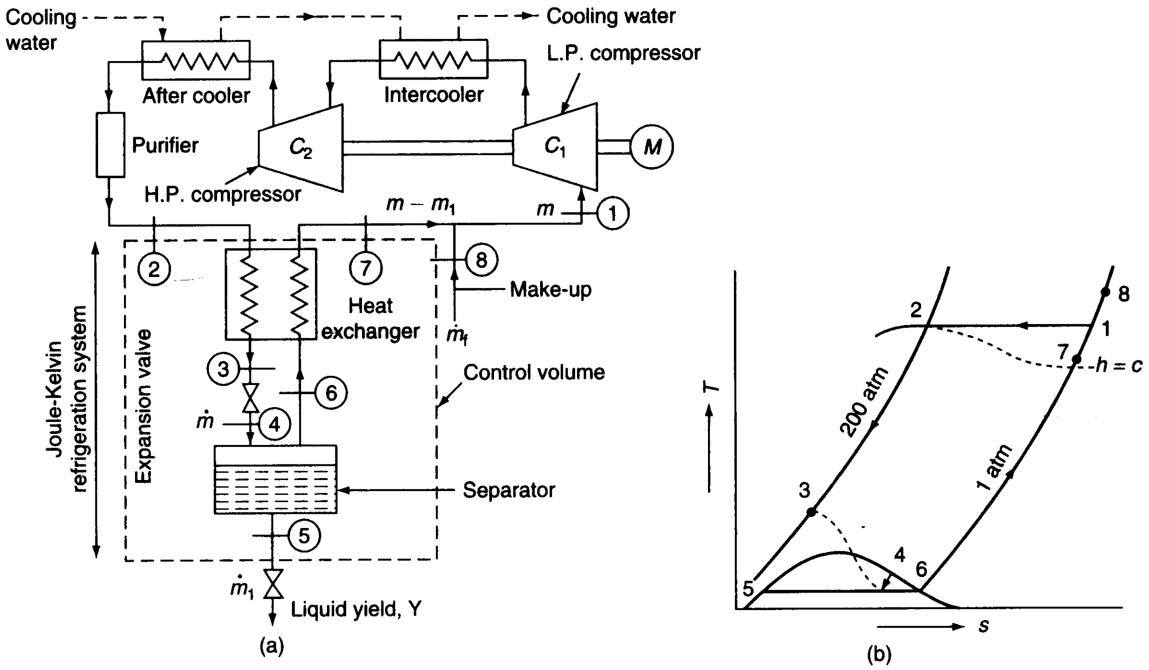
(a) (b)

Fig. 14.39 *Thermodynamic cycle for bootstrap system*

expansion through the throttle valve may yield a temperature decrease only when the temperature before throttling is below the maximum inversion temperature.

14.11.1 Linde–Hampson System for Liquefaction of Air

In this system, Joule-Kelvin effect is utilized for cooling, and ultimately, liquefying the air. The schematic diagram and the *T-s* diagram are shown in Fig. 14.40. Ideally, the compression would be isothermal as shown on the *T-s* diagram. A two-stage compressor with intercooling and aftercooling is shown. The *yield*, *Y*, of the system is defined as the ratio of the mass of liquid produced to the mass of gas compressed. The energy required per unit mass of liquid produced is known as the *specific work* consumption, *W*.



(a) (b)

Fig. 14.40 *Linde-hampson cycle for air liquefaction*

The theoretical yield, assuming perfect insulation, can be determined by a mass and energy balance for the control volume (Joule-Kelvin refrigeration system) as shown in Fig. 14.40. Let $\dot{m}_f$ be the rate at which liquid air is produced (the same given to the system as make-up), and $\dot{m}$ the rate at which air is compressed and then expanded. Then the yield is

$$Y = \frac{\dot{m}_f}{\dot{m}}$$

and the energy balance gives

$$\dot{m}h_2 - \dot{m}_f h_5 - (\dot{m} - \dot{m}_f)h_7 = 0$$

$$\therefore \quad \dot{m}(h_2 - h_7) - \dot{m}_f(h_5 - h_7) = 0$$

$$Y = \frac{\dot{m}_f}{\dot{m}} = \frac{h_2 - h_7}{h_5 - h_7}$$

$$\therefore \quad Y = \frac{h_7 - h_2}{h_7 - h_5} \tag{14.6}$$

No yield is thus possible unless h_7 is greater than h_2. The energy balance for the compressor gives

$$\dot{m}h_1 + W_c = \dot{m}h_2 + Q_R$$

Where Q_R is the heat loss to the surroundings from the compressor

$$\therefore \quad \frac{W_c}{\dot{m}} = T_1(s_1 - s_2) - (h_1 - h_2)$$

This is the *minimum work requirement.*

Specific work consumption, W

$$= \frac{W_c}{\dot{m}} \times \frac{\dot{m}}{\dot{m}_f} = \frac{W_c}{\dot{m}}\frac{1}{Y} = \frac{h_7 - h_5}{h_7 - h_2}\left[T_1(s_1 - s_2) - (h_1 - h_2)\right]$$

14.11.2 Claude System of Air Liquefaction

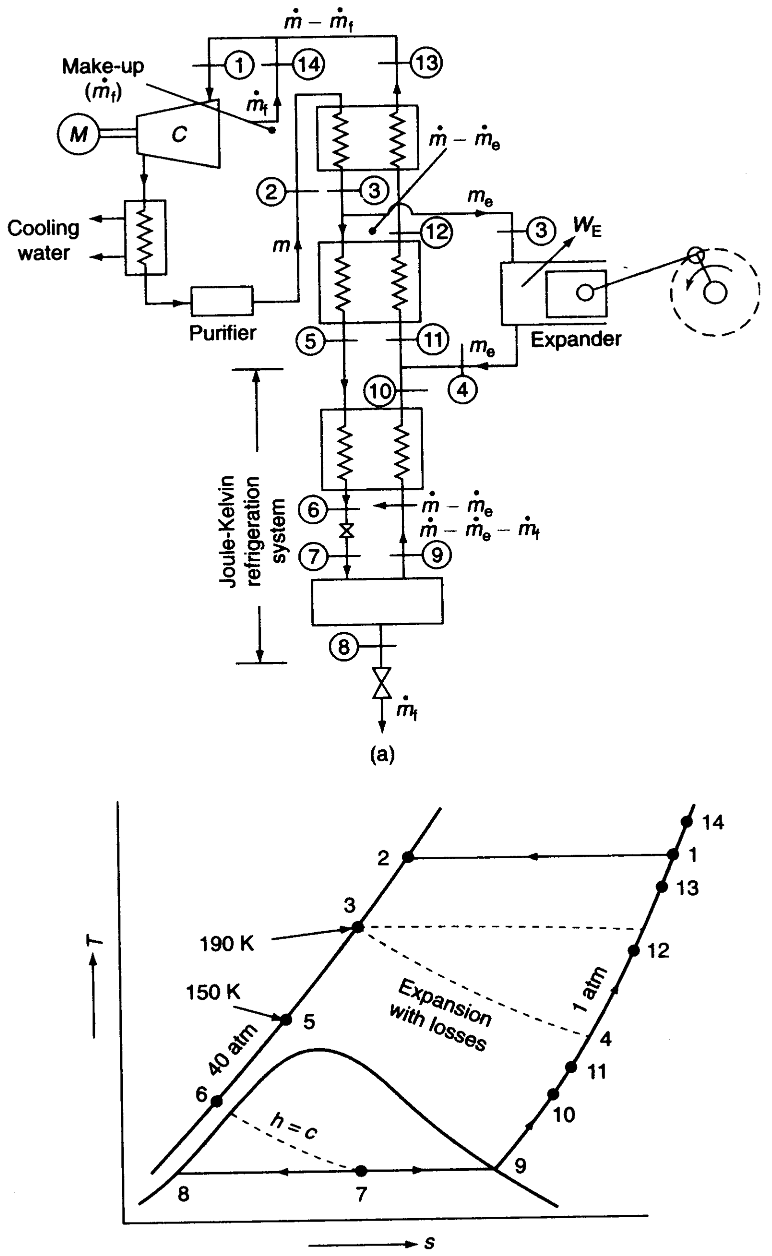
In the Claude system, energy is removed from the gas stream by allowing it to do some work in an expander. The flow and *T-s* diagrams are given in Fig. 14.41.

The gas is first compressed to pressures of about 40 atm and then passed through the first heat exchanger. Approximatly 80% of the gas is then diverted from the main stream, expanded through an expander, and reunited with the return stream below the second heat exchanger. The stream to be liquefied continues through the second and third heat exchangers, and is finally expanded through an expansion valve to the liquid receiver. The cold vapour from the liquid receiver is returned through the heat exchangers to cool the incoming gas.

The yield and the specific work consumption may be computed by making the mass and energy balance as in the Linde-Hampson system.

14.12 PRODUCTION OF SOLID ICE

Dry ice is used for low temperature refrigeration, such as to preserve ice cream and other perishables. The property diagram of CO_2 on the *p-h* coordinates is given in Fig. 14.42. The schematic diagram of producing solid CO_2 and the corresponding *p-h* diagram are shown in Fig. 14.43 and Fig. 14.44 respectively.



(a)

(b)

Fig. 10.41 *Claude cycle for air liquefaction*

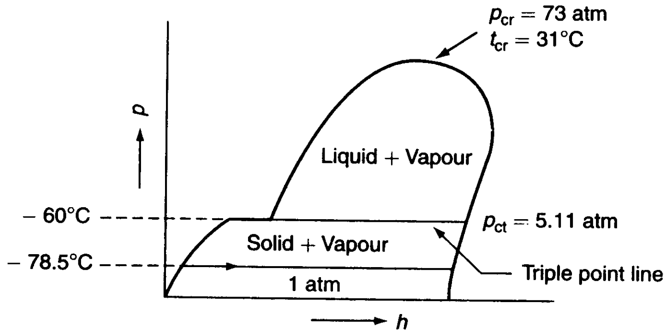


Fig. 14.42 p-h diagram of CO_2

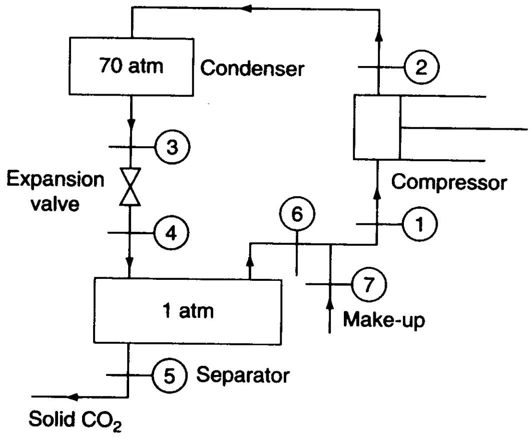


Fig. 14.43 Production of dry ice-flow diagram

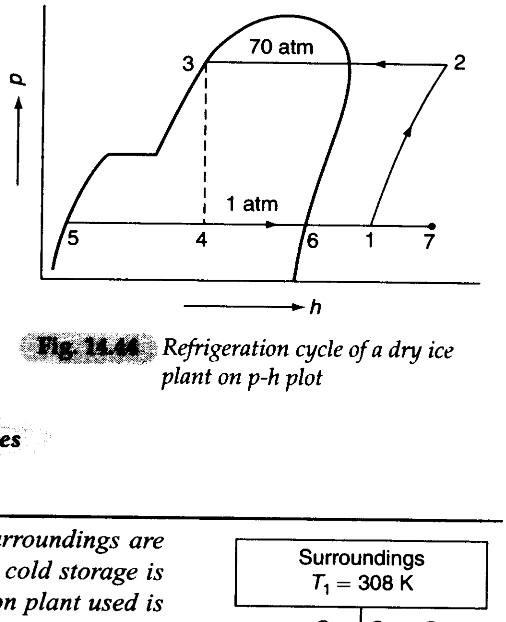


Fig. 14.44 Refrigeration cycle of a dry ice plant on p-h plot

Solved Examples

Example 14.1

A cold storage is to be maintained at – 5°C while the surroundings are at 35°C. The heat leakage from the surroundings into the cold storage is estimated to be 29 kW. The actual COP of the refrigeration plant used is one-third that of an ideal plant working between the same temperatures. Find the power required (in kW) to drive the plant.

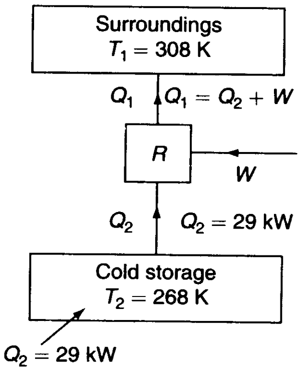


Fig. Ex. 14.1

Solution $$\text{COP (Ideal)} = \frac{T_2}{T_1 - T_2} = \frac{268}{308 - 268} = 6.7$$

$\therefore$ $\quad$ $\text{Actual COP} = 1/3 \times 6.7 = 2.23 = \frac{Q_2}{W}$

$\therefore$ $\quad$ Power required to drive the plant (Fig. Ex. 14.1)

$$W = \frac{Q_2}{2.23} = \frac{29}{2.23} = \mathbf{13\ kW}$$

Example 14.2

A refrigerator uses R-134a as the working fluid and operates on an ideal vapour compression cycle between 0.14 MPa and 0.8 MPa. If the mass flow rate of the refrigerant is 0.06 kg/s, determine (a) the rate of heat removal from the refrigerated space, (b) the power input to the compressor, (c) the heat rejection rate in the condenser, and (d) the COP.

Solution From the R-134a tables, the enthalpies at the four states (Fig. Ex. 14.2) are:

$h_1 = 236.04$ kJ/Kg

$s_1 = 0.9322$ kJ/kg K $= s_2$

For $p_2 = 0.8$ MPa, $s_2 = 0.9322$ kJ/kgK,

$h_2 = 272.05$ kJ/kg, $h_3 = h_4 = 93.42$ kJ/kg

$Q_2 = 0.06\ (236.04 - 93.42) = \mathbf{8.56\ kW}$

$W_c = 0.06\ (272.05 - 236.04) = \mathbf{2.16\ kW}$

$Q_1 = 0.06\ (272.05 - 93.42) = \mathbf{10.72\ kW}$

$$\text{COP} = \frac{Q_2}{W_c} = \frac{8.56}{2.16} = \mathbf{3.963}$$

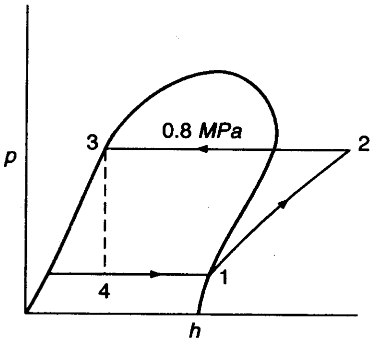


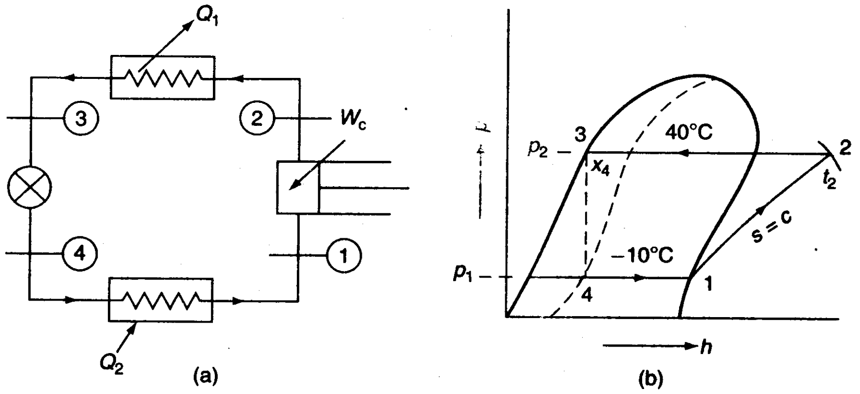
Fig. Ex. 14.2

Example 14.3

A simple R-12 plant is to develop 5 tonnes of refrigeration. The condenser and evaporator temperatures are to be 40°C and −10°C respectively. Determine (a) the refrigerant flow rate in kg/s, (b) the volume flow rate handled by the compressor in m³/s. (c) the compressor discharge temperature, (d) the pressure ratio, (e) the heat rejected to the condenser in kW, (f) the flash gas percentage after throttling, (g) the COP, and (h) the power required to drive the compressor.

How does this COP compare with that of a Carnot refrigerator operating between 40°C and −10°C?

Solution From the table of the thermodynamic properties of a saturated Refrigerant-12 (Fig. Ex. 14.3), $p_1 = (p_{\text{sat}})_{-10°\text{C}} = 2.1912$ bar, $h_1 = 183.19$ kJ/kg, $s_1 = 0.7019$ kJ/kg K, $v_1 = 0.077\text{m}^3/\text{kg}$,



(a) (b)

Fig. Ex. 14.3

$p_2 = (p_{sat})_{40°C} = 9.6066$ bar, and $h_3 = 74.59$ kJ/kg $= h_4$. From the superheated table of R-12, when $p_2 = 9.6066$ bar, and $s_2 = s_1 = 0.7019$ kJ/kg K, by interpolation, $t_2 = 48°C$, and $h_2 = 209.41$ kJ/kg. The capacity of the plant $= 5 \times 14{,}000 = 70{,}000$ kJ/h. If w is the refrigerant flow rate in kg/s

$$w(h_1 - h_4) = \frac{70.000}{3600} = 19.44 \text{ kW}$$

$$\therefore \quad w = \frac{19.44}{183.19 - 74.59} = \mathbf{0.18\ kg/s}$$

Volume flow rate $= w \cdot v_1 = 0.18 \times 0.077 =$ **0.0139 m³/s**

Compressor discharge temperature = **48°C**

$$\text{Pressure ratio } = \frac{p_2}{p_1} = \frac{9.6066}{2.1912} = \mathbf{4.39}$$

Heat rejected to the condenser $= w(h_2 - h_3)$

$$= 0.18\,(209.41 - 74.59) = \mathbf{24.27\ kW}$$

$$h_4 = h_f + x_4 h_{fg} = 26.87 + x_4 \times 156.31 = 74.59$$

$$x_4 = \frac{47.72}{156.31} = 0.305$$

$\therefore$ Flash gas percentage = **30.5%**

$$\text{COP} = \frac{h_1 - h_4}{h_2 - h_1} = \frac{183.19 - 74.59}{209.41 - 183.19}$$

$$= \frac{108.60}{26.22} = \mathbf{4.14}$$

Power required to drive the compressor

$$= w(h_2 - h_1) = 0.18 \times 26.22 = \mathbf{4.72\ kW}$$

$$\text{COP (Reversible)} = \frac{T_2}{T_1 - T_2} = \frac{263}{50} = 5.26$$

$$\therefore \frac{\text{COP(Vap. Comp. cycle)}}{\text{COP(Carnot cycle)}} = \frac{4.14}{5.26} = \mathbf{0.787}$$

Example 14.4

*A Refrigerant-*12 *vapour compression plant producing* 10 *tonnes of refrigeration operates with condensing and evaporating temperatures of* 35°C *and* –10°C *respectively. A suction line heat exchanger is used to subcool the saturated liquid leaving the condenser. Saturated vapour leaving the evaporator is superheated in the suction line heat exchanger to the extent that a discharge temperature of* 60°C *is obtained after isentropic compression. Determine* (*a*) *the subcooling achieved in the heat exchanger,* (*b*) *the refrigerant flow rate in kg/s,* (*c*) *the cylinder dimensions of the two-cylinder compressor, if the speed is* 900 *rpm, stroke-to-bore ratio is* 1.1, *and the volumetric efficiency is* 80% (*d*) *the COP of the plant, and* (*e*) *the power required to drive the compressor in kW.*

Solution From the p-h chart of R-12, the property values at the states, as shown in Fig. Ex. 14.4

$$h_3 = 882,\ h_2 = 1034$$
$$h_6 = 998,\ h_1 = 1008 \text{ kJ/kg}$$
$$v_1 = 0.084 \text{ m}^3\text{/kg}$$

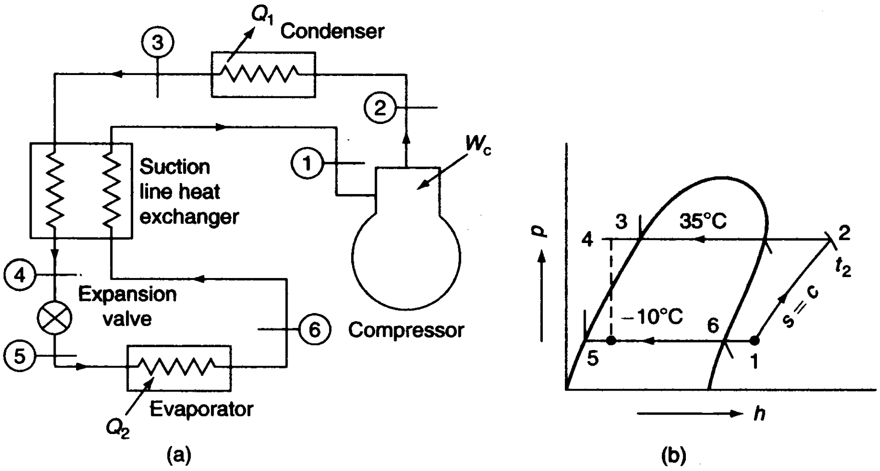


Fig. Ex. 14.4

$$h_3 - h_4 = h_1 - h_6$$
$$882 - h_4 = 1008 - 998 = 10$$
$$\therefore \quad h_4 = 872 \text{ kJ/kg}$$
$$\therefore \quad t_4 = 25°\text{C}$$

So 10°C subcooling is achieved in the heat exchanger.

Refrigeration effect $= h_6 - h_5 = 998 - 872 =$ **126 kJ/kg**

$$\therefore \quad \text{Refrigerant flow rate } \frac{10 \times 14000}{126} = \mathbf{1110\ kg/h = 0.31\ kg/s}$$

$$\text{Volume flow rate} = w \cdot v_1 = 1110 \times 0.084 = 93 \text{ m}^3\text{/h}$$

$$\text{Compressor displacement} = \frac{93}{0.8} = 116 \text{ m}^3\text{/h} = 1.94 \text{ m}^3\text{/min}$$

This is equal to $\frac{\pi}{4} D^2$ LNn

Where D = diameter

L = stroke

N = rpm

n = number of cylinders of the compressor.

$$\frac{\pi}{4} D^2 \times 1.1D \times 900 \times 2 = 1.94 \text{ m}^3\text{/min}$$

$$D^3 = 1250 \text{ cm}^3$$

or $$D = \mathbf{10.8\ cm} \quad \text{and} \quad L = \mathbf{11.88\ cm}$$

$$\text{COP} = \frac{h_6 - h_5}{h_2 - h_1} = \frac{126}{1034 - 1008} = \mathbf{4.85}$$

Power required to drive the compressor

$$= w(h_2 - h_1) = \frac{1110 \times 26}{3600} = \mathbf{8.02\ kW}$$

Example 14.5

A two-stage vapour compression refrigeration system with a direct contact heat exchanger (flash chamber) operates with ammonia as the refrigerant. The evaporator and condenser temperatures are –30 *and* 40°C *respectively. If the capacity of the plant is* 30 *tonnes of refrigeration, estimate the total work of compression and the COP. Had the compression been done in a single stage, what would have been the percentage increase in the work of compression? What is the percentage increase in the COP owing to the staging of the compression process?*

Solution Using tables for ammonia given in the appendix,

at 40°C, $p_2 = 1554.3$ kPA

at – 30°C, $p_1 = 119.5$ kPa

$\therefore \quad p_i = \sqrt{1554.3 \times 119.5} = 431$ kPa

$\therefore \quad h_1 = 1404.6\ s_2 = s_1,\ h_2 = 1574.3$

$h_3 = 1443.5\ s_4 = s_3,\ h_4 = 1628.1$

$h_5 = 371.7 = h_6,\ h_7 = 181.5$ hg

$$\therefore \quad \dot{m}_2 = \frac{3.89 \times 30}{1404.6 - 181.5} = \frac{116.7}{1223.1} = 0.0954 \text{ kg/s}$$

$$\dot{m}_1 = \dot{m}_2 \frac{h_2 - h_7}{h_3 - h_6} = 0.0954 \times \frac{1392.8}{1071.8} = 0.124 \text{ kg/s}$$

$$\dot{W}_c = \dot{m}_c (h_2 - h_1) + \dot{m}_1 (h_4 - h_3)$$

$$= 0.0954 \times 169.7 + 0.124 \times 184.6$$

$$= 16.19 + 22.89 = 39.08 \text{ kW}$$

$$\text{COP} = \frac{30 \times 3.89}{39.08} = 2.986$$

Single stage

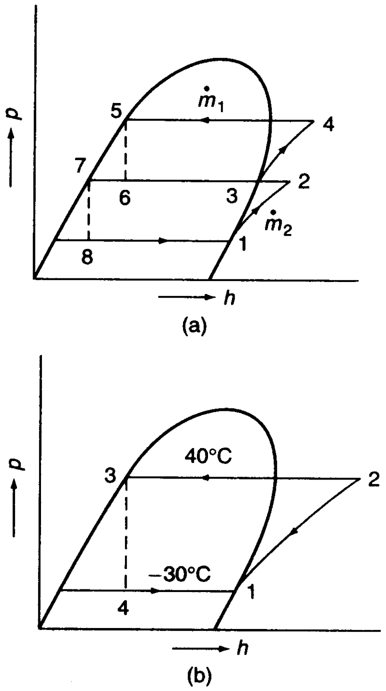
$h_1 = 1404.6 \quad h_2 = 1805.1$

$h_3 = 371.7 = h_4$

$$\dot{m} = \frac{30 \times 3.89}{1404.6 - 371.7} = \frac{116.7}{1032.9} = 0.113 \text{ kg/s}$$

$$W_c = \dot{m}(h_2 - h_1) = 0.113 \times 400.5 = 45.26 \text{ kW}$$

$$\therefore \quad \text{COP} = \frac{116.7}{45.26} = 2.578$$



(a)

(b)

Fig. Ex. 14.5

Increase in work of compression (for single stage)

$$= \frac{45.26 - 39.08}{39.08} \times 100 = \mathbf{15.81\%}$$

Increase in COP for 2-stage compression

$$= \frac{2.986 - 2.578}{2.578} \times 100 = \mathbf{15.82\%}$$

Example 14.6

*A vapour compression plant uses R-*134*a as refrigerant. The evaporator temperature is* –10°*C. The condenser pressure is* 7.675 *bar and there is no subcooling of the condensate. The flash chamber pressure is* 4.139 *bar and the dry saturated vapour bled off from the flash chamber is mixed with refrigerant from the LP compressor before entering the HP compressor. The liquid from the flash chamber is throttled before entering the evaporator. Assuming isentropic compression, determine* (*a*) *the COP of the plant,* (*b*) *the mass flow rate of refrigerant in the evaporator when the power input to the compressor is* 100 *kW.*

Solution From property tables of R-134a, the enthalpy of saturated liquid leaving the condenser at 30°C (p_{sat} = 7.675 bar) is

$$h_7 = h_8 = h_f + x_8 h_{fg}$$

$$\therefore \quad x_8 = \frac{140.96 - 113.29}{300.5 - 113.29} = 0.1478 \text{ kg/kg refrigerant}$$

Now, h_1 = 288.86 kJ/kg, s_1 = 1.7189 kJ/kg. K = s_2

By interpolation, h_2 = 303.468 kJ/kg

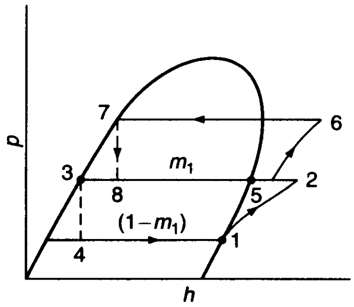


Fig. Ex. 14.6

By energy balance,

$$h_5 = (1 - m_1)\, h_2 + m_1 h_g$$

$$= (1 - 0.1478) \times 303.468 + 0.1478 \times 300.5$$

$$= 303.0295 \text{ kJ/kg}$$

By interpolation, $s_5 = s_6 = 1.7174$ kJ/kgK

$$\therefore \quad h_6 = 315.79 \text{ kJ/kg}$$

Since work input = 100 kW,

$$\dot{m}(h_6 - h_5) + (1 - m_1)\dot{m}(h_2 - h_1) = 100$$

$$\therefore \quad \dot{m}(315.79 - 303.0295) + (1 - 0.1478)\dot{m}(303.468 - 288.86) = 100$$

$$\therefore \quad \dot{m} = 3.966 \text{ kg/s}$$

Mass flow rate of refrigerant through the evaporator

$$= (1 - m_1)\dot{m} = (1 - 0.1478) \times 3.966$$

$$= 3.38 \text{ kg/s.}$$

Ans. (*b*)

$$\text{COP} = \frac{3.38(288.96 - 113.29)}{100} = 5.93$$

Ans. (*a*)

Example 14.7

In an aqua-ammonia absorption refrigerator system, heat is supplied to the generator by condensing steam at 0.2 *MPa,* 90% *quality. The temperature to be maintained in the refrigerator is* –10°C, *and the ambient temperature is* 30°C. *Estimate the maximum COP of the refrigerator.*

If the actual COP is 40% *of the maximum COP and the refrigeration load is* 20 *tonnes, what will the required steam flow rate be?*

Solution At 0.2 MPa, from the steam table

$$t_{\text{sat}} = 120.2°\text{C},\ h_{\text{fg}} = 2201.9 \text{ kJ/kg}$$

The maximum COP of the absorption refrigeration system is given by Eq. (14.4)

$$(\text{COP})_{\max} = \frac{(T_1 - T_2)T_R}{(T_2 - T_R)T_1}$$

where T_1 = generator temperature

$= 120.2 + 273 = 393.2$ K

T_2 = condenser and absorber temperature

$= 30 + 273 = 303$ K

T_R = evaporator temperature

$= -10 + 273 = 263$ K

$$\therefore \quad (\text{COP})_{\max} = \frac{(393.2 - 303) \times 263}{(303 - 263) \times 393.2} = \frac{90.2 \times 263}{40 \times 393.2} = 1.5$$

$\therefore$ Actual COP $= 1.5 \times 0.4 = 0.60$

Since $\text{COP} = \dfrac{Q_E}{Q_G}$

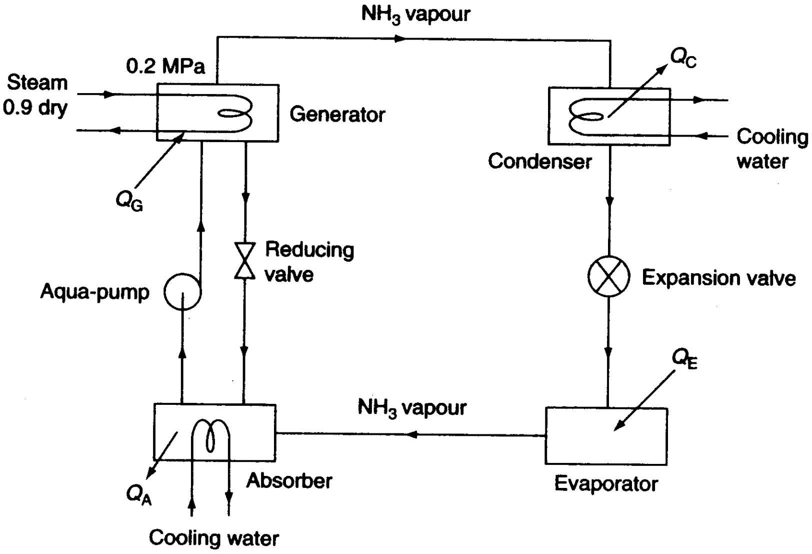


Fig. Ex. 14.7

$$Q_G = \frac{Q_E}{\text{COP}} = \frac{20 \times 14000}{0.60 \times 3600} = 129.6 \text{ kW}$$

Heat transferred by 1 kg of steam on condensation

$$= (h_f + xh_{fg}) - h_f = 0.9 \times 2201.9 = 1981.71 \text{ kJ/kg}$$

∴ Steam flow rate required

$$= \frac{129.6}{1981.71} = \mathbf{0.0654\ kg/s}$$

Example 14.8

In a steam-jet refrigeration system, the flash chamber is maintained at 5°C*. The quality of water vapour leaving the evaporator is* 0.98 *and the chilled water returns to the flash chamber at* 14°C *and the make-up water is available at* 30°C*. Estimate the COP of the system if the mass-flow rate of the chilled water is* 12 *kg/s, compressor efficiency is* 0.80 *and the condenser pressure is* 0.10 *bar.*

Solution From steam tables, at 14°C, $h_f = 58.62$ kJ/kg

at 5°C, $h_f = 20.93$ kJ/kg

at 30°C, $h_f = 125.73$ kJ/kg

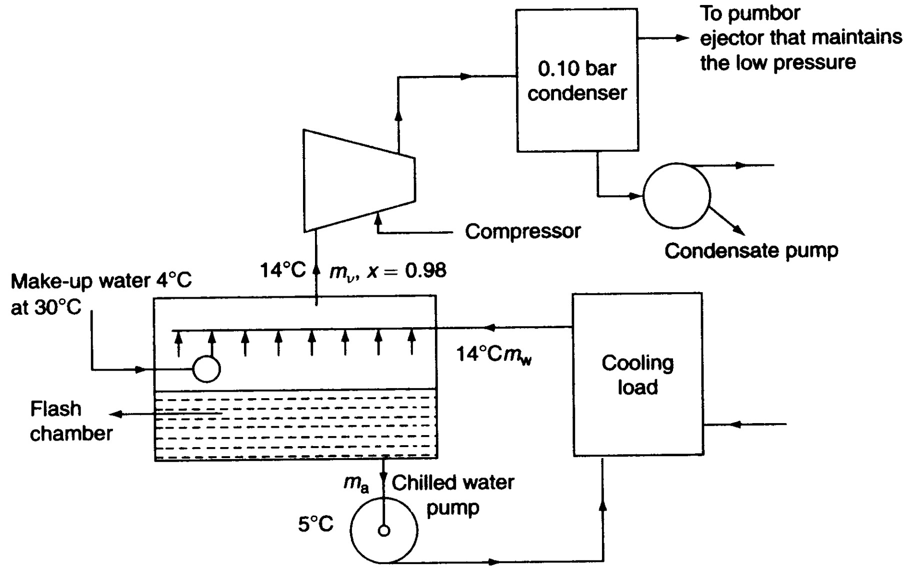
Enthalpy at water vapour at 5°C and 0.98 quality

$$h_v = 0.98 \times 2510.7 = 2460.49 \text{ kJ/kg}$$

$$\text{Refrigerating capacity} = \dot{m}_w (h_{w_i} - h_{w_o})$$

$$= 12(58.62 - 20.93)$$

$$= 452.28 \text{ kJ/s} / 3.5 = 129.22 \text{ TR}$$



[illegible]

By making an energy balance,

$$\dot{m}_w(h_{w_i} - h_{w_o}) = \dot{m}_\upsilon(h_{\upsilon_i} - h_{m,k})$$

where $h_{m,k}$ is the enthalpy of make-up water and $\dot{m}_\upsilon$ is the mass of vapour discharged from the evaporator/flash chamber.

$$\dot{m}_\upsilon = \frac{452.28}{2460.49 - 125.73} = 0.1937 \text{ kg/s}$$

For isentropic compression, the enthalpy of vapour leaving the compressor at 0.10 bar, $h_g = 2800$ kJ/kg

$$\text{Work input} = 0.1937\,(2800 - 2460.49)/0.8 = 82.204 \text{ kW}$$

$$\therefore \qquad \text{COP} = \frac{452.28}{82.204} = 5.5 \qquad \textit{Ans.}$$

Example 14.9

In an aircraft cooling system, air enters the compressor at 0.1 *MPa,* 4°C, *and is compressed to* 0.3 *MPa with an insentropic efficiency of* 72%. *After being cooled to* 55°C *at constant pressure in a heat exchanger the air then expands in a turbine to* 0.1 *MPa with an isentopic efficiency of* 78%. *The low temperature air absorbs a cooling load of* 3 *tonnes of refrigeration at constant pressure before re-entering the compressor which is driven by the turbine. Assuming air to be an ideal gas, determine the COP of the refrigerator, the driving power required, and the air mass flow rate.*

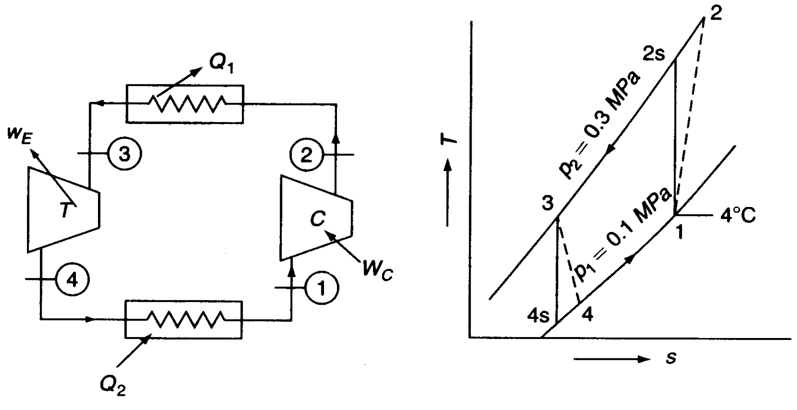
Solution Given: (Fig. Ex. 14.9)

$$T_1 = 277 \text{ K}, \; T_3 = 273 + 55 = 328 \text{ K}$$

$$\frac{T_{2s}}{T_1} = \left(\frac{p_2}{p_1}\right)^{(\gamma-1)/\gamma}$$

$$\therefore \qquad T_{2s} = 277(3)^{0.4/1.4} = 379 \text{ K}$$

$$T_{2s} - T_1 = 102 \text{ K}$$



(a) (b)

Fig. Ex. 14.9

$$\therefore \qquad T_2 - T_1 = \frac{102}{0.72} = 141.8\ \text{K}$$

$$\frac{T_{4s}}{T_3} = \left(\frac{p_2}{p_1}\right)^{(\gamma-1)/\gamma}$$

$$\therefore \qquad T_{4s} = 328(3)^{0.4/1.4} = \frac{328}{1.368} = 240\ \text{K}$$

$$T_3 - T_{4s} = 88\ \text{K}$$

$$\therefore \qquad T_3 - T_4 = 0.78 \times 88 = 68.6\ \text{K}$$

$$\therefore \qquad T_4 = 259.4\ \text{K}$$

Refrigerating effect = $c_p\,(T_1 - T_4) = 17.6\,c_p$ kJ/kg

Net work input = $c_p[(T_2 - T_1) - (T_3 - T_4)]$

$= c_p[141.8 - 68.6] = 73.2\,c_p$ kJ/kg

$$\text{COP} = \frac{17.6\,c_p}{73.2\,c_p} = \mathbf{0.24}$$

$$\text{Driving power required} = \frac{3 \times 14000}{0.24 \times 3600} = \mathbf{48.6\ kW}$$

$$\text{Mass flow rate of air} = \frac{3 \times 14000}{1.005 \times 17.6} = 2374.5\ \text{kg/h} = \mathbf{0.66\ kg/s}$$

Example 14.10

A vapour-compression heat pump system uses R-12 as the working fluid. The refrigerant enters the compressor at 2.4 bar. 0°C with a volumetric flow rate of 0.6 m³/min. Compression is adiabatic to 9 bar, 60°C and the saturated liquid exits the condenser at 9 bar. Determine (a) the power input to the compressor, (b) the heating capacity of the system, (c) the coefficient of performance, (d) the isentropic compressor efficiency.

Solution

At $p_1 = 2.4$ bar, $T_1 = 0$°C

$h_1 = 188.99$ kJ/kg

$s_1 = 0.7177$ kJ/kg K

$v_1 = 0.0703$ m³/kg

At $p_2 = 9$ bar, $T_2 = 60$°C

$h_2 = 219.37$ kJ/kg

$h_2s = 213.27$ kJ/kg

At $p_2 = 9$ bar, sat. liquid

$h_3 = 71.93$ kJ/kg $= h_4$

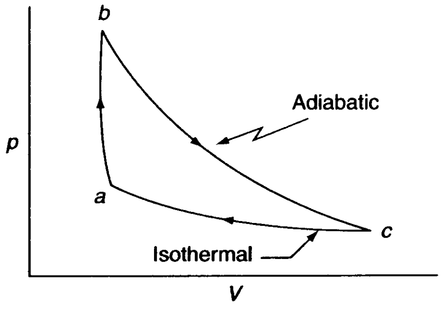


Fig. Ex. 14.10

$$\dot{m} = \frac{A_1V_1}{v_1} = \frac{0.6}{60}\frac{m^3}{s} \times \frac{1}{0.0703}\,\text{kg m}^3 = 0.1422\ \text{kg/s}$$

(a) Power input $\dot{W}_c = \dot{m}(h_2 - h_1)$

$= 0.1422\,(219.37 - 188.99) = 4.32$ kW *Ans.*

(b) Heating capacity, $\dot{Q}_1 = \dot{m}(h_2 - h_3)$

$= 0.1422\,(219.37 - 71.93) = 20.97$ kW $= 5.963$ tonnes *Ans.*

(c) $\text{COP} = \dfrac{\dot{Q}_1}{\dot{W}_c} = \dfrac{20.97}{4.32} = 4.854$ *Ans.*

(d) $\eta_{is} = \dfrac{h_{2s} - h_1}{h_2 - h_1} = \dfrac{213.27 - 188.99}{219.37 - 188.99} = 0.799$ or 79.9% *Ans.*

Example 14.11

In air-refrigeration system working on reversed Brayton cycle, the temperature of air at entrance to compressor (pressure ratio = 4, efficiency = 0.8) is 275 K and the inlet pressure is 1 bar. The pressure loss in the cooler is 0.1bar and in the cold chamber it is 0.08 bar. The temperature of air at turbine (efficiency = 0.85) inlet is 310 K. Estimate the pressure ratio for the turbine and the COP of the cycle.

Solution $T_1 = 275$ K, $T_3 = 310$ K

$\dfrac{p_2}{p_1} = 4, p_1 = 1$ bar

$T_{2s} = T_1\,(p_2/p_1) = 275 \times 40.286 = 408.81$ K

$T_2 = T_1 + (T_{2s} - T_1)\,\eta_c = 442.26$ K

$p_3 = p_2 - pr$ loss in the cooler $= 4 - 0.1 = 3.9$ bar

$p_4 = p_1 + pr$ loss in the cold chamber $= 1 + 0.08$

$= 1.08$ bar

∴ Pressure ratio for the turbine $= \dfrac{3.9}{1.08} = 3.611$ *Ans.*

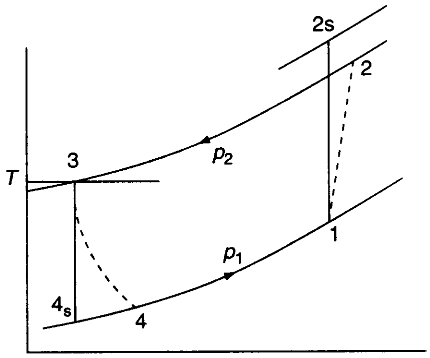


Fig. Ex. 14.11

$$\frac{T_3}{T_{4s}} = (p_3/p_{4s})^{0.286} = (3.611)^{0.286} = 1.4437$$

$T_{4s} = 214.72$ K

$T_4 = T_3 - (T_3 - T_{4s})\eta_t = 310 - (310 - 214.72) \times 0.85 = 229.015$ K

$$\text{COP} = \frac{T_1 - T_4}{(T_2 - T_3) - (T_1 - T_4)} = \frac{275 - 229.015}{(442.26 - 310) - (275 - 229.015)}$$

$= 0.533$ *Ans.*

Example 14.12

The cabin of a jet plane having a cooling load of 60 kW is to be maintained at 1 bar, 20°C. The aircraft is flying at a speed of 90 km/h in air where the pressure is 0.35 bar and temperature 255 K. The air flows through the diffuser of efficiency 85% and a compressor of pressure ratio 6 and efficiency 85% before entering the air cooler having an effectiveness of 0.9. The pressure drop in the air cooler is 0.08 bar. The air should leave the turbine having an efficiency of 88% at 1.08 bar. Determine the mass flow rate of air flowing through the cooling system and the COP.

Solution With reference to Fig. 14.37,

$$p_1 = 0.35 \text{ bar}, T_1 = 255 \text{ K}$$

Speed of aircraft, $V = \dfrac{900,000}{36,00} = 250$ m/s

Stagnation temperature, $T_2' = T_2 = T_1 + \dfrac{V^2}{2c_p}$

$\therefore$ $T_2' = T_2 = 255 + \dfrac{250^2}{2 \times 1.005} = 286.1 \text{ K}$

Stagnation pressure, $p_2' = p_1 \left(\dfrac{T_2'}{T_1}\right)^{\frac{\gamma}{\gamma-1}} = 0.35 \left(\dfrac{286.1}{2.55}\right)^{3.5} = 0.523$ bar

Actual pressure, $p_2 = p_1 + 0.85\,(p_2' - p_1) = 0.497$ bar

$$p_3 = 6p_2 = 6 \times 0.497 = 2.982 \text{ bar}$$

$$T_3' = T_2 \left(\frac{p_3}{p_2}\right)^{\frac{\gamma-1}{\gamma}} = 286.1\,(6)^{0.286} = 477.6 \text{ K}$$

$$T_3 = T_2 + \frac{T_3' - T_2}{\eta_c} = 286.1 + \frac{477.6 - 286.1}{0.85} = 511.28 \text{ K}$$

Power required for compressor work per kg

$$= c_p(T_3 - T_2) = 1.005\,(511.28–286.1) = 226.3 \text{ kJ/kg}$$

Pressure at turbine inlet, $p_4 = p_3 -$ losses in cooler

$$= 2.982 - 0.08 = 2.902 \text{ bar}$$

Since the air is cooled by the air coming out of the diffuser, the effectiveness

$$\varepsilon = \frac{T_3 - T_4}{T_3 - T_2}$$

$\therefore$ $T_4 = T_3 - \varepsilon\,(T_3 - T_2)$

$$= 511.28 - 0.9\,(511.28 - 286.1) = 308.6 \text{ K}$$

$$T_5' = T_4 / (p_4 / p_5)^{0.286} = 308.6 / (2.902 / 1.08)^{0.286} = 232.6 \text{ K}$$

$$T_5 = T_4 - \frac{T_4 - T_5'}{\eta_t} = 308.6 - \frac{308.6 - 232.6}{0.88} = 241.75 \text{ K}$$

Refrigerating (cooling) effect $= c_p\,(T_{\text{cabin}} - T_5)$

$$= 1.005\,(293 - 241.75) = 51.5 \text{ kJ/kg}$$

Cooling load = 60 kW = $\dot{m} \times 51.5$

where $\dot{m}$ = mass flow rate of air through the cooling system $= \dfrac{60}{51.5} = 1.165$ kg/s *Ans.*

Power required to drive the compressor

$$= \dot{m}(h_3 - h_2) = 1.165 \times 226.3 = 263.55 \text{ kW}$$

$$\therefore \quad \text{COP} = \frac{60}{263.55} = 0.23$$ *Ans.*

Review Questions

14.1 What is refrigeration ? How is (a) ice and (b) dry ice used for the purpose of refrigeration?

14.2 Explain the vapour compression cycle with the help of flow, *T–s* and *p–h* diagrams. Can this cycle be reversible? If not, why?

14.3 What is superheat horn?

14.4 What do you understand by dry and wet compression? Which is preferred and why?

14.5 What is refrigerating effect?

14.6 Explain the effect of evaporator pressure on the performance of a vapour compression refrigeration plant.

14.7 Estimate the effect of suction vapour superheat on the vapour compression cycle.

14.8 What is the effect of liquid subcooling on the vapour compression cycle?

14.9 What is a tonne of refrigeration?

14.10 Explain the effect of superheat and subcooling on the vapour compression cycle.

14.11 How does the actual vapour compression cycle differ from the ideal one?

14.12 What is a suction line heat exchanger? When is it used?

14.13 What are the expansion devices used in vapour compression plant? When are they used?

14.14 What are the different types of compressors used in vapour compression plants and what are their applications?

14.15 What is a multistage vapour compression plant? When is it used?

14.16 What is a flash chamber? What is its advantage?

14.17 What are the most widely used refrigerants?

14.18 How are refrigerants numbered?

14.19 Why is the use of halogenated hydrocarbons as refrigerants now discouraged?

14.20 What are the effects of CFCs on the environment? How do they affect the ozone layer?

14.21 What is ODP? Why has R-22 less ODP than R-12?

14.22 What are the parameters to be considered in the selection of a refrigerant?

14.23 What do you understand by cascade refrigeration system? Explain it with the help of flow and *T-s* diagrams.

14.24 Evaluate ammonia as a refrigerant.

14.25 What is an absorption refrigeration cycle? How does it differ from a vapour compression cycle?

14.26 How is the refrigerant liberated from the absorbent in an aqua-ammonia system?

14.27 What are the functions of the analyzer and the rectifier?

14.28 What is the advantage of using a suction line heat exchanger in an absorption refrigeration system?

14.29 In a lithium bromide-water absorption system, which is the refrigerant? What is its limitation?

14.30 Derive the expression for the maximum COP of an absorption refrigeration system.

14.31 With a neat sketch explain the mechanism of operation of an electrolux refrigerator.

14.32 Evaluate water as a refrigerant. Explain the principle of steam-jet refrigeration with a neat sketch. What are its applications?

14.33 How does a heat pump upgrade low grade reject heat?

14.34 How can a heat pump be used for (a) space heating (b) year-round airconditioning?

14.35 How is a reversed Brayton cycle used for refrigeration?

14.36 Why is the COP of a gas cycle refrigeration system low?

14.37 Explain the flow and *T-s* diagrams of a simple aircraft refrigeration cycle.

14.38 What is a bootstrap system? How is it different from the simple aircraft refrigeration cycle?

14.39 Why is gas cycle refrigeration preferred in aircraft?

14.40 What is the principle of the Linde-Hampson system for liquefaction of air?

14.41 Derive the expressions of liquid yield and the minimum work requirement in a Linde-Hampson system.

14.42 How does Claude cycle differ from a Linde-Hampson cycle in the context of the liquefaction of air?

14.43 With the help of flow and *p–h* diagrams, explain how dry ice is produced.

Problems

14.1 A refrigerator using R-134*a* operates on an ideal vapour compression cycle between 0.12 and 0.7 MPa. The mass flow of refrigerant is 0.05 kg/s. Determine (a) the rate of heat removal from the refrigerated space, (b) the power input to the compressor, (c) the heat rejection to the environment, and (d) the COP.

Ans. (a) 7.35 kW, (b) 1.85 kW, (c) 9.20 kW, (d) 3.97

14.2 A Refrigerant-12 vapour compression cycle has a refrigeration load of 3 tonnes. The evaporator and condenser temperatures are −20°C and 40°C respectively. Find (a) the refrigerant flow rate in kg/s, (b) the volume flow rate handled by the compressor in m^3/s, (c) the work input to the compressor in kW. (d) the heat rejected in the condenser in kW, and (e) the isentropic discharge temperature.

If there is 5 C deg. of superheating of vapour before it enters the compressor, and 5 C deg. subcooling of liquid before it flows the through the expansion valve, determine the above quantities.

14.3 A 5 tonne R-12 plant maintains a cold store at −15°C. The refrigerant flow rate is 0.133kg/s. The vapour leaves the evaporator with 5 C deg. superheat. Cooling water is available in plenty at 25°C. A suction line heat exchanger subcools the refrigerant before throttling. Find (a) the compressor discharge temperature, (b) the COP, (c) the amount of subcooling in C deg., and (d) the cylinder dimensions of the compressor, if the speed is 900 rpm, stroke-to-bore ratio is 1.2, and volumetric efficiency is 95 %.

Allow approximately 5°C temperature difference in the evaporator and condenser.

Ans. (a) 66°C, (b) 4.1 (c) 125°C, (d) 104.5 mm, 125mm

14.4 A vapour compression refrigeration system uses R-12 and operates between pressure limits of 0.745 and 0.15 MPa. The vapour entering the compressor has a temperature of −10°C and the liquid leaving the condenser is at 28°C. A refrigerating load of 2 kW is required. Determine the COP and the swept volume of the compressor if it has a volumetric efficiency of 76% and runs at 600 rpm.

Ans. 4.15, 243 cm^3

14.5 A food-freezing system requires 20 tonnes of refrigeration at an evaporator temperature of −35°C and a condenser temperature of 25°C. The refrigerant, R-12, is subcooled 4°C before entering the expansion valve, and the vapour is superheated 5°C before leaving the evaporator. A six-cylinder single-acting compressor with stroke equal to bore is to be used, operating at 1500 rpm. Determine (a) the refrigerating effect, (b) the refrigerant flow rate, (c) the theoretical piston displacement per sec, (d) the theoretical power required in kW, (e) the COP, the (f) the heat removed in the condenser, and (g) the bore and stroke cf the compressor.

14.6 A R-12 vapour compression refrigeration system is operation at a condenser pressure of 9.6 bar and an evaporator pressure of 2.19 bar. Its refrigeration capacity is 15 tonnes. The values of enthalpy at the inlet and outlet of the evaporator are 64.6 and 195.7 kJ/kg. The specific volume at inlet to the reciprocating compressor is 0.082 m^3/kg. The index of compression for the compressor is 1.13. Determine: (a) the power input in kW required for the compressor, and (b) the COP. Take 1 tonne of refrigeration as equivalent to heat removal at the rate of 3.517 kW.

Ans. (a) 11.57 kW, (b) 4.56

14.7 A refrigeration plant produces 0.139 kg/s of the ice at −5°C from water at 30°C. If the power required to drive the plant is 22 kW, determine the capacity of the ice plant in tones and the actual COP (c_p of ice = 2.1 kJ/kg K).

14.8 An air conditioning unit using R-12 as a refrigerant is mounted in the window of a room. During steady operation 1.5 kW of heat is transferred from the air in the room to evaporator coils of R-12. If this air is at 22°C and the temperature of R-12 in the evaporator is 15°C, determine (a) the refrigerant flow rate, and (b) the minimum power required to drive the compressor if the outside air is at 43°C and the temperature of the refrigerant during condensation is 50°C.

14.9 In a solar energy operated aqua-ammonia absorption refrigeration system, water is cooled at the rate of 10 kg/s from 38°C to 13°C. If the incident solar energy is 640 W/m^2 and the COP of the system is 0.32, estimate the area of the solar collector needed.

14.10 A gas refrigerating system using air as a refrigerant is to work between -12°C and 27°C using an ideal reversed Brayton cycle of pressure ratio 5 and minimum pressure 1 atm, and to maintain a load of 10 tonnes. Find (a) the COP, (b) the air flow rate in kg/s, (c) the volume flow rate entering the compressor in m^3/s, and (d) the maximum and minimum temperatures of the cycle.

14.11 An open cycle (Brayton) aircraft cabin cooler expands air at 27°C through a turbine which is 30% efficient from 2 to 1 atm. The cabin temperature is not to exceed 24°C. Estimate the mass flow rate of air required (kg/s) for each tonne of cooling.

14.12 Determine the ideal COP of an absorption refrigerating system in which the heating, cooling, and refrigeration take place at 197°C, 17°C, and -3°C respectively. Ans. 5.16

14.13 Heat pump is to use an R-12 cycle to operate between outdoor air at -1°C and air in a domestic heating system at 40°C. The temperature difference in the evaporator and the condenser is 8°C. The compressor efficiency is 80%, and the compression begins with saturated vapour. The expansion begins with saturated liquid. The combined efficiency of the motor and belt drive is 75%. If the required heat supply to the warm air is 43.6 kW, what will be the electrical load in kW?

14.14 An ideal (Carnot) refrigeration system operates between the temperature limits of -30°C and 25°C. Find the ideal COP and the power required from an external source to absorb 3.89 kW at high temperature.

14.15 A heat pump that operates on the ideal vapour compression cycle with R-134*a* is used to heat a house and maintain it at 20°C, using underground water at 10°C as the heat source. The house is losing heat at a rate of 75 MJ/h. The evaporator and condenser pressures are 320 and 800 kPa respectively. Determine the power input to the heat pump and the electric power saved by using a heat pump instead of a resistance heater.
Ans. 2.27 kW, 18.56 kW

14.16 An ammonia-absorption system has an evaporator temperature of -12°C and a condenser temperature of 50°C. The generator temperature is 150°C. In this cycle, 0.42 kJ is transferred to the ammonia in the evaporator for each kJ transferred to the ammonia solution in the generator from the high temperature source.

It is desired to compare the performance of this cycle with the performance of a similar vapour compression cycle. For this, it is assumed that a reservoir is available at 150°C, and that heat is transferred from this reservoir to a reversible engine which rejects heat to the surroundings at 25°C. This work is then used to drive an ideal vapour compression system with ammonia as the refrigerant. Compare the amount of refrigeration that can be achieved per kJ from the high temperature source in this case with the 0.42 kJ that can be achieved in the absorption system.

14.17 An R-12 plant is to cool milk from 30°C to 1°C involving a refrigeration capacity of 10 tonnes. Cooling water for the condenser is available at 25°C and 5 C deg. rise in its temperature is allowable. Determine the suitable condensing and evaporating temperatures, providing a minimum of 5 C deg. differential, and calculate the theoretical power required in kW and the cooling water requirement in kg/s. Also, find the percentage of flash gas at the end of the throttling. Assume a 2 C deg. subcooling in the liquid refrigerant leaving the condenser.

14.18 The following data pertain to an air cycle refrigeration system for an aircraft.

Capacity 5 tonnes
Cabin air inlet temperature 15°C and outlet temperature 25°C
Pressure ratio across the compressor 5

The aircraft is flying at 0.278 km/s where the ambient conditions are 0°C and 80 kPa. Find the COP and the cooling effectiveness of the exchanger. The cabin is at 0.1 MPa, and the cooling turbine powers the circulating fans.

14.19 A water cooler supplies chilled water at 7°C when water is supplied to it at 27°C at a rate of 0.7 litres/min., while the power consumed amounts to 200 watts. Compare the COP of this refrigeration plant with that of the ideal refrigeration cycle for a similar situation.

14.20 A refrigerating plant of 8 tonnes capacity has an evaporation temperature of – 8°C and condenser temperature of 30°C. The refrigerant, R-12, is subcooled 5°C before entering the expansion valve and the vapour is superheated 6°C before leaving the evaporator coil. The compression of the refrigerant is isentropic. If there is a suction pressure drop of 20 kPa through the valves, and discharge pressure drop of 10 kPa through the valves, determine the COP of the plant, theoretical piston displacement per sec. and the heat removal rate in the condenser.

14.21 An ultra-low-temperature freezer system employs a coupling of two vapour compression cycles of R-12 and R-13, as shown in Fig. P. 14.21. The states and properties of both cycles are shown on the *T–s* plot. Determine the ratio of the circulation rates of the two refrigerants, w_1/w_2 and the overall COP. How does this COP compare with the Carnot COP operating between 42°C and −70°C?

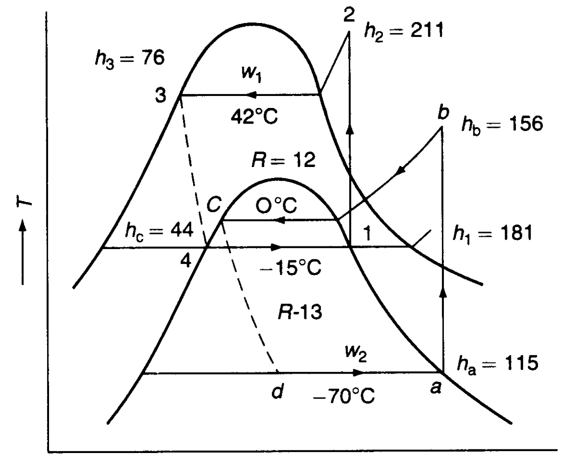


Fig. P. 14.21

14.22 Derive an expression for the COP of an ideal gas refrigeration cycle with a regenerative heat exchanger. Express the result in terms of the minimum gas temperature during heat rejection (T_h) maximum gas temperature during heat absorption (T_l), and pressure ratio for the cycle (p_2/p_1).

$$\text{Ans. COP} = \frac{T_l}{T_h r_p^{(\gamma-1)/\gamma} - T_l}$$

14.23 Large quantities of electrical power can be transmitted with relatively little loss when the transmission cable is cooled to a superconducting temperature. A regenerated gas refrigeration cycle operating with helium is used to maintain an electrical cable at 15 K. If the pressure ratio is 10 and heat is rejected directly to the atmosphere at 300 K, determine the COP and the performance ratio with respect to the Carnot cycle.

Ans. 0.02, 0.38

14.24 A 100 tonne refrigerating plant using R-12 has a condensing temp. of 35°C and an evaporating temp. of 5°C. Calculate the power requirement of the compressor in kW, the volume flow rate of compressor and the compressor displacement volume if the volumetric effy. is 75% and the mechanical efficiency is 80%.

If a liquid suction heat exchanger is installed in the above plant which subcools the condensed refrigerant to 30°C, what would be the refrigeration capacity of the plant and the power required by the compressor?

14.25 A heat pump installation is proposed for a home heating unit with an output rated at 30 kW. The evaporator temperature is 10°C and the condenser pressure is 0.5 bar. Using an ideal vapour cycle, estimate the power required to drive the compressor if steam/water mixture is used as the working fluid, the COP and the mass flow rate of the fluid. Assume saturated vapour at compressor inlet and saturated liquid at condenser outlet. Ans. 8.0 kW, 3.77, 0.001012 kg/s

14.26 A 100 tonne low temperature R-12 system is to operate on a 2-stage vapour compression refrigeration cycle with a flash chamber, with the refrigerant evaporating at −40°C, an intermediate pressure of 2.1912 bar, and condensation at 30°C. Saturated vapour enters both the compressors and saturated liquid enters each expansion valve. Consider bothe stages of compression to be isentropic. Determine:

(a) The flow rate of refrigerant handled by each compressor. (b) the total power required to drive the compressor, (c) the piston displacement of each compressor, if the clearance is 2.5% for each machine, and (d) the COP of the system, (e) What would have been the refrigerant flow rate, the total work of compression, the piston displacement in each compressor and the compressor and the COP, if the compression had occurred in a single stage?

Ans. (a) 2.464, 3.387 kg/s, (b) 123 kW, (c) 0.6274, 0.314 m^3/s, (d) 2.86, (e) 3.349 kg/s, 144.54 kW, 1.0236 m^3/s, 2.433

14.27 A vapour compression plant uses R-134a as refrigerant. The evaporator temperature is −10°C. The condenser pressure is 7.675 bar and there is no subcooling of the condensate. The flash chamber pressure is 4.139 bar and the dry saturated vapour bled off from the flash chamber is mixed with the refrigerant from the LP compressor before entering the HP compressor. The liquid from the flash chamber is throttled before entering the evaporator. Assuming isentropic compression, calculate (a) COP of the plant (b) mass flow of refrigerant in the evaporator when the power input to the plant is 100 kW. Ans. (a) 5.93, (b) 3.38 kg/s

14.28 The working fluid in a heat pump installation is ammonia. The ammonia after evaporation to a dry saturated state at 2°C is compressed to a pressure of 12.38 bar at which it is cooled and condensed to a saturated liquid state. It then passes through a throttle valve and returns to the evaporator. Calculate the COP assuming that the isentropic efficiency of the compressor is 0.85. Ans. 7.88

14.29 (a) A R-12 simple saturation cycle operates at temperatures of 35°C and −15°C for the condenser and evaporator respectively. Determine the COP and power input per TR.

(b) If a liquid-vapour heat exchanger is installed in the system, with the temperature of the vapour leaving the heat exchanger at 15°C, what is the change in COP and power input per TR.

Ans. (a) 4.09, 0.865 kW/TR, (b) +2.56%, −2.5%

14.30 The cabin of a jet plane has an air-cooling system operating on a simple cycle. It is maintained at 25°C. The ambient air condition at the altitude of flight is 0.35 bar, −15°C. The pressure ratio of the compressor is 3. The plane is flying at a speed of 1000 km/h. The pressure drop in the air cooler is 0.1 bar. Air leaves the cooling turbine at 1.06 bar. The pressure in the cabin is 101.325 kpa. The cooling load of the cabin is 58 kW. Determine (a) the stagnation temperature and pressure of the air entering the compressor, (b) mass-flow rate of air flowing through the cooling system, (c) volume flow rate of air handled by the compressor and expander, (d) net power delivered by the engine to the cooling system, (e) the COP of the system.

Ans. (a) 296.5 K, 0.57 bar, (b) 5950 kg/h, (c) 9050 m^3/h, 430 m^3/h, (d) kW, (e) 0.3

14.31 A simple R-134a heat pump for space heating operates between temperature limits of 15 and 50°C. The heat required to be pumped is 100 MJ/h. Determine (a) the quality of refrigerant entering the evaporator, (b) the discharge temperature from the compressor, assuming the specific heat of vapour as 0.996 kJ/kgK, (c) the theoretical piston displacement of the compressor, given the specific volume at suction as 0.04185 m^3/kg, (d) the theoretical power input, (e) the COP. Ans. (a) 0.2675, (b) 327.15 K, (c) 7.156×10^{-3} m^3/s, (d) 3.56 kW, (e) 8.1

CHAPTER

15

Psychrometrics and Air-Conditioning Systems

The singlemost important application of refrigeration is in air conditioning which means simultaneous control of the dry bulb temperature, humidity, cleanliness, ventilation and distribution of air and air motion in a place besides the control of contaminated gases.

15.1 PROPERTIES OF ATMOSPHERIC AIR

The working substance in air conditioning is the atmospheric or *moist air* which is a mixture of two gases, viz., *dry air* which is a mixture of a number of gases like N_2, O_2, A, CO_2 etc., as given in Table 15.1 and *water vapour* which may exist in a saturated or superheated state. A stated in the first chapter, a pure substance is homogeneous and invariable in chemical composition. Both dry air and water vapour are individually pure substances. But moist air is not a pure substance when condensation or evaporation of moisture can take place which varies the composition of the mixture. Thus, moist air consists of two parts: one comprising dry air, considered as the *fixed part*, and the other, solely of water vapour, considered as the *variable part.*

Completely dry air does not exist in nature. Water vapour in varying amounts is diffused through it. Both dry air and water vapour can be considered as ideal gases since both exist in the atmosphere at low pressures. Hence, ideal gas laws can be applied to them individually. If p_a and p_w are the partial pressures of dry air and water vapour respectively then by *Dalton's law of partial pressures*

$$p = p_a + p_w$$

where p is the atmospheric pressure.

Mole fraction of dry air, x_a

$$x_a = \frac{p_a}{p} = p_a, \text{ since } p = 1 \text{ atm.}$$

and mole fraction of water vapour, x_w

Table 15.1

Composition of Dry Air

Component	*Molecular mass*	*Part by volume*	*Part by mass*
N_2	28.02	0.7803	0.7547
O_2	32.0	0.2099	0.2319
Ar	39.91	0.0094	0.0129
CO_2	44.0	0.0003	0.0005
H_2	2.02	0.0001	0.0000

$$x_w = \frac{p_w}{p} = p_w$$

Let a dry air–water vapour mixture of mass m be contained in a chamber of volume V at the total pressure p and temperature T. If V_1 is the volume of dry air at p and T of the mixture, and V_2 is the volume of water vapour at the same p and T then by *Amagat's law of partial volumes*

$$V = V_1 + V_2$$

where $V_1 = \frac{n_1 \bar{R} T}{p}$ and $V_2 = \frac{n_2 \bar{R} T}{p}$ are the partial volumes of dry air and water vapour respectively, n_1 and n_2 being the respective mole numbers. Therefore, the mole fraction of dry air is

$$x_1 = p_1/p = V_1/V = n_1/n.$$

Now, if M is the molecular mass of the mixture

$$mM = M_1 m_1 + M_2 m_2$$

$$\therefore M = x_1 M_1 + x_2 M_2$$

The *Gibb's theorem* states that the internal energy of a mixture of gases is equal to the sum of the internal energies of individual gases, taken each at the temperature and volume of the mixture. Thus, we have

$$mu = m_1 u_1 + m_2 u_2,\ u = \frac{m_1 u_1 + m_2 u_2}{m_1 + m_2}$$

Similary,

$$mh = m_1 h_1 + m_2 h_2,\ h = \frac{m_1 h_1 + m_2 h_2}{m_1 + m_2}$$

$$mc = m_1 c_1 + m_2 c_2,\ c = \frac{m_1 c_1 + m_2 c_2}{m_1 + m_2}$$

for enthalpy and specific heat respectively.

The molecular mass of atmospheric air is

$$M = x_{N_2} M_{N_2} + x_{O_2} M_{O_2} + x_{Ar} M_{Ar} = 0.78 \times 28 + 0.21 \times 32 + 0.94 \times 40 = 28.96 \text{ kg/kg mol.}$$

15.2 PSYCHROMETRIC PROPERTIES OF AIR

Dry air and water vapour form a binary mixture. From Gibbs phase rule (Eq. 11.45), $f = C - \phi + 2$, where $C = 2$, the number of components, and ϕ = number of phases = 1; therefore, $f = 3$. Thus, three properties are required to completely define its thermodynamic state, unlike a pure substance which requires only two. One of the three properties can be the composition. The properties of moist air are called *psychrometric properties,* and the subject which deals with the behaviour of moist air is known as *psychrometry* or *psychrometrics.*

In air-conditioning practice, all calculations are based on the dry-air part (fixed), since the water-vapour part is continuously variable. For defining and calculating the relevant psychrometric properties, a certain volume V of moist air at pressure p and temperature T is considered (Fig. 15.1). It contains G kg of dry air and m_w kg of water vapour. The actual temperature t of moist air is called the *dry bulb temperature* (DBT). The total pressure p which is equal to the *barometric pressure* is constant.

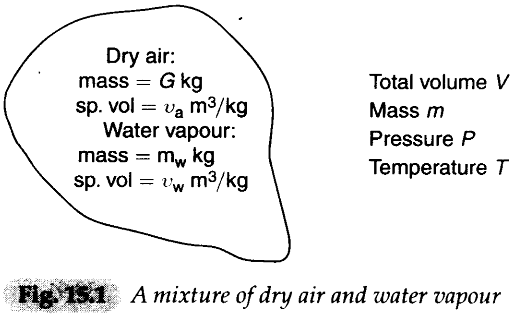


Fig. 15.1 *A mixture of dry air and water vapour (moist air)*

15.2.1 Specific Humidity or Humidity Ratio, W

The specific humidity of humidity ratio is defined as the mass of water vapour or moisture per unit mass of dry air in a mixture of air and water vapour. If G = mass of dry air and m = mass of water vapour, then

$$W = \frac{m}{G} = \frac{V/v_w}{V/v_a} = \frac{v_a}{v_w} \tag{15.1}$$

Since p_w is very small, the saturation temperature at p_w is less than atmospheric temperature t (Fig. 15.2). So the water vapour in air exists in *superheated state*, and air is said to be *unsaturated.*

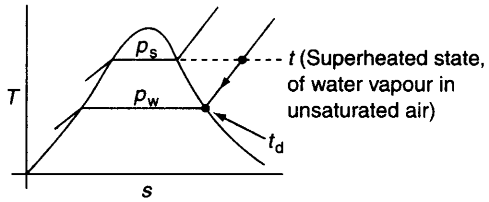


Fig. 15.2 *State of water vapour in moist air*

Since both dry air and water vapour behave individually as ideal gases,

$$p_a v_a = \frac{\bar{R}}{\bar{M}_a} T, \quad p_a v = G\frac{\bar{R}}{\bar{M}_a} T$$

$$p_w v_w = \frac{\bar{R}}{M_w} T, \quad p_w v = m_w \frac{\bar{R}}{M_w} T$$

where subscripts 'a' and 'w' refer to dry air and water vapour respectively and M is the molecular weight.

Substituting in Eq. (15.1), we obtain

$$W = \frac{M_w p_w}{M_a p_a} = \frac{18.016}{28.96}\frac{p_w}{p_a} = 0.622\frac{p_w}{p_a} \tag{15.2}$$

where W is in kg of water vapour per kg of dry air

Since

$$p = p_a + p_w,$$

$$\therefore \ W = 0.622\frac{p_w}{p - p_w} \tag{15.3}$$

Since the total atmospheric pressure p remains constant, we see that only

$$W = f(p_w) \tag{15.4}$$

If we take 1 kg of dry air, Viz.,

$$G = 1 \text{ kg}$$

then the mass of water vapour associated with this dry air is

$$m_w = W \text{kg}.$$

then the total mass of this volume of moist air is

$$m = (1 + W) \text{ kg} \tag{15.5}$$

The specific humidity thus is not a mass fraction of water vapour which would have been $W/(1+W)$, but a ratio of the mass of water vapour to that of dry air in a certain volume of the mixture.

15.2.2 Dew Point Temperature

If a sample of unsaturated moist air containing superheated water vapour is cooled at constant pressure p_w, the mixture will eventually reach the saturation temperature t_d of water vapour corresponding to its partial pressure p_w (Fig. 15.2) at which it starts condensing and dews start appearing. This temperature t_d is called the *dew point temperature* (DPT). It is therefore, the temperature to which moist air must be cooled at constant pressure before condensation of moisture takes place. Moisture can thus be removed from humid air by bringing the air in contact with a cold surface or cooling coil whose temperature is below its dew point temperature. During the process of cooling, the partial pressure p_w of water vapour and specific humidity W remain constant until the vapour starts condensing.

Now, unsaturated moist air with superheated water vapour in a control volume V (Fig. 15.1) at dry bulb temperature T and partial pressure p_w (Fig. 15.3) is considered. If now more water vapour is added to this control volume V at this temperature T, the partial pressure p_w will go on increasing, until it reaches a value p_s corresponding to state 2, after which it cannot increase further, since p_s is the saturation pressure or the maximum possible pressure of vapour at temperature T. The water vapour at state 2 is now saturated and the air is said to be *saturated*. In this state, the air is holding the maximum amount of water vapour at temperature T and W is maximum.

$$\therefore W_{\max} = W_s = 0.622 \frac{p_s}{p - p_s} \tag{15.6}$$

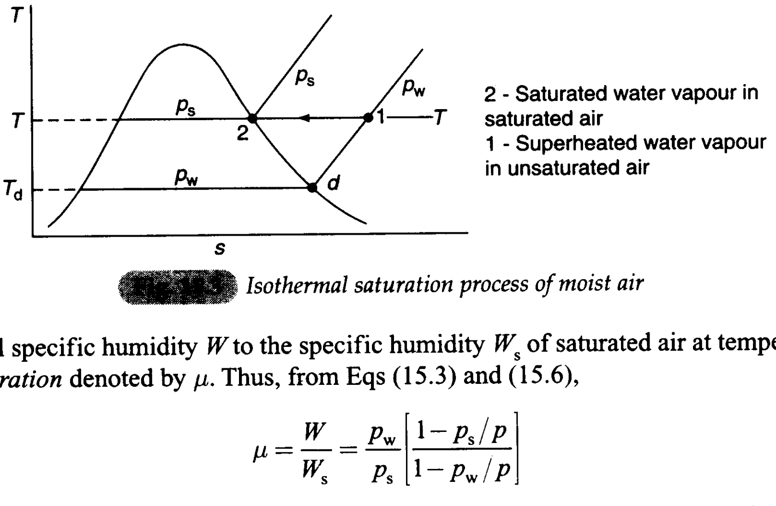


Fig. 15.3 *Isothermal saturation process of moist air*

The ratio of actual specific humidity W to the specific humidity W_s of saturated air at temperature T is called the *degree of saturation* denoted by μ. Thus, from Eqs (15.3) and (15.6),

$$\mu = \frac{W}{W_s} = \frac{p_w}{p_s}\left[\frac{1 - p_s/p}{1 - p_w/p}\right] \tag{15.7}$$

The degree of saturation μ is a measure of the capacity of air to absorb moisture. For dry air, $p_w = 0$ and $\mu = 0$ and for saturated air, $p_w = p_s$, $\mu = 1$, Thus μ varies between 0 and 1.

15.2.3 Relative Humidity (Denoted by ϕ or RH)

Relative humidity is defined as the ratio of the mass of water vapour m_w in a certain volume of moist air at a given temperature to the mass of water vapour $(m_w)_s$ in the same volume of saturated air at the same temperature. Thus if v_w and v_s are the specific volumes of water vapour in the moist air and saturated air respectively at temperature T and in volume V, viz., at points 1 and 2 respectively in Fig. 15.3, we have

$$\phi = \frac{m_w}{(m_w)_s} = \frac{p_w V/\bar{R}T}{p_s V/\bar{R}T} = \frac{p_w}{p_s} \tag{15.8}$$

Also,

$$\phi = \frac{V/v_w}{V/v_s} = \frac{v_s}{v_w} \tag{15.9}$$

Using ideal-gas relationship between states 1 and 2,

$$p_1 v_1 = p_2 v_2, \quad \text{or} \quad p_w v_w = p_s v_s,$$

We have

$$\phi = \frac{p_w}{p_s} = \frac{v_s}{v_w}$$

The relative humidity can thus be defined as the ratio of partial pressure of water vapour in a given unsaturated moist air at a certain temperature T to the saturation pressure of water vapour at the same temperature T. It is usually measured in percentage. When $p_w = p_s$, ϕ is equal to unity, and air is saturated with 100% RH.

From Eq. (15.3),

$$W = 0.622 \frac{p_w}{p - p_w} = 0.622 \frac{p_w}{p_a}$$

$$\therefore \phi = \frac{p_w}{p_s} = \frac{W}{0.622} \frac{p_a}{p_s} \qquad (15.10)$$

Also, from Eqs (15.6) and (15.7),

$$\mu = \phi \left[\frac{1 - p_s/p}{1 - p_w/p} \right] \qquad (15.11)$$

$$\text{or, } \phi = \frac{\mu}{1 - (1 - \mu) p_s/p} \qquad (15.12)$$

15.2.4 Enthalpy of Moist Air

According to the Gibbs theorem, the enthalpy of a mixture of ideal gases is equal to the sum of the enthalpies of the constituent gases. Thus, the enthalpy of moist air is equal to the sum of the enthalpies of dry air and associated water vapour.

$$h = h_a + W h_w \qquad (15.13)$$

per kg of dry air.

The enthalpy of the dry-air part above a datum of 0°C is expressed as

$$h_a = c_{p_a} t = 1.005 t \text{ kJ/kg}, \qquad (15.14)$$

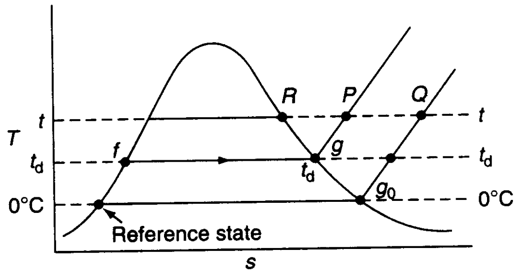
t being the dry-bulb temperature in °C.

Taking the reference state enthalpy as zero for saturated water at 0°C (Fig. 15.4), the enthalpy of the water-vapour part at point p is expressed as

$$h_w = h_p = c_{p_w} t_d + (h_{fg})_{t_d} + c_{p_v} (t - t_d) \text{ kJ/kg} \qquad (15.15)$$

$$= 4.187 t_d + (h_{fg})_{t_d} + 1.88 (t - t_d) \qquad (15.16)$$

where the specific heat of liquid water is taken as 4.187 kJ/kg K and that of superheated vapour as 1.88 kJ/kg K.



Enthalpy of water-vapour part

To simplify the above expression for h_w, since the pressure is low and the enthalpy is a function of temperature only,

$$h_P = h_Q = h_R = h_{g_0} + c_{p_v} (t - 0) = 2500 + 1.88 t \qquad (15.17)$$

where the enthalpy of saturated vapour at 0°C is taken as 2500 kJ/kg. Therefore, the enthalpy of moist air is

$$h = 1.005 t + W(2500 + 1.88 t) \text{ kJ/kg d.a.} \qquad (15.18)$$

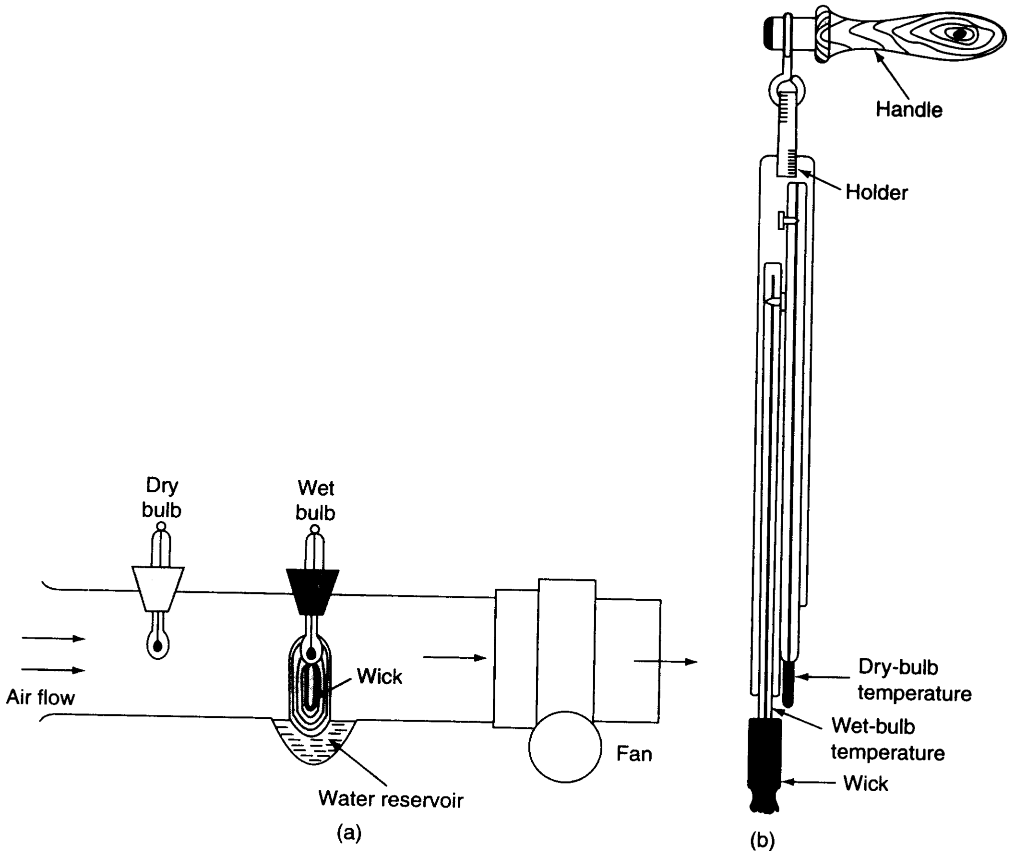
15.2.5 Wet-Bulb Temperature

The wet-bulb temperature (WBT) is the temperature recorded by a thermometer when the bulb is enveloped by a cotton wick saturated with water. As the air stream flows past it, some water evaporates, taking the latent heat from the water-soaked wick, thus decreasing its temperature. Energy is then transferred from the air to the wick. When the equilibrium condition is reached, there is a balance between energy removed from the water film by evaporation and energy supplied to the wick by heat transfer, and the minimum temperature recorded is the wet-bulb temperature.

A *Psychrometer* is an instrument which measures both the dry-bulb and wet-bulb temperatures of air. Figure 15.5(a) shows a continuous psychrometer with a fan for drawing air over the thermometer bulbs. A *sling psychrometer* (Fig.15.5(b)) has the two thermometers mounted on a frame with a handle. The handle is rotated fast (150–300 rpm) so that there is good air motion. The wet bulb temperature is the *lowest temperature* recorded by the moistened bulb.

The difference between the DBT and the WBT is called the *wet-bulb depression* (WBD). Thus,

$$\text{WBD} = \text{DBT} - \text{WBT} = t - t'$$



(a) (b)

Fig. 15.5 (a) *Dry and wet bulb temperatures,* (b) *Sling psychrometer*

If the ambient air is saturated and RH is 100%, there will be no evaporation of water on the bulb, and hence WBT and DBT will be equal. The wet-bulb depression will be zero. The WBT is an indirect measure of the dryness of air.

The wet-bulb temperature is essentially not a thermodynamic property. It is the temperature of equilibrium reached by heat transfer from air to water in the wick due to temperature difference $(t - t')$ causing the evaporation of water and consequent diffusion of water vapour into air due to partial pressure difference $(p'_w - p_w)$, where p'_w is the saturation water vapour-pressure at temperature t' (Fig. 15.6). At any DBT, the greater the depression, the smaller is the amount of water vapour held in the mixture.

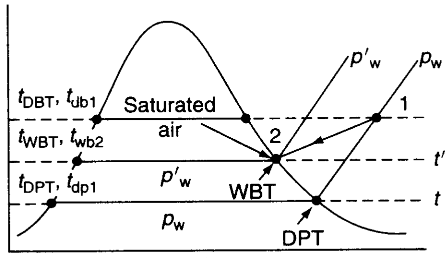


Fig. 15.6 *Wet bulb temperature and adiabatic saturation process*

15.2.6 Adiabatic Saturation Process and Thermodynamic Wet-Bulb Temperature

When unsaturated air flows over a long sheet of water (Fig. 15.7) in an insulated chamber, the water evaporates, and the specific humidity of the air increases. Both the air and water are cooled as evaporation takes place. The process continues until the energy transferred from the air to the water is equal to the energy required to vaporize the water. When this point is reached, thermal equilibrium exists with respect to the water, air and water vapour, and consequently the air is saturated. The equilibrium temperature is called the *adiabatic saturation temperature* or the *thermodynamic wet-bulb temperature*. The make-up water is introduced at this temperature to make the water level constant.

The 'adiabatic cooling' process is shown in Fig. 15.6 on *T-s* plot for the vapour in the air-water vapour mixture. Although the total pressure of the mixture is constant, the partial pressure of the vapour increases from p_w to p'_w, and in the saturation state corresponds to the adiabatic saturation temperature. The vapour is initially at t_{db1} and is adiabatically cooled to t_{wb2} which is equal to the adiabatic saturation temperature. The adiabatic saturation temperature and the wet-bulb temperature are taken to be equal for all practical purposes. The WBT lies between DBT and DPT.

Since the system is insulated and no work is done, the first law yields

$$Gh_{a1} + m_1 h_{w1} + (m_2 - m_1)h_{f2} = Gh_{a2} + m_2 h_{w2} \tag{15.19}$$

where $(m_2 - m_1)$ is the mass of water added, h_{f2} is the enthalpy of liquid water at $t_2(= t_{wb2})$, h_a is the specific enthalpy of dry air, and h_w is the specific enthalpy of water vapour in air. Dividing by G, and since $h_{w2} = h_{g2}$

$$h_{a1} + W_1 h_{w1} + (W_2 - W_1)h_{f2} = h_{g2} + W_2 h_{g2} \tag{15.20}$$

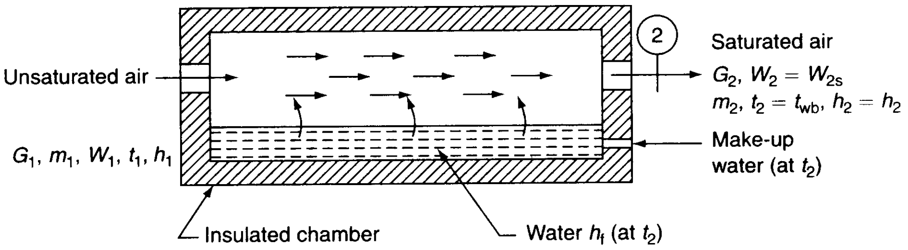


Fig. 15.7 *Adiabatic saturation process*

Solving for W_1,

$$W_1 = \frac{(h_{a2} - h_{a1}) + W_2(h_{g2} - h_{f2})}{h_{f2} - h_{w1}}$$

$$= \frac{c_{pa}(T_2 - T_1) + W_2 h_{fg2}}{h_{f2} - h_{w1}} \qquad (15.21)$$

where $$W_2 = \frac{m_2}{G} = \frac{m_s}{G} = 0.622\frac{p_s}{p - p_s}.$$

The enthalpy of the air–water vapour mixture is given by

$$Gh = Gh_a + mh_w$$

where h is the enthalpy of the mixture per kg of dry air.

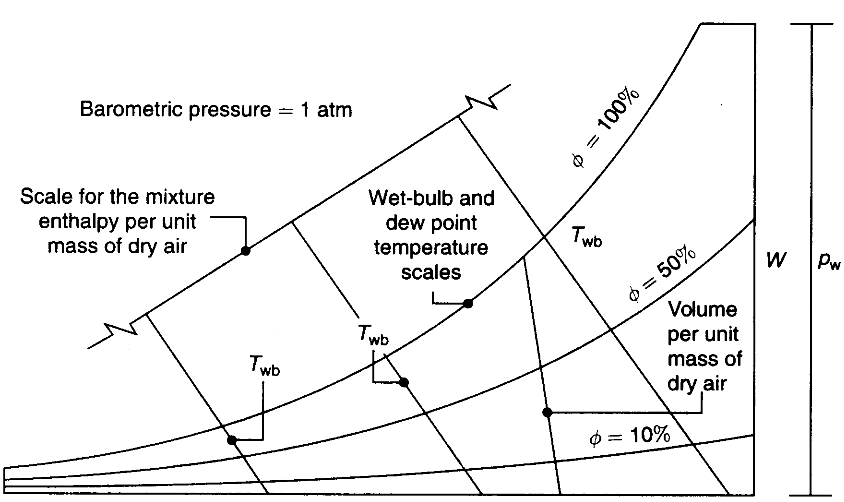
$$h = h_a + Wh_w$$

which was stated earlier in Eq. (15.13).

15.3 PSYCHROMETRIC CHART

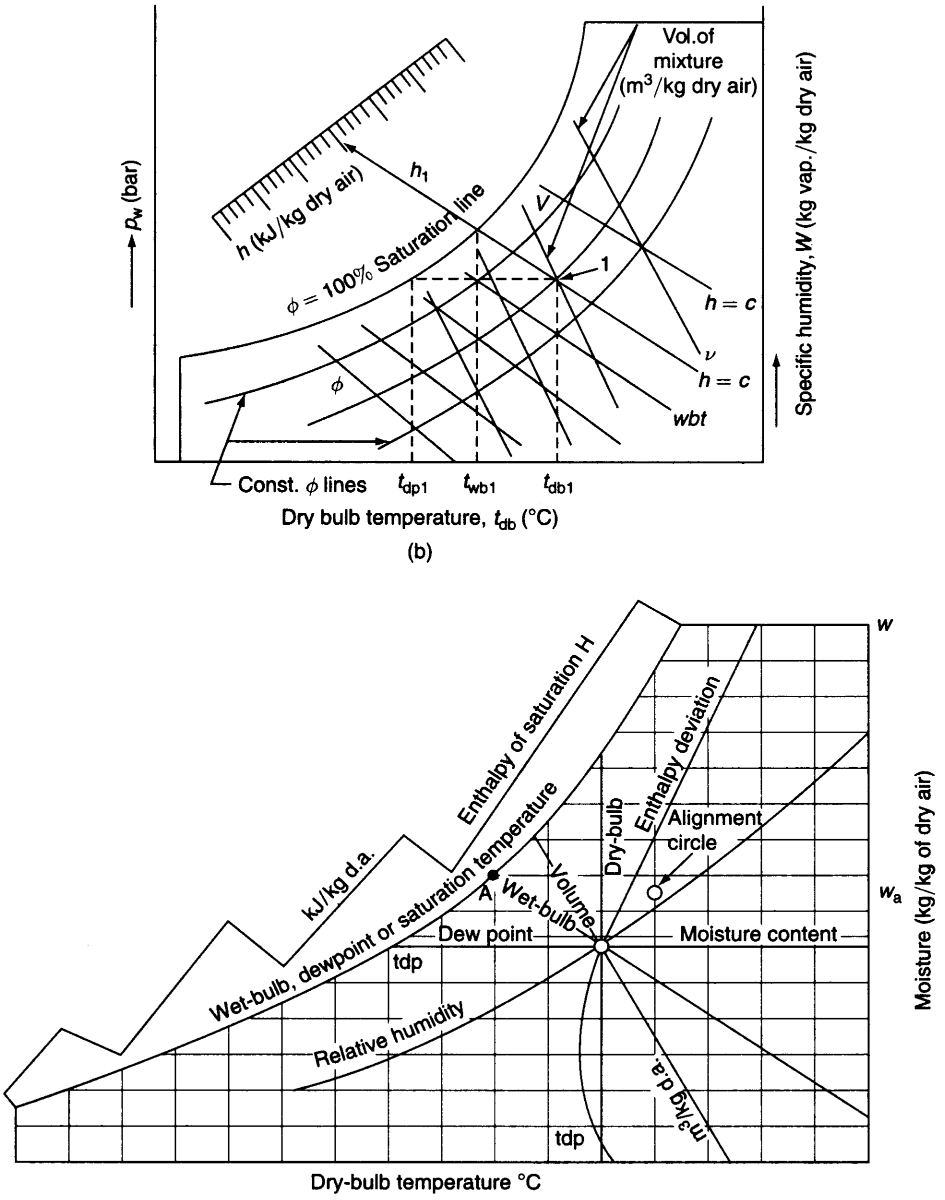
The psychrometric chart is a graphical plot (Fig. 15.8) with specific humidity and partial pressure of water vapour as ordinate, and dry bulb temperature as abscissa. The volume of the mixture (m^3/kg dry air), wet-bulb temperature, relative humidity, and enthalpy of the mixture appear as parameters. The chart is plotted for one atmospheric pressure, usually 760 mm Hg.

The constant WBT line represents the adiabatic saturation process. It also coincides with the constant enthalpy line. To show this, let us consider the energy balance for the adiabatic saturation process (Fig. 15.7).



(a)

Fig. 15.8 *(Continued)*



(b)

(c)

Psychrometric chart

$$h_{a1} + W_1 h_{w1} + (W_2 - W_1)h_{f2} = h_{a2} + W_2 h_{w2}$$

Since $h = h_a + W h_w$ kJ/kg d.a.,

$$h_1 - W_1 h_{f2} = h_2 - W_2 h_{f2}$$

where the subscript 2 refers to the saturation state, and the subscript 1 denotes any state along the adiabatic saturation path. Therefore,

$$h - Wh_{f2} = \text{constant} \tag{15.22}$$

Since Wh_f is small compared to h (of the order of 1 or 2%)

$$h = \text{constant}$$

indicating that the enthalpy of the mixture remains constant during an adiabatic saturation process.

15.3.1 Enthalpy Deviation

For any state of unsaturated moist air, there exists a temperature t^* at which air becomes adiabatically saturated by the evaportation of water into air, at exactly the same temperature t^*. In the adiabatic saturation process (Fig. 15.7), the leaving air is saturated at temperature t^*. The specific humidity is correspondingly increased to W^*. The enthalpy is increased from a given initial value h to the value h^*. The weight of water added per kg of dry air is $(W^* - W)$ which adds energy to the moist air of amount equal to $(W^* - W)\, h_f^*$ where h_f^* is the specific enthalpy of injected water at t^*. By energy balance, since the process is adiabatic,

$$h + (W^* - W)\, h_f^* = h^*$$

It was stated, in Eq. 15.12 that the difference of enthalpies at the saturation point A (15.8c) and any other point on the constant WBT line is very small. The difference denoted by the symbol D is called *enthalpy deviation* and is given by

$$D = h - h^* = (W - W^*)h_f^* \tag{15.23}$$

If it is sufficiently large, separate lines of constnat WBT and constnat h can be shown on the psychrometric chart. However, usually D is very small.

15.4 PSYCHROMETRIC PROCESSES

Four basic thermodynamic processes and four combinations of processes by which the state of moist air can be altered are shown in Fig. 15.9. They are

(i) Sensible heating process OA
(ii) Sensible cooling process OB
(iii) Humidifying process OC
(iv) Dehumidifying process OD
(v) Heating and humidifying process OE
(vi) Cooling and dehumidifying process OF
(vii) Cooling and humidifying process OG
(viii) Heating and dehumidifying process OH

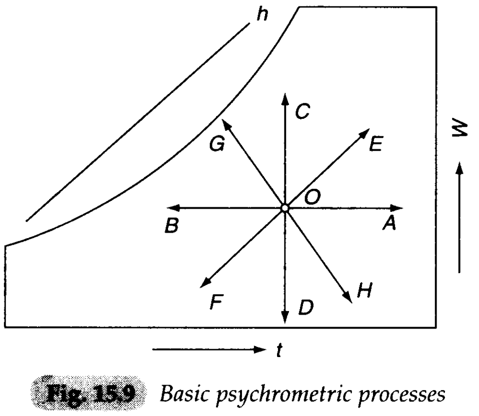


Fig. 15.9 Basic psychrometric processes

Sensible heating and cooling processes involve only a change in the dry bulb temperature, whereas the processes of humidifying and dehumidifying involve a change in the specific humidity. Thus, when the state of air moves from O to A or to B, there is no change in the moisture content of the air. If the state changes from O to C or to D, the DBT remains constant. The last four fundamental processes listed above involve both changes in temperature as well as in humidity.

15.4.1 Sensible Heating or Cooling (at W = constant)

When the state of moist air is altered along the W = constant line such as 1–2 in Fig. 15.10 with only DBT changing, we have

Balance of
Dry air $G_1 = G_2$
Moisture $m_1 = m_2$
Energy $G_1h_1 + Q_{1-2} = G_2h_2$

$$\therefore Q_{1-2} = G(h_2 - h_1) = G\,[h_{a2} + W_2h_{w2} - (h_1 + W_1h_w)]$$

$$= G[1.005(t_2 - t_1) + W_2\,[h_{g2} + 1.88(t_2 - t_{d2})] - W_1[h_{g1} + 1.88(t_1 - t_{d1})] = Q_s \qquad (15.24)$$

where the C_p of water vapour in the superheated state is assumed to be 1.88 kJ/kgK and t_d is the dew point temperature.

Since $\quad W_1 = W_2,\ h_{g2} = h_{g1},\ t_{d2} = t_{d1},\ Q_{1-2} = G(1.005 + 1.88\,W)(t_2 - t_1) = Q_s \qquad (15.25)$

Similar equations will hold good for sensible cooling at constant W. Simple heating of moist air can be done to any desired temperature, simple cooling can be done only up to the dew-point temperature.

If a building to be air conditioned receives or loses heat due to transmission through the walls, it is supposed to have *sensible heat load* (Q_c). Heat gain in buildings will require the conditioning of air to lower temperatures, causing a *cooling load* on the air-conditioning equipment. However, heat loss in buildings will require the heating of air causing a *heating load* on the equipment.

15.4.2 Latent Heat Load: Humidification or Dehumidification

When the state of air is altered along the DBT= constant line, such as 3–4 in Fig. 15.11, moisture in the form of water vapour is transferred to change the specific humidity of the air. Thus the amount of moisture transfer is

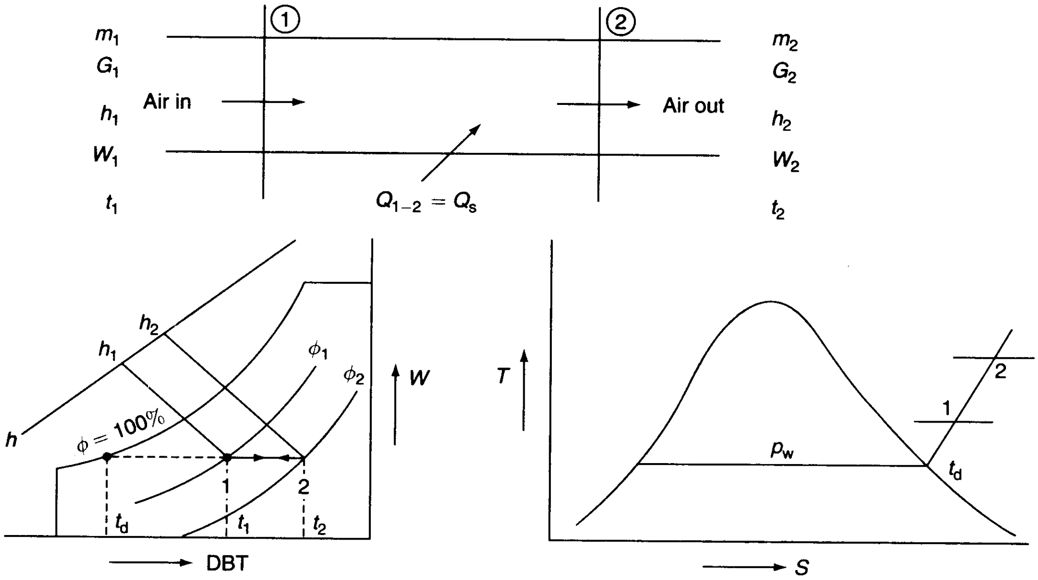


Fig. 15.10 *Sensible heating*

$$m = G(W_3 - W_4)$$

Because of this change in specific humidity, there is also a change in enthalpy of the air given by $(h_3 - h_4)$. In air-conditioning practice, this change of enthalpy due to the change in W is considered to cause *latent heat transfer* given by

$$Q_L = G(h_3 - h_4) = G[(c_p t_3 + h_{fgo} W_3) - (c_p t_4 + h_{fgo} W_4)]$$

$$= G h_{fgo} (W_3 - W_4) = m h_{fgo} = 2500 \text{ m kJ} \qquad (15.26)$$

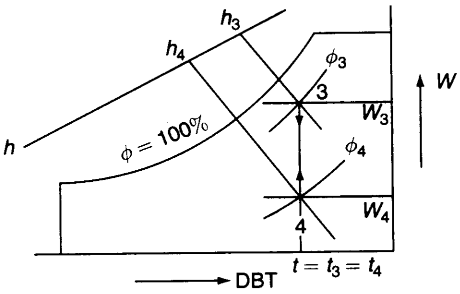


Fig. 15.11 *Latent heat process*

The latent heat load is proportional to the latent heat of vaporization h_{fgo}. Accordingly, if a building gains or loses moisture, it is supposed to have a *latent heat load.* A gain of moisture will require the condensation of moisture (water vapour) for the dehumidification of air in the conditioning apparatus, and hence a cooling load. On the other hand, a loss of moisture will require the evaporation of water for the humidification of air in the apparatus and hence a heating load.

15.4.3 Total Heat Load

Let us now consider a change in the state of air along the path 1–3 as shown in Fig. 15.12. This involves both a change in temperature as well as in the humidity ratio. The change in temperature causes a sensible heat load (SHL)given by

$$Q_S = Q_{1-2} = G(h_2 - h_1) = G c_p (t_2 - t_1)$$

The change in the humidity ratio causes a moisture transfer given by

$$m = G(W_3 - W_1)$$

and a latent heat load (LHL) given by

$$Q_L = Q_{2-3} = G(h_3 - h_2) = G h_{fgo} (W_3 - W_1)$$

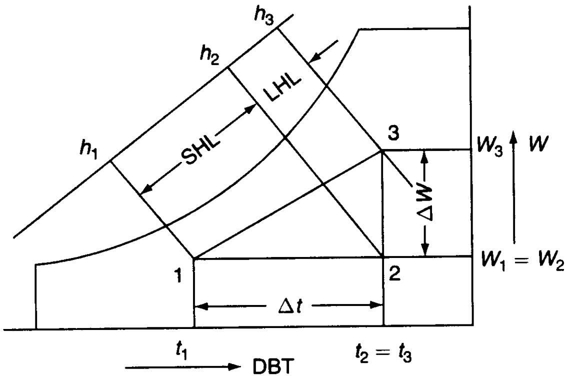


Fig. 15.12 *Total heat load process*

The *total heat load* is then expressed as

$$Q = Q_s + Q_L = G(h_3 - h_1) = G[c_p(t_3 - t_1) + h_{fgo}(W_3 - W_1)] \qquad (15.27)$$

15.4.4 Sensible Heat Factor (SHF)

The ratio of the sensible heat transfer to the total heat transfer is called the *sensible heat factor.* Thus

$$\text{SHF} = \frac{Q_s}{Q_s + Q_L} = \frac{Q_s}{Q}$$

$$= \frac{h_2 - h_1}{(h_2 - h_1) + (h_3 - h_2)} = \frac{h_2 - h_1}{h_3 - h_1} \qquad (15.28)$$

15.4.5 Humid Specific Heat

The enthalpy of moist air can be written in the form

$$h = (c_{pa} + W c_{pw})t + W(h_{fg})_{0°C} = c_p t + W(h_{fg})_{0°C}$$

where $$c_p = c_{pa} + Wc_{pw} = (1.005 + 1.88c_{pw})\ \text{kJ/(kg d.a.)(K)}$$

is termed as the *humid specific heat*. It is the specific heat of moist air $(1+W)$ kg/kg d.a. The term $C_p t$ governs the change in enthalpy of moist air with temperature at constant W, and the term $W(h_{fg})_{0°C}$ governs the change in enthalpy with the change in W, i.e. due to addition or removal of moisture in air.

Normally, the second term 1.88 W is very small compared to the first term 1.005. An approximate value of C_p of 1.0216 kJ/(kg d.a.)(K) may be taken for all practical purposes in air-conditioning calculations.

The flow rate of air is measured in terms of m^3/min or cmm. Then the mass flow rate of dry air is

$$G = \dot{Q}_v \rho / 60 \text{ kg d.a./s}$$

where Q_v is the volume flow rate of dry air (m^3/min) and for standard air at 20°C and 50% RH, the density ρ is about 1.2 kg/m^3 d.a.

Sensible heat load (SHL) is then

$$\dot{Q}_s = \frac{cmm \times 1.2 \times 1.0216}{60}\Delta t = 0.0204(cmm)\ \Delta t \text{ kW} \tag{15.29}$$

The *latent heat load* (LHL) is from Eq. (15.16)

$$\dot{Q}_L = 2500\ \dot{m} \text{ kW} = \frac{2500(cmm)\times 1.2 \times 2500}{60}\Delta W = 50(cmm)\ \Delta W \text{kW} \tag{15.30}$$

The *total heat load* (THL)

$\dot{Q} = (\text{cmm})(0.0204)\Delta t + 50(\text{cmm})\ \Delta W$

The *sensible heat factor* (SHF) is from

$$\text{SHF} = \frac{\dot{Q}_s}{\dot{Q}} = \frac{0.0204(cmm)\Delta t}{(cmm)(0.0204)\Delta t + 50(cmm)\Delta W} = \frac{0.0204\Delta t}{0.02\Delta h} \tag{15.31}$$

15.4.6 Cooling and Dehumidification

When the humidity radio of air decreases, air is said to be dehumidified, and when it increases, air is humidified. Air may be cooled and dehumidified (a) by placing the evaporator coil across the air flow (Fig. 15.13(b)), (b) by circulating chilled water or brine (NaCl or CaCl$_2$) in a tube placed across the air flow (Fig.15.13(c)), or (c) by spraying chilled water to air in the form of mist (15.13(d)) to expose a large surface area. The temperature of the cooling surface or the spraywater must be below the dew point at state 1, t_d (Fig. 15.13(a)). If the cooling surface or the spray shower is of large magnitude, the air may come out at the saturation state 2s, known as the *apparatus dew point* (adp).

Balance gives $$G_1 = G_2 = G$$

If L is the amount of water vapour removed,

$$m_1 = m_2 + L, \quad L = m_1 - m_2 = G(W_1 - W_2).$$

The energy equation gives $$G_1 h_1 = G_2 h_2 + Q_{1-2} + L\, h_{f2}$$

where h_{f2} is the specific enthalpy of water at temperature t_2.

$$\therefore Q_{1-2} = G[(h_1 - h_2) - (W_1 - W_2)h_{f2}]$$

If $(W_1 - W_2)h_{f2}$ is small, the amount of heat removed is

$$Q_{1-2} = G(h_1 - h_2) = \text{Total heat load on the cooling coil (kJ/h).}$$

Cooling and dehumidification of air is common in summer air conditioning.

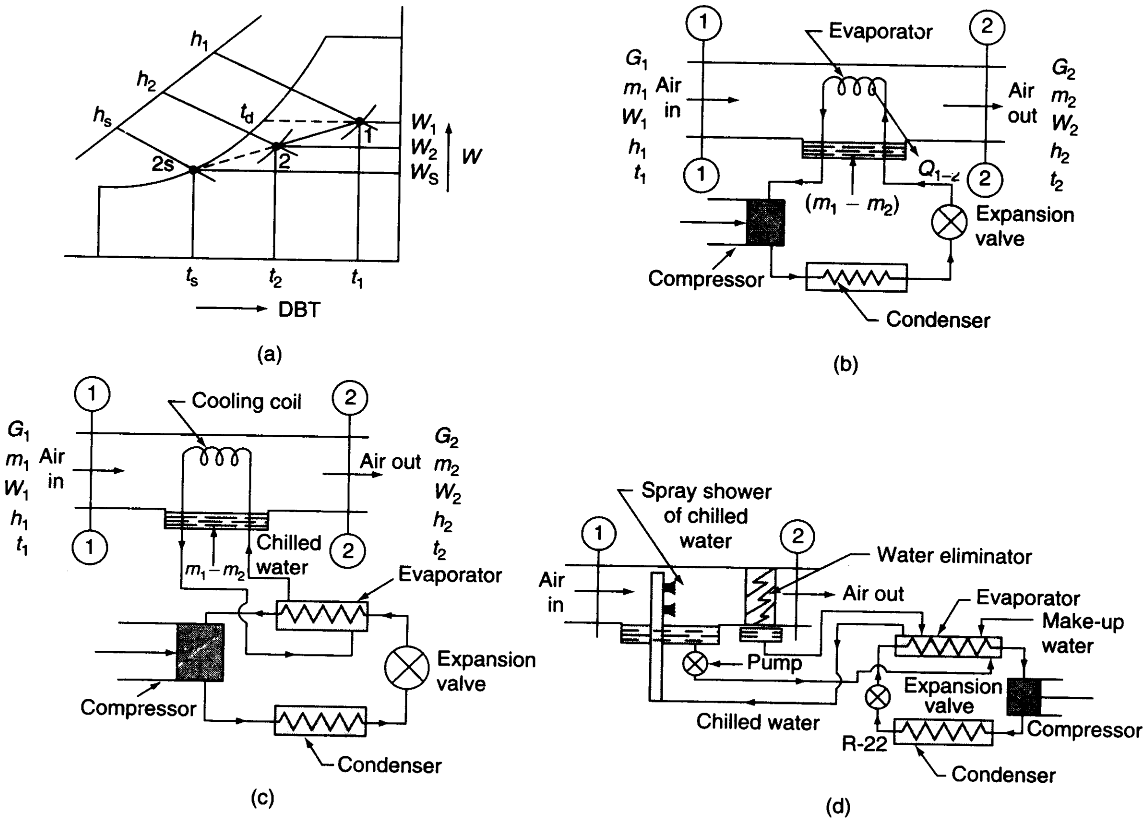


Fig. 15.13 *Cooling and dehumidification*

15.4.7 Heating and Humidification

The addition of heat and moisture to air is a problem for winter air conditioning (Fig. 15.14). The water added may be liquid or vapour. The following equations apply

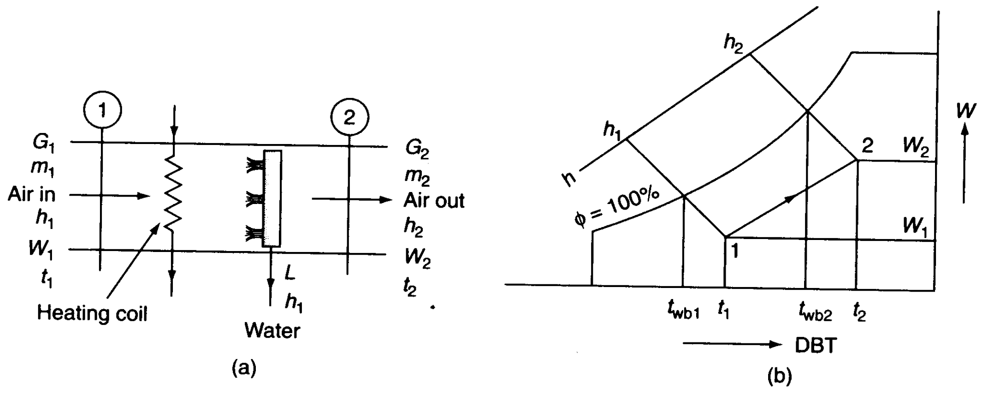


Fig. 15.14 *Heating and humidification*

$$G_1 = G_2 = G$$

$$m_1 + L = m_2$$

$$L = m_2 - m_1 = G(W_2 - W_1)$$

$$G_1 h_1 + L\,h_f + Q_{1-2} = G_2 h_2$$

$$Q_{1-2} = G(h_2 - h_1) - G(W_2 - W_1)h_f$$

Or, $Q_{1-2} = G[(h_2 - h_1) - (W_2 - W_1)h_f]$

15.4.8 Dehumidification and Heating

In winter with cold and dry ambient air, it is often required to dehumidify and heat it, as shown in Fig. 15.15.

15.4.9 Adiabatic Mixing of Two Streams

This is a common problem in air conditioning, where ventilation air and some recirculated room air are mixed prior to processing it to the desired state, and supplying it to the conditioned space (Fig. 15.16).

The following equations hold good:

$$G_1 + G_2 = G_3$$

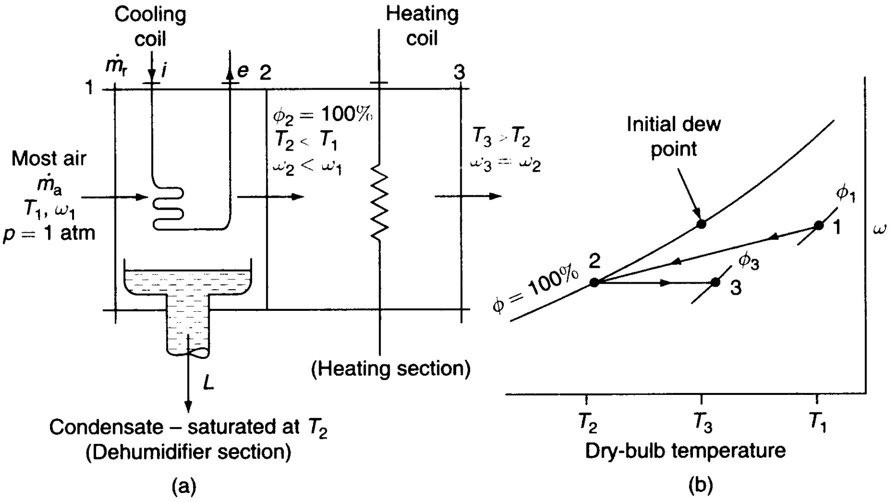
$$G_1\,W_1 + G_2\,W_2 = G_3\,W_3$$

$$G_1\,h_1 + G_2\,h_2 = G_3\,h_3$$

Combining these equations and rearranging,

$$\frac{G_1}{G_2} = \frac{h_3 - h_2}{h_1 - h_3} = \frac{W_3 - W_2}{W_1 - W_3}$$

The points 1, 2 and 3 fall in a straight line and the division of the line is inversely proportional to the ratio of the mass flow rates.



(a) (b)

Fig. 15.15 *Dehumidification with heating* (a) *equapment schematic* (b) *psychrometric chart representation*

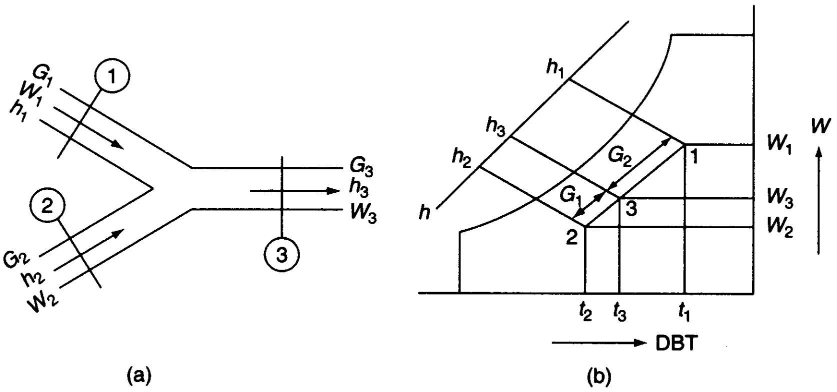
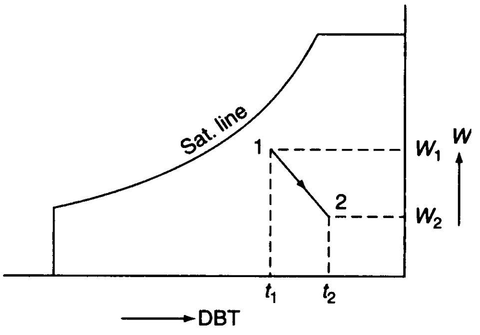


Fig. 15.16 Adiabatic mixing of two air streams

15.4.10 Chemical Dehumidification

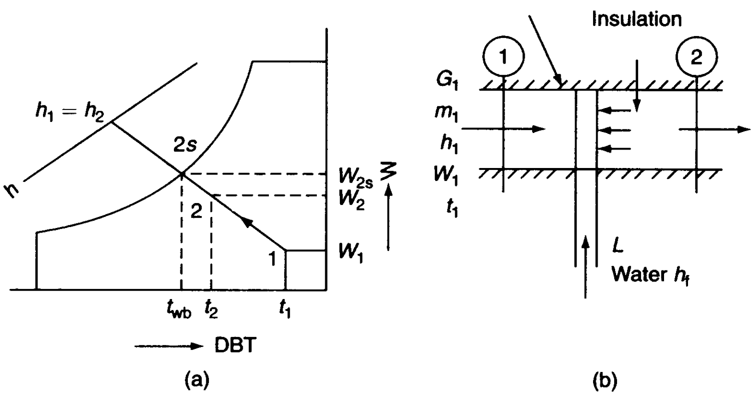
Some substances like silica gel (product of fused sodium silicate and sulphuric acid) and activated alumina have great affinity with water vapour. They are called *adsorbents*. When moist air passes through a bed of silica gel, water vapour molecules get adsorbed on its surface. Latent heat of condensation is released. So the DBT of air increases. The process is shown in Fig. 15.17.



Chemical dehumidification

15.4.11 Adiabatic Evaporative Cooling

A large quantity of water is constantly circulated through a spray chamber. The air-vapour mixture is passed through the spray and, in doing so, evaporates some of the circulated water. The air may leave at a certain humidity ratio or in a saturation state (Fig. 15.18). The increase in specific humidity is equal to the quantity of water evaporated per unit mass of dry air. No heat transfer takes place between the chamber and the surroundings.



Adiabatic evaporative cooling

Therefore, the energy required for evaporation is supplied by the air, and so the DBT is lowered. After the process has been in operation for a sufficiently longtime, the circulating water approaches the WBT of the air. The following equations apply to the system.

$$G_1 = G_2 = G$$

$$G_1 W_1 + L = G_2 W_2$$

$$L = G(W_2 - W_1)$$

$$G_1 h_1 + L h_f = G_2 h_2$$

$$G(h_1 - h_2) + G(W_2 - W_1) h_f = 0 \quad \text{or,} \quad h_1 - W_1 h_f = h_2 - W_2 h_f$$

It is the same as Eq. 15.22 derived earlier. Since Wh_f is small, enthalpy of the mixture remains constant in adiabatic evaporative cooling.

The *cooling tower* utilizes the phenomenon of evaporative cooling to cool warm water below the dbt of the air. However, the water never reaches the minimum temperature, i.e., the wbt, since an excessively large cooling tower would then be required. Also, since warm water is continuously introduced to the tower (Fig. 15.19), the equilibrium conditions are not achieved, and the dbt of the air is increased. Hence, while the water is cooled, the air is heated and humidified.

The warm water is introduced at the top of the tower in the form of spray to expose a large surface area for evaporation to take place. The more the water evaporates, the more is the effect of cooling. Air leaves from the top very nearly saturated. The following equations apply

$$G_1 = G_2 = G$$

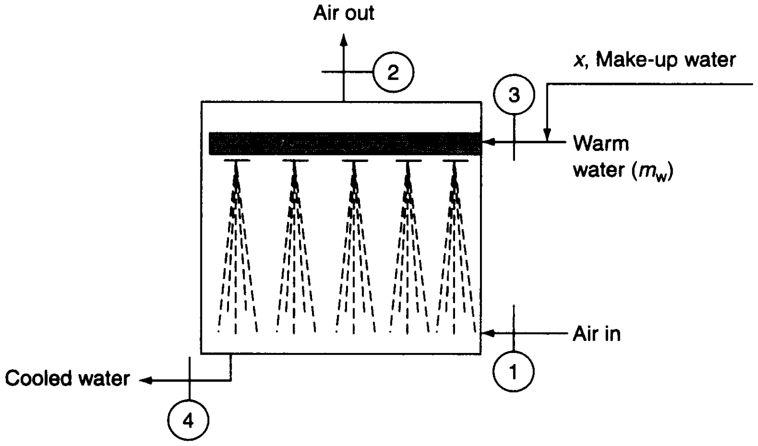
$$G_1 W_1 + m_{w3} = G_2 W_2 + m_{w4}$$

$$m_{w3} - m_{w4} = G(W_2 - W_1)$$

$$G_1 h_1 + m_{w3} h_{w3} = G_2 h_2 + m_{w4} h_{w4}$$

$$G(h_1 - h_2) + m_{w3} h_{w3} = m_{w4} h_{w4}$$

The difference in temperature of the cooled-water temperature and the wet bulb temperature of the entering air is known as the *approach*. The *range* is the temperature difference between the inlet and exit states of water. Cooling towers are rated in terms of approach and range.



[illegible] *Cooling tower*

If x is the make-up water supplied (Fig. 15.19), then

$$x = G(W_2 - W_1) \text{ and } m_{w3} = m_{w4} = m_w$$

By energy balance,

$$G_1 h_1 + m_{w3} h_{w3} + x h_w = G_2 h_2 + m_{w3} h_{w4}$$

$$m_w (h_{w3} - h_{w4}) = G(h_2 - h_1) - G(W_2 - W_1) h_w$$

$$h_{w3} - h_{w4} = \frac{G}{m_w}\left[(h_2 - h_1) - (W_2 - W_1) h_w\right]$$

$$\therefore \text{Range} = t_{w3} - t_{w4} = \frac{G}{m_w c_{pw}}\left[(h_2 - h_1) - (W_2 - W_1) h_w\right]$$

where c_{pw} is the specific heat of water and h_w is the enthalpy of the make-up water.

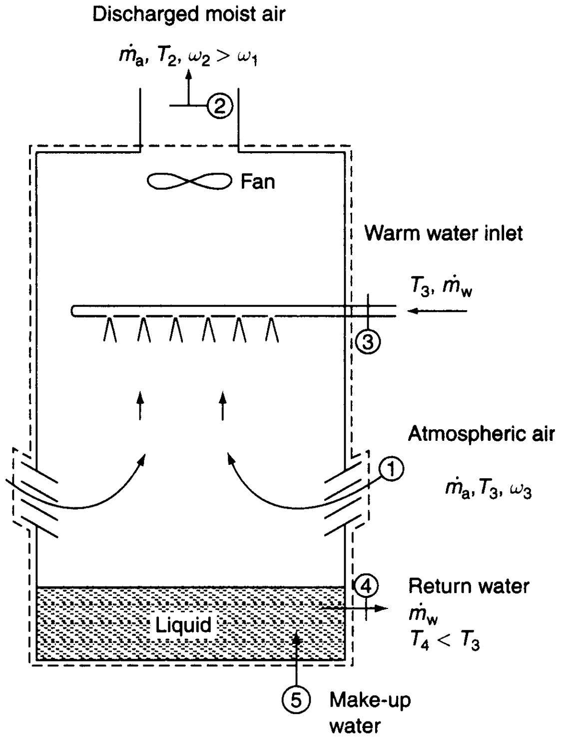
$$\text{Approach} = t_{w3} - t_{wb1}$$

The active portion of the tower in which energy exchange occurs is filled with a packing which breaks up the flow and exposes a large surface area of water in contact with air.

The schematic layout of a cooling tower is shown in Fig. 15.20.

15.4.12 Bypass Factor

Figure 15.21 shows the process that the moist air undergoes while flowing over a surface. The air enters at 1 and leaves at 2 when the surface is maintained at s. In the transfer of heat and water of vapour in any conditioning



Schematic of a cooling tower

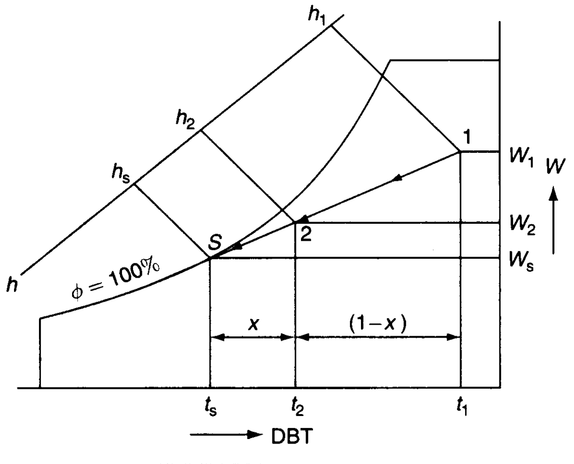


Fig. 15.21 Bypass factor(x)

process, the particles of air stream come in contact with the surface. The state of the *contacted air* is that of the saturated air at t_s. The *uncontacted air* remains in the entering state. The end state 2 of the air is produced by the mixing of contacted and uncontacted particles. The *bypass factor* (BPF) is defined as the fraction of the uncontacted air in terms of the states 1, 2 and *s*, as

$$\text{BPF}, X = \frac{t_2 - t_s}{t_1 - t_s} = \frac{W_2 - W_s}{W_1 - W_s} = \frac{h_2 - h_s}{h_1 - h_s}$$

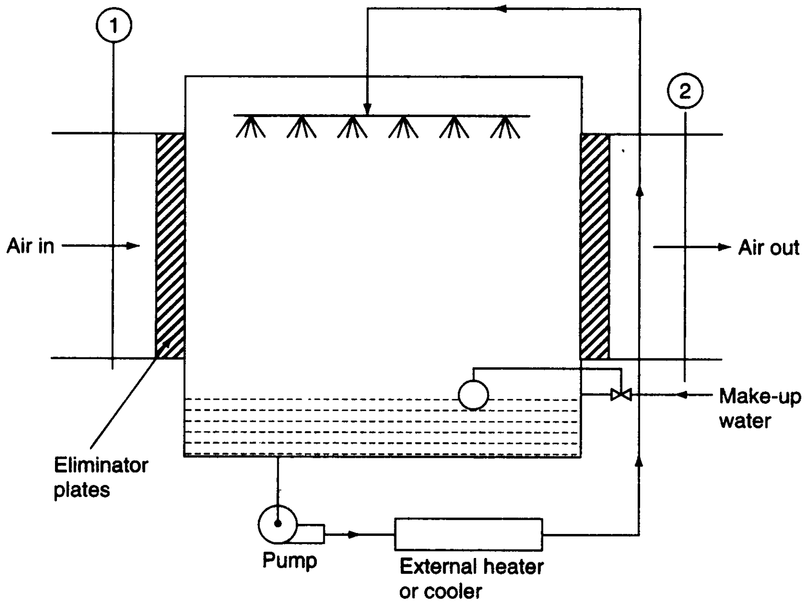
The *contact factor* $(1 - x)$ represents the fraction of the contacted air.

15.4.13 Air Washer

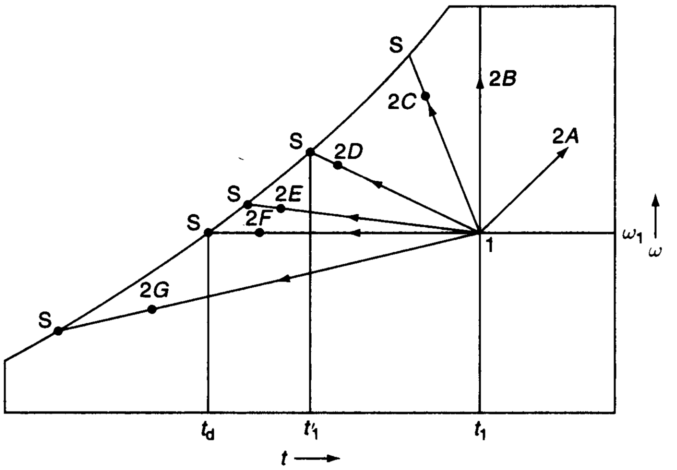
An *air washer* is shown schematically in Fig. 15.22. It involves the flow of air through a spray of water. During the course of flow, the air may be cooled or heated, humidified or dehumidified, or simply adiabatically saturated, depending on the mean surface temperature of water spray. The water is, accordingly, cooled or heated externally, or simply recirculated by a pump. Make-up water is added for any loss due to humidification. Eliminator plates are provided to minimise the loss of water droplets.

The thermodynamic changes of state of air along paths 1–2 in an air washer are shown in Fig. 15.23. The following processes are possible:

1. *Process* 1–2*A* Heating and humidification $(t_s > t_1)$.
2. *Process* 1–2*B* Humidification $(t_s = t_1)$.
3. *Process* 1–2*C* Cooling and humidification $\left(t_1' < t_s < t_1\right)$ where t' is the WBT and t_1 the DBT.
4. *Process* 1–2*D* Adiabatic saturation $\left(t_1' = t_s\right)$.
5. *Process* 1–2*E* Cooling and humidification $\left(t_d < t_s < t_1'\right)$ where t_d is the DPT.



[illegible] *Air washer*



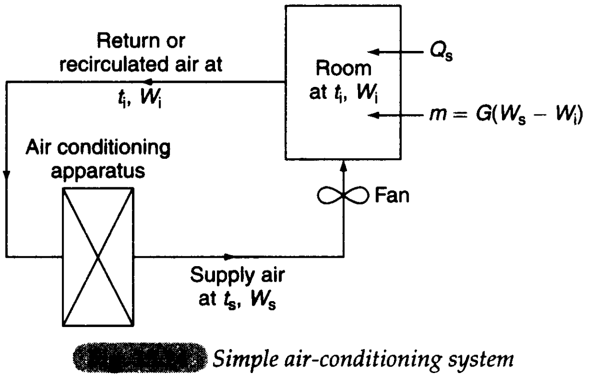
Range of psychrometric processes with an air washer

6. *Process* 1–2*F* Cooling ($t_s = t_d$).
7. *Process* 1–2*G* Cooling and dehumidification ($t_s < t_d$).

It is thus seen that the air washer can be used for *year-round air conditioning.*

15.5 SIMPLE AIR-CONDITIONING SYSTEM

The problem of air conditioning a space is to pick up its sensible and latent heat loads and to calculate the state and mass rate of flow of air to be supplied to the space. For a simple air-conditioning system (Fig. 15.24), let us consider a space which is to be maintained at the room or inside conditions of DBT t_i and humidity ratio W_i. Let Q_s be the sensible heat gain and *m*, the moisture gain $G(W_2 - W_1)$ of the room from internal and external sources. The room sensible heat (RSH) and the room latent heat (RLH) make the room total heat (RTH) which requires to be removed. Thus



Simple air-conditioning system

$$\text{RTH} = \text{RSH} + \text{RLH}$$

In the case of an air-conditioning apparatus, the room or recirculated air from the room is conditioned to a supply DBT t_s and a specific humidity W_s. The processed air is supplied to the room by a fan. Assuming steady-state conditions and the supply air flow rate as (cmm), we have:

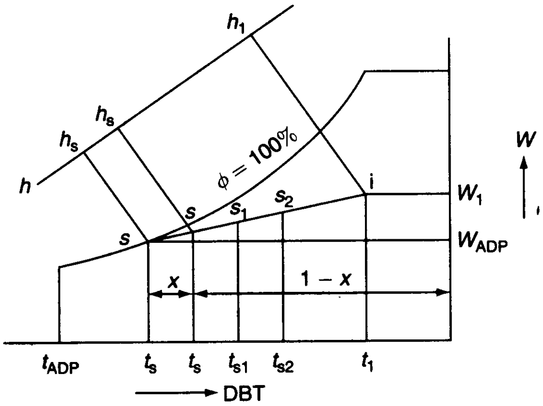
$$\text{RSH} = Q_s = Gc_p\,(t_i - t_s) = 0.0204(\text{cmm})(t_i - t_s)$$

$$\text{RLH} = \dot{Q}_L = G(h_{fgo})(W_i - W_s) = 2500G = 50(\text{cmm})(W_i - W_s)$$

15.5.1 Summer Air-Conditioning—Apparatus Dew Point

In summer, the outside air temperature and humidity are both high. The room, therefore gains heat as well as moisture. It is thus required to cool and dehumidify the recirculated room air in the air – conditioning apparatus either by the use of a cooling coil or by an air washer in which chilled water is sprayed. The process follows the room sensible heat factor (RSHF) line. The room sensible heat factor is the ratio of the room sensible heat to the room total heat, i.e.,

$$\text{RSHF} = \frac{\text{RSH}}{\text{RSH} + \text{RLH}} = \frac{\text{RSH}}{\text{RTH}}$$



[redacted] *Locus of supply air states for cooling and dehumidifying*

In a cooling and dehumidifying process, the temperature at which the RSFH or condition line intersects the saturation curve is called the room apparatus dew point (RADP). Thus, t_{ADP} in Fig. 15.25 denotes the effective surface temperature t_s. The condition line *i-s* represents the locus of all possible supply air states like s, s_1, s_2, etc. The minimum supply air quantity will be

$$(\text{cmm})_{\text{min.}} = \frac{\text{RSH}}{0.0204(t_i - t_{ADP})}$$

$$= \frac{\text{RLH}}{50(W_i - W_{ADP})} = \frac{\text{RTH}}{0.02(h_i - h_{ADP})}$$

In the case of an actual coil with a bypass factor of x, the leaving air state will be at s. It is seen that the effect of bypass factor is to decrease the difference in temperature between the room air and supply air, and hence to increase the supply air quantity over its minimum value.

15.5.2 Summer Air-Conditioning System with Ventilation Air–Bypass Factor X

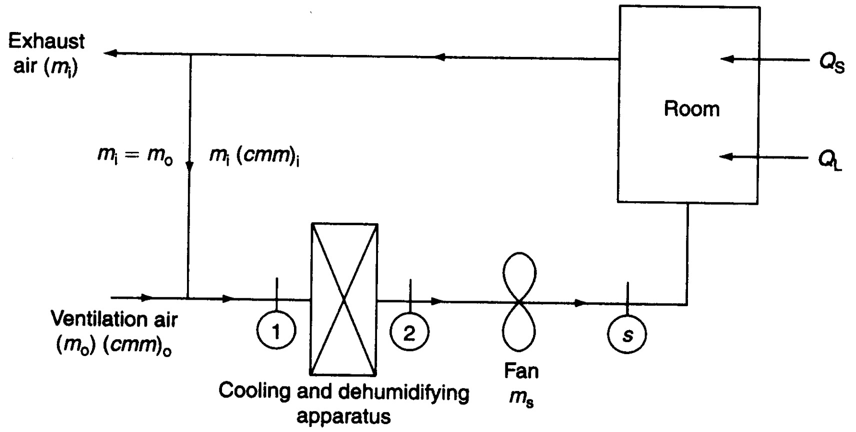
The introduction of the fresh outside air for the ventilation of the conditioned space is necessary to dilute the carbon dioxide and adours and other air contaminants for maintaining the purity of room air. The supply air to the room thus comprises fresh air and recirculated room air. An amount equal to the fresh air is ejected from the room (Fig. 15.26). In the figure, *o* and *i* represent the outside and inside air states and 1 is the state of air after mixing of recirculated room air (m_i) and ventilation air (m_o). The room sensible heat factor (RSHF) line is drawn from *i* to intersect the saturation curs *c* at room ADP at 2. Point 2 indicates the supply air state for a minimum rate of air supply. The line 1–2 represents the condition line for the apparaturs called the grand sensible heat factor (GSHF) line. Figure 15.27 shows psychrometric processes with zero and finite bypass factors. The total load on the air-conditioning apparatus from state 1 to 2 is

$$\dot{Q} = \dot{m}(h_1 - h_2) = (\dot{m}_i h_i + \dot{m}_o h_o) - \dot{m}_s h_2$$

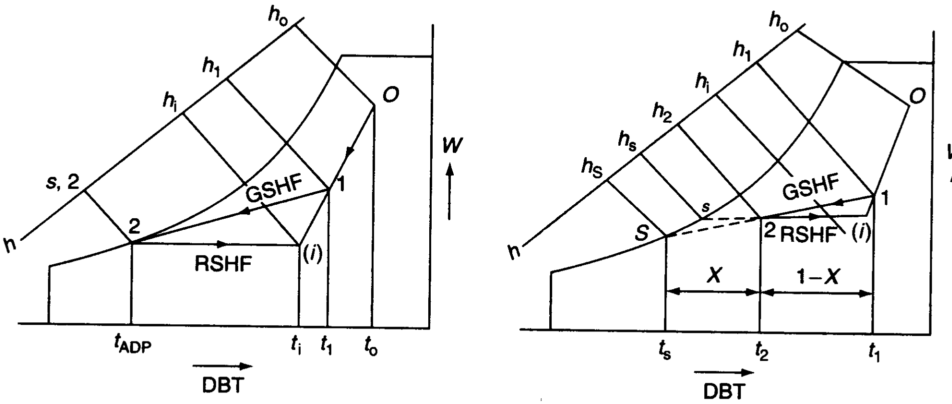
$$= (\dot{m}_i - \dot{m}_o) h_i + \dot{m}_o h_o - \dot{m}_s h_2$$

$$= \dot{m}_i (h_i - h_2) + \dot{m}_o (h_o - h_i)$$

$$= \text{Room load} + \text{Ventilation air load}$$



Summer air-conditioning scheme with ventilation air



(a) With zero bypass factor

(b) With bypass factor

Psychrometric processes for summer air-conditioning with zero and finite bypass factor

The outside air sensible heat (OASH) is $\left(\dot{Q}_S\right)_o = 0.0204\,(\text{cmm})_o(t_o - t_i)$

and the outside air latent heat load (OALH) is $\left(\dot{Q}_L\right)_o = 50(\text{cmm})_o\,(W_o - W_i)$

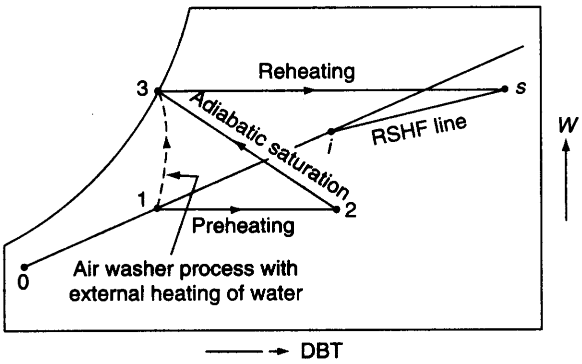
Thus, the outside air total load is $\dot{Q}_o = \left(\dot{Q}_s\right)_o + \left(\dot{Q}_L\right)_o = 0.02(\text{cmm})_o\,(h_o - h_i)$

15.5.3 Winter Air Conditioning

The processes in the conditioning apparatus for winter air conditioning for comfort usually involve heating and humidifying. Two typical processes are

1. Preheating the air with steam or hot water in a coil followed by adiabatic saturation and then reheat.
2. Heating and humidifying air in an air washer with pumped recirculation and external heating of water followed by reheat.

The processes for the two systems are shown in Fig. 15.28. The first system with preheating and adiabatic saturation follows processes 1–2 and 2–3 respectively. The second system replaces the two processes with heated water spray in the air washer and the process line is 1–3 (dotted). The reheating process 3-s is common to both.



Winter air-conditioning processes

15.6 LOAD CALCULATIONS

The major components of load in buildings are due to the direct solar radiation through the west glass, transmission through building structures and fresh air for ventilation, which depend on the *external environment*. The sensible and latent heat gains due to occupants, lights, appliances, machines, piping, etc. within the conditioned space, form the components of load of the *internal heat gains*.

15.6.1 Occupancy Load

The occupants in a conditioned space give out heat at a metabolic rate that depends on their rate of working. The typical values of sensible heat (*S*) and latent heat (*L*) given out by a person are given in Table 15.2.

15.6.2 Lighting Load

Electric lights generate sensible heat equal to the electric power consumed.

Incandescent light: Q = Total watts

Fluorescent tube: $Q = 1.25 \times$ total watts

15.6.3 Appliance Load

Most appliances contribute both sensible and latent heats, as given in Table 15.3 below.

Table 15.2

Heat Liberated due to Occupancy

Activity	*Metabolic rate (W)*	*Heat liberated (W) Room DBT in °C*					
		20		24		26	
		S	*L*	*S*	*L*	*S*	*L*
Seated at rest	115	90	25	75	40	65	50
Office Work	140	40	90	80	60	70	70
Standing	150	105	45	82	68	72	78
Light work in factory	235	130	105	100	135	80	155
Dancing	265	140	125	105	160	90	175

Table 15.3

Appliance Load, W

Appliance	*Sensible heat*	*Latent heat*
Coffee brewer	265	65
Egg boiler	**353**	**253**
Food warmer/m^2 of plate	1150	1150
Toaster, 360 slices/h	**1500**	**382**

15.6.4 Piping, Tank, Steam

Heat is added to conditioned space from running pipes carrying hot or cold fluids. Open tanks containing warm water contribute both SHL and LHL to the space due to evaporation.

15.6.5 Product Load

In the case of cold storages, the enclosures are insulated with at least 10–15 cm of thermocole and are almost sealed. In addition to the heat to be removed from products at the time of initial loading, there is also the heat produced by the commodities during storage. The *heat of respiration* forms a sizeable product load even at a storage temperature of 0°C. At higher temperatures, it is more, as given below.

[illegible]

Heat of Respiration of Products in J/kg per 24 hours

Product	*Storage temperature*	
	0°C	**15.6°C**
Apples	312–1500	2300–8215
Cabbage	**1248**	**4265**
Carrots	2183	8420
Cauliflower	**4680**	**10,500**
Grapes	416	2290
Lemon	**520**	**2390**
Orange	728	2495
Potato	**1350**	**1560**
Tomato	1040	5820

15.7 AIR-CONDITIONING SYSTEMS

Among many applications of air conditioning, the important ones are

(a) Cold storage
(b) Industrial air conditioning
(c) Comfort air conditioning

15.7.1 Cold Storage

Though cold storage is understood to be merely an application of refrigeration, it is in fact a complete air-conditioning system in which room air is cooled to much lower temperatures over a cooling coil and supplied back to the storage space. The conditions maintained inside the storage space depend on the nature of the product stored.

15.7.2 Industrial Air Conditioning

One category of industries requires constant temperature like metrology laboratories, precision-machine tools, computer centres, etc. In these, a variation of 10 to 20% in RH will not have much effect. The other category like paper and textile mills requires a constant RH. In a textile mill, e.g., an RH of 70 to 75% is required.

15.7.3 Comfort Air Conditioning

There is a problem of measuring comfort in terms of a single parameter which would include all three governing factors, namely, air temperature, humidity and air velocity in addition to air purity. Often, a single parameter called the *effective temperature* is used as an index of comfort.

Effective temperature (ET) is defined as that temperature of saturated air at which a person would experience the same feeling of comfort as experienced in the actual unsaturated environment. Based on the concept of effective temperatures, some *comfort charts* have been developed. The general practice is to recommend the following optimum inside design conditions for comfort for summer air conditioning:

ET 21.7°C
DBT 25 ± 1°C
RH 50 ± 5%

The corresponding room air velocity is 0.4 m/s.

During winter, the body gets acclimatized to withstand lower temperatures. Consequently, a DBT of 21°C at 50% RH and 0.15 – 0.2 m/s air velocity is quite comfortable. In addition to the maintenance of temperature, humidity and air velocity it is also important to maintain the purity of room air. To achieve this, it is necessary to introduce fresh air or *ventilation air*. In the case of theatres and auditoriums, ventilation air requirement is very large due to very large occupancy.

Solved Examples

Example 15.1

Atmospheric air at 1.0132 *bar has a dbt of* 32°C *and a wbt of* 26°C. *Compute* (*a*) *the partial pressure of water vapour,* (*b*) *the specific humidity,* (*c*) *the dew point temperature,* (*d*) *the relative humidity,* (*e*) *the degree of saturation,* (*f*) *the density of the air in the mixture,* (*g*) *the density of the vapour in the mixture and* (*h*) *the enthalpy of the mixture.*

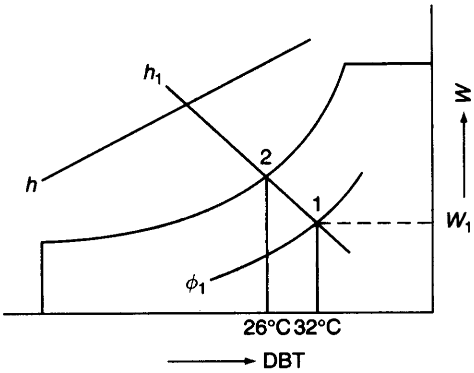
Solution The state of air is shown on the DBT-W plot in Fig. Ex. 15.1. The path 1–2 represents the constant wbt and enthalpy of the air, which also holds good approximately for an adiabatic saturation process. From Eq. (15.1), the specific humidity at state 2 is given by

$$W_2 = 0.622 \frac{p_s}{p - p_s}$$

The saturation pressure p_s at the wbt of 26°C is 0.03363 bar.

$$\therefore W_2 = 0.622\ \frac{0.03363}{1.0132 - 0.3363}$$

$$= 0.021148 \text{ kg vap./kg dry air}$$



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From Eq. (15.3), for adiabatic saturation

$$W_1 = \frac{c_{pa}\,(T_2' - T_1) + W_2 \cdot h_{fg2}}{h_{w1} - h_{f2}}$$

From the steam tables, at 26°C

$h_{fg2} = 2439.9$ kJ/kg, $h_{f2} = 109.1$ kJ/kg

At 32°C, $h_{w1} = h_g = 2559.9$ kJ/kg

(a)
$$W_1 = \frac{1.005(26-32) + 0.021148\,(2439.9)}{2559.9 - 109.1}$$

$$= 0.0186 \text{ kg vap./kg dry air} \qquad \textit{Ans.}$$

(b)
$$W_1 = 0.622\ \frac{p_w}{p - p_w} = 0.0186$$

$$\frac{p_w}{p - p_w} = \frac{0.622}{0.0186} = 33.44$$

$$p_w = 0.03 \text{ bar} \qquad \textit{Ans.}$$

(c) Saturation temperature at 0.03 bar, dpt = 24.1°C *Ans.*

(d) Relative humidity, $\phi = \dfrac{p_w}{p_{sat}}$

At 32°C, $p_{sat} = 0.048$ bar

$$\phi = \frac{0.03}{0.048} = 0.625 \text{ or } 62.5\% \qquad \textit{Ans.}$$

(e) Deg. of saturation $\mu = \dfrac{W}{W_s} = \dfrac{p_w}{p_s}\dfrac{p - p_s}{p - p_w} = \dfrac{0.03\,(1.0132 - 0.048)}{0.048\,(1.0132 - 0.03)} = 0.614$

(f) Partial pressure of dry air

$$p_a = p - p_w = 1.0132 - 0.03 = 0.9832 \text{ bar}$$

$\therefore$ Density of dry air

$$\rho_a = \frac{p_a}{R_a T_{db}} = \frac{0.9832 \times 100}{0.287 \times (273 + 32)}$$

$$= 1.12 \text{ kg/m}^3 \text{ dry air} \qquad \textit{Ans.}$$

(g) Density of water vapour

$$\rho_w = 0.0186 \frac{\text{kg vap.}}{\text{kg dry air}} \times 1.12 \frac{\text{kg dry air}}{\text{m}^3 \text{ dry air}}$$

$$= 0.021 \text{ kg vap/m}^3 \text{ dry air}$$ *Ans.*

(h) Enthalpy of the mixture

$$h = h_a + Wh_w = c_p t_a + W[h_g + 1.88\,(t_{db} - t_{dp})]$$

$$= 1.005 \times 32 + 0.0186\,[2559.9 + 1.88\,(32 - 24.1)]$$

$$= 80.55 \text{ kJ/kg}$$ *Ans.*

Example 15.2

An air-water vapour mixture enters an adiabatic saturator at 30°C *and leaves at* 20°C, *which is the adiabatic saturation temperature. The pressure remains constant at* 100 *kPa. Determine the relative humidity and the humidity ratio of the inlet mixture.*

Solution The specific humidity at the exit

$$W_2 = 0.622 \frac{p_s}{p - p_s} = 0.622 \left(\frac{2.339}{100 - 2.339}\right) = 0.0149 \frac{\text{kg vap.}}{\text{kg dry air}}$$

The specific humidity at the inlet (Eq. 15.3)

$$W_1 = \frac{c_{pa}(T_2 - T_1) + W_2 h_{fg2}}{h_{w1} - h_{f2}} = \frac{1.005\,(20 - 30) + 0.0149 \times 2454.1}{2556.3 - 83.96}$$

$$= 0.0107 \text{ kg vap./kg dry air}$$

$$W_1 = 0.622 \left(\frac{p_{w1}}{100 - p_{w1}}\right) = 0.0107$$

$$p_{w_1} = 1.691 \text{ kPa}$$

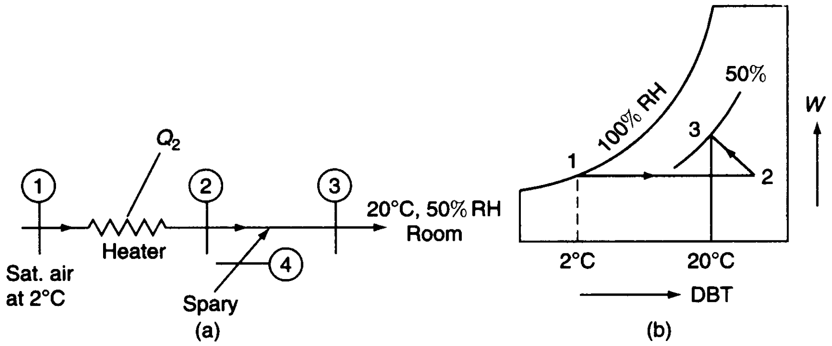
$$\therefore \quad \phi_1 = \frac{p_{w1}}{p_{s1}} = \frac{1.691}{4.246} = 0.398 \text{ or } 39.8\%$$ *Ans.*

Example 15.3

Saturated air at 2°C *is required to be supplied to a room where the temperature must be held at* 20°C *with a relative humidity of* 50%. *The air is heated and then water at* 10°C *is sprayed in to give the required humidity. Determine the temperature to which the air must be heated and the mass of spray water required per* m³ *of air at room conditions. Assume that the total pressure is constant at* 1.013 *bar and neglect the fan power.*

Solution The process is shown in Fig. Ex. 15.3. From the steam tables, at 20°C, $p_{sat} = 2.339$ kPa

$$\phi_3 = \frac{p_{w3}}{(p_{sat})_{t3}} = \frac{p_{w3}}{2.339} = 0.50$$



(a) (b)

[illegible]

$$\therefore \quad p_{w3} = 1.17 \text{ kPa}$$

$$\therefore \quad p_{a3} = 101.3 - 1.17 = 100.13 \text{ kPa}$$

$$W_3 = 0.622 \frac{p_{w3}}{p_{a3}} = 0.622 \times \frac{1.17}{100.13} = 0.00727$$

$$\phi_1 = \frac{p_{w1}}{(p_{sat})_{2°C}} = 1.00$$

At $2°C, p_{sat} = 0.7156$ kPa

$$\therefore \quad p_{w1} = 0.7156 \text{ kPa}$$

$$p_{a1} = 101.3 - 0.7156 = 100.5844 \text{ kPa}$$

$$W_1 = 0.622 \frac{0.7156}{100.5844} = 0.00442$$

$$W_3 - W_1 = 0.00727 - 0.00442 = 0.00285 \text{ kg vap./kg dry air}$$

$$v_{a3} = \frac{R_a T_3}{p_{a3}} = \frac{0.287 \times 293}{100.13} = 0.84 \text{ m}^3\text{/kg dry air}$$

$$\therefore \quad \text{Spray water} = 0.00285 \frac{\text{kg vap.}}{\text{kg dry air}} \times \frac{\text{kg dry air}}{0.84 \text{ m}^3}$$

$$= 0.00339 \text{ kg moisture/m}^3$$ *Ans.*

$$G_2 h_2 + m_{w4} h_4 = G_3 h_3$$

$$\therefore \quad h_2 + (W_3 - W_2) h_4 = h_3$$

$$h_{a2} + W_2 h_{w2} + (W_3 - W_2) h_4 = h_{a3} + W_3 h_{w3}$$

$$\therefore \quad c_p(t_3 - t_2) + W_3 h_{w3} - W_2 h_{w2} - (W_3 - W_2) h_4 = 0$$

From the steam tables, at $p_w = 1.17$ kPa

$$h_g = 2518 \text{ kJ/kg and } t_{sat} = 9.65°C$$

$$1.005\,(20 - t_2) + 0.00727\,[2518 + 1.884\,(20 - 9.65)]$$
$$-\,0.00442\,[2518 + 1.884\,(t_2 - 9.65)] - 0.00285 \times 10 = 0$$
$$\therefore \quad t_2 = 27.2°\text{C} \qquad \textit{Ans.}$$

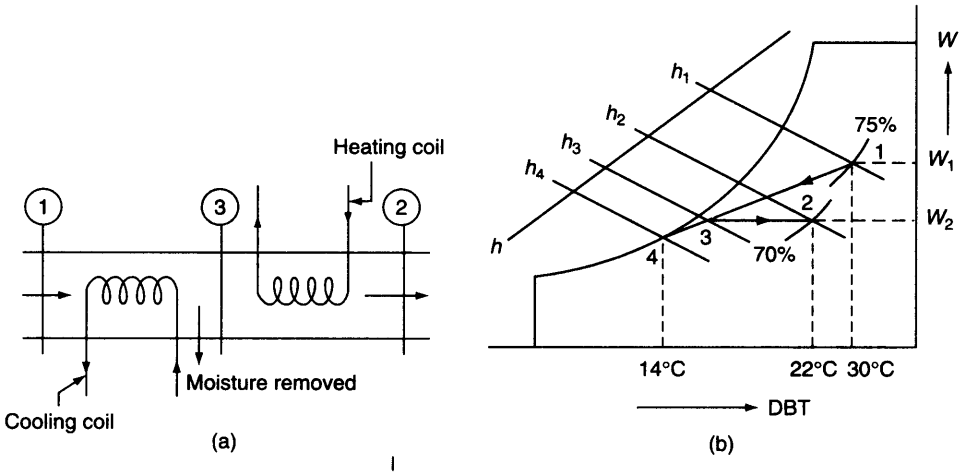
Example 15.4

An air conditioning system is designed under the following conditions:
Outdoor conditions—30°C dbt, 75% R.H.
Required indoor condition—22°C dbt, 70% R.H.
Amount of free air circulated—3.33 m³/s
Coil dew point temperature—14°C

The required condition is achieved first by cooling and dehumidification and then by heating. Estimate (a) the capacity of the cooling coil in tonnes, (b) the capacity of the heating coil in kW, and (c) the amount of water vapour removed in kg/s.

Solution The processes are shown in Fig. Ex. 15.4. The property values, taken from the psychrometric chart, are

$$h_1 = 82,\ h_2 = 52,\ h_3 = 47,\ h_4 = 40 \text{ kJ/kg dry air}$$
$$W_1 = 0.020,\ W_2 = W_3 = 0.0115 \text{ kg vap./kg dry air}$$
$$v_1 = 0.887 \text{ m}^3\text{/kg dry air}$$
$$G = \frac{3.33}{0.887} = 3.754 \text{ kg dry air/sec}$$
$$\therefore \quad \text{Cooling coil capacity} = G(h_1 - h_3) = 3.754\,(82 - 47) \text{ kJ/s}$$
$$= \frac{3.754 \times 35 \times 3600}{14{,}000} = 33.79 \text{ tonnes} \qquad \textit{Ans.}\ \text{(a)}$$
$$\text{Capacity of the heating coil} = G(h_2 - h_3) = 3.754\,(52 - 47) \text{ kJ/s}$$
$$= 3.754 \times 5 = 18.77 \text{ kW} \qquad \textit{Ans.}\ \text{(b)}$$



Rate of water vapour removed $= G\,(W_1 - W_3) = 3.754 \times (0.0200 - 0.0115)$

$= 0.0319$ kg/s *Ans.* (c)

Example 15.5

Air at 20°C, 40% RH is mixed adiabatically with air at 40°C, 40% RH in the ratio of 1 kg of the former with 2 kg of the latter (on dry basis). Find the final condition of air.

Solution Fig. Ex. 15.5 shows the mixing process of two air streams. The equations

$$G_1 + G_2 = G_3$$

$$G_1W_1 + G_2W_2 = G_3W_3$$

$$G_1h_1 + G_2h_2 = G_3h_3$$

result in

$$\frac{W_2 - W_3}{W_3 - W_1} = \frac{h_2 - h_3}{h_3 - h_1} = \frac{G_1}{G_2}$$

From the psychrometric chart

$$W_1 = 0.0058,\ W_2 = 0.0187 \text{ kg vap./kg dry air}$$

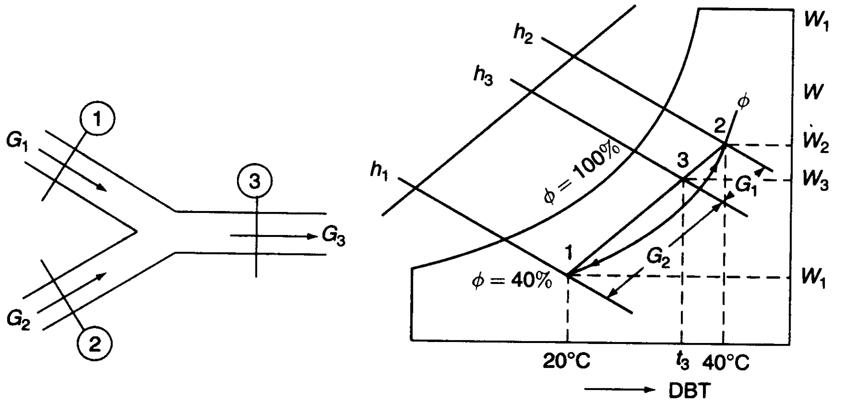
$$h_1 = 35,\ h_2 = 90 \text{ kJ/kg dry air}$$

$$\therefore \quad \frac{0.0187 - W_3}{W_3 - 0.0058} = \frac{G_1}{G_2} = \frac{1}{2}$$

$$\therefore \quad W_3 = \frac{2}{3} \times 0.187 + \frac{1}{3} \times 0.0058 = 0.0144 \text{ kg vap./kg dry air}$$

Again

$$\frac{h_2 - h_3}{h_3 - h_1} = \frac{G_1}{G_2} = \frac{1}{2}$$



(a) (b)

$$\therefore \qquad h_3 = \frac{2}{3}\,h_2 = \frac{1}{3}\,h_1 = \frac{2}{3} \times 90 + \frac{1}{3} \times 35 = 71.67 \text{ kJ/kg dry air}$$

$\therefore$ Final condition of air is given by

$$W_3 = 0.0144 \text{ kg vap./kg dry air}$$

$$h_3 = 71.67 \text{ kJ/kg dry air}$$

Example 15.6

Saturated air at 21°C is passed through a drier so that its final relative humidity is 20%. The drier uses silica gel adsorbent. The air is then passed through a cooler until its final temperature is 21°C without a change in specific humidity. Find out (a) the temperature of air at the end of the drying process, (b) the heat rejected in kJ/kg dry air during the cooling process, (c) the relative humidity at the end of the cooling process, (d) the dew point temperature at the end of the drying process, and (e) the moisture removed during the drying process in kg vap./kg dry air.

Solution From the psychrometric chart (Fig. Ex. 15.6)

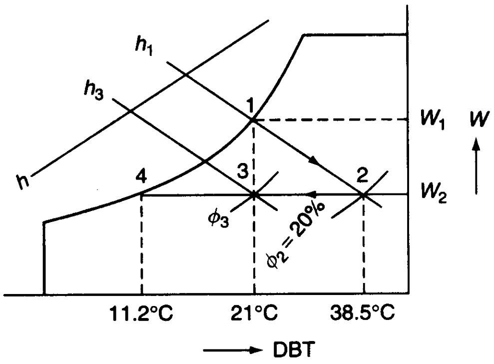
$T_2 = 38.5°\text{C}$ *Ans.* (a)

$h_1 - h_3 = 60.5 - 42.0 = 18.5$ kJ/kg dry air *Ans.* (b)

$\phi_3 = 53\%$ *Ans.* (c)

$t_4 = 11.2°\text{C}$ *Ans.* (d)

$W_1 - W_2 = 0.0153 - 0.0083 = 0.0070$ kg vap/kg dry air *Ans.* (e)



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Example 15.7

For a hall to be air-conditioned, the following conditions are given

Outdoor condition—40°C dbt, 20°C wbt

Required comfort condition—20°C dbt, 60% RH

Seating capacity of hall—1500

Amount of outdoor air supplied—0.3 m³/min per person

If the required condition is achieved first by adiabatic humidification and then by cooling, estimate (a) the capacity of the cooling coil in tonnes, and (b) the capacity of the humidifier in kg/h.

Solution From the psychrometric chart (Fig. Ex. 15.7)

$h_1 = h_2 = 57.0,\ h_3 = 42.0$ kJ/kg dry air

$W_1 = 0.0065,\ W_2 = W_3 = 0.0088$ kg vap./kg dry air

$t_2 = 34.5°\text{C}$, $v_1 = 0.896\ \text{m}^3/\text{kg dry air}$

Amount of dry air supplied

$$G = \frac{1500 \times 0.3}{0.896} = 502\ \text{kg/min}$$

$\therefore$ Capacity of the cooling coil $= G(h_2 - h_3)$
$= 502\,(57 - 42)$ kJ/min

$$= \frac{502 \times 15 \times 60}{14{,}000} = 32.27 \text{ tonnes} \qquad \textit{Ans. (a)}$$

Capacity of the humidifier $= G\,(W_2 - W_1)$
$= 502\,(0.0088 - 0.0065)$ kg/min

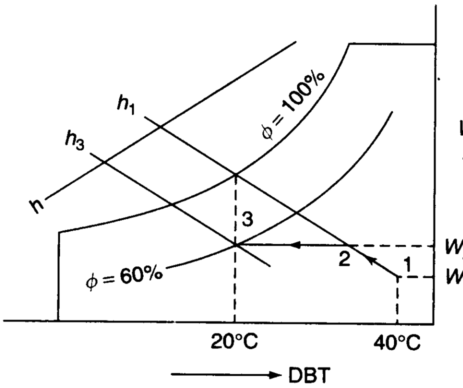


Fig. Ex. 15.7

$= 502 \times 23 \times 10–4 \times 60 = 69.3$ kg/h *Ans.* (b)

Example 15.8

Water at 30°C *flows into a cooling tower at the rate of* 1.15 *kg per kg of air. Air enters the tower at a dbt of* 20°C *and a relative humidity of* 60% *and leaves it at a dbt of* 28°C *and* 90% *relative humidity. Make-up water is supplied at* 20°C. *Determine:* (i) *the temperature of water leaving the tower,* (ii) *the fraction of water evaporated, and* (iii) *approach and range of the cooling tower.*

Solution Properties of air entering and leaving the tower (Fig. 15.13) are

$$t_{\text{wb1}} = 15.2°\text{C}$$

$$t_{\text{wb2}} = 26.7°\text{C}$$

$$h_1 = 43\ \text{kJ/kg dry air}$$

$$h_2 = 83.5\ \text{kJ/kg dry air}$$

$$W_1 = 0.0088\ \text{kg water vapour/kg dry air}$$

$$W_2 = 0.0213\ \text{kg water vapour/kg dry air}$$

Enthalpies of the water entering the tower and the make-up water are

$$h_{\text{w3}} = 125.8\ \text{kJ/kg} \qquad h_{\text{m}} = 84\ \text{kJ/kg}$$

From the energy balance Eq. (15.5),

$$h_{\text{w3}} - h_{\text{w4}} = \frac{G}{m_{\text{w}}}\left[(h_2 - h_1) - (W_2 - W_1)\,h_{\text{w}}\right]$$

$$= \frac{1}{1.15}\left[(83.5 - 43) - (0.0213 - 0.0088)\,84\right] = 34.2\ \text{kJ/kg}$$

Temperature drop of water

$$t_{\text{w3}} - t_{\text{w4}} = \frac{34.2}{4.19} = 30 - t_{\text{w4}}$$

$$\therefore \qquad t_{w4} = 21.8°\text{C}$$

$$\therefore \qquad \text{Approach} = t_{w4} = t_{wb1} = 21.8 - 15.2 = 6.6°\text{C}$$

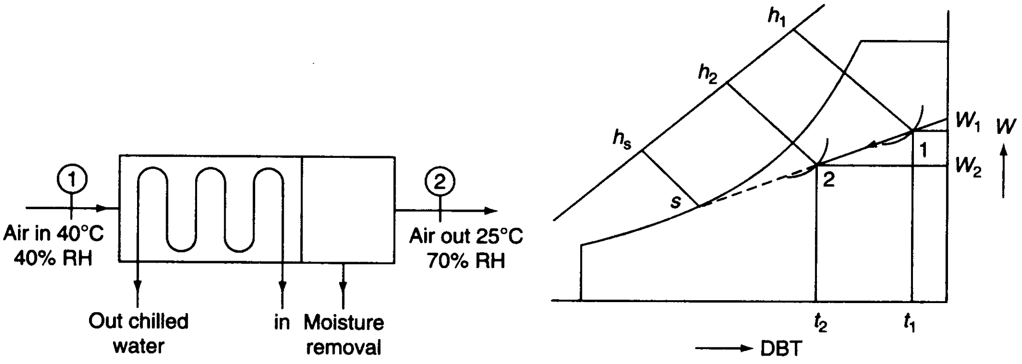
$$\text{Range} = t_{w3} = t_{w4} = 30 - 21.8 = 8.2°\text{C}$$

Fraction of water evaporated, $x = G(W_2 - W_1) = 1(0.0213 - 0.0088) = 0.0125$ kg/kg dry air

Example 15.9

Air having DBT of 40°C and RH 40% has to be cooled and dehumidified such that its DBT is 25°C and RH 70%. Determine the amount of moisture removed and the tons of refrigeration required when the air flow rate is 30 cmm. Estimate the bypass factor of the cooling coil.

Solution



Cooling and dehumidification

From psychrometric chart (fig. above)

$$v_1 = 0.9125 \text{ m}^3/\text{kg d.a. (at 40°C, 40\% RH)}$$

Mass of dry air entering the cooling coil

$$G = \frac{30\,\text{m}^3/\text{min}}{0.9125} = 32.88 \text{ kg/min}$$

$$W_1 = 0.0182 \text{ kg vapour/kg d.a.}, \; h_1 = 86 \text{ kJ/kg d.a.}$$

$$W_2 = 0.0136 \text{ kg/kg d.a.}, \; h_2 = 60 \text{ kJ/kg d.a.}$$

$$\text{Cooling load} = G(h_1 - h_2) = \frac{32.88(86 - 60)}{60 \times 3.5} = 4.07 \text{ tonnes of refrigeration} \qquad \textit{Ans.}$$

$$\text{Rate of moisture removal} = G\,(W_1 - W_2)$$

$$= 32.88\,(0.0182 - 0.0136)$$

$$= 0.151 \text{ kg/min} \qquad \textit{Ans.}$$

$$\text{Bypass factor} = \frac{h_2 - h_s}{h_1 - h_s}$$

$$= \frac{60 - 41.5}{86 - 41.5} = 0.468 \qquad \textit{Ans.}$$

Example 15.10

A classroom with seating capacity of 75 *persons has to be air conditioned, first by heating and then humidifying, during winter. The outdoor conditions are: DBT* 10°*C, WBT* 8°*C. The indoor conditions: DBT* 20°*C, RH* 50%. *An amount of* 0.3 *cmm per person is circulated Calculate the capacity of the heating coil and its surface temperature when the bypass factor is* 0.5 *and the capacity of the humidifier.*

Solution In Fig. Ex.15.10 above, line 1–4 is sensible heating and line 2–3 is adiabatic saturation when $h_2 = h_3$. From the chart

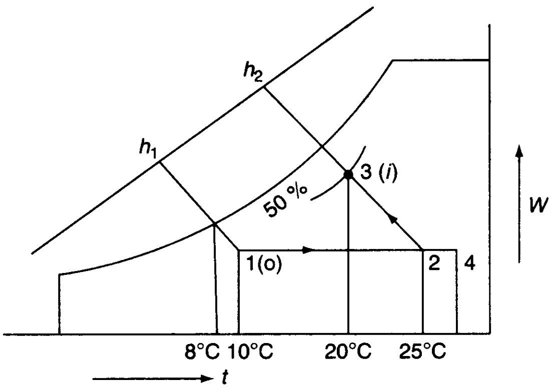


Fig. Ex. 15.10

$W_1 = 0.0058$ kg moisture/kg d.a.,

$h_1 = 24.5$ kJ/kg d.a.

$h_2 = h_3 = 39.5$ kJ/kg d.a, $t_db_2 = 25$°C.

$W_3 = 0.0074$ kg moisture/kg d.a.

$\upsilon_1 = 0.81$ m3/kg d.a.

Mass of dry air circulated per min

$$G = \frac{0.3 \times 75}{0.81} = 27.78 \text{ kg d.a./min}$$

Capacity of the heating coil $= G(h_2 - h_1)$

$= 27.78\ (39.5 - 24.5)/60 = 6.94$ kW *Ans.*

Bypass factor of the heating coil

$$= \frac{t_4 - t_2}{t_4 - t_1} = \frac{t_4 - 25}{t_4 - 10} = 0.5$$

$\therefore\ t_4 = 40°\text{C} = t_s$ *Ans.*

Capacity of the humidifier $= G(W_3 - W_1) = 27.78\ (0.0074 - 0.0058) \times 60$

$= 2.667$ kg/h *Ans.*

Example 15.11

A mixture of recirculated room air and outdoor air enters a cooling coil at 31°*C DBT and* 18.5°*C WBT at the rate of* 39.6 *cmm. The effective surface temperature of the coil is* 4.4°*C. The surface area of the coil is such as would gives* 12.5 *kW of refrigeration. Determine the DBT and WBT of the air leaving the coil and the coil bypass factor.*

Solution From Fig. Ex. 15.11, at the ADP, of 4.4°C,

$W_s = 5.25$g/kg d.a.

$h_s = 17.7$ kJ/kg.d.a.

State of entering air: $\upsilon_1 = 0.872$ m^3/kg d.a.

$h_1 = 52.5$ kJ/kg d.a.

$w_1 = 8.2$g/kg d.a.

Mass flow rate of dry air,

$$G = \frac{39.6}{0.872} = 44.4 \text{ kg d.a./min}$$

Cooling load, $\dot{Q} = G(h_1 - h_2)$

$$\therefore \quad h_1 - h_2 = \frac{12.5 \times 60}{44.4} = 16.89 \text{ kJ/kg d.a.}$$

$$h_2 = 52.5 - 16.89 = 35.61 \text{ kJ/kg d.a.}$$

For the condition line 1–5,

$$\frac{h_1 - h_2}{h_1 - h_s} = \frac{w_1 - w_2}{w_1 - w_s}$$

$$\frac{52.5 - 25.61}{52.5 - 17.7} = \frac{8.2 - w_2}{8.2 - 5.25}$$

$\therefore W_2 = 6.77$ g water vapour/kg d.a.

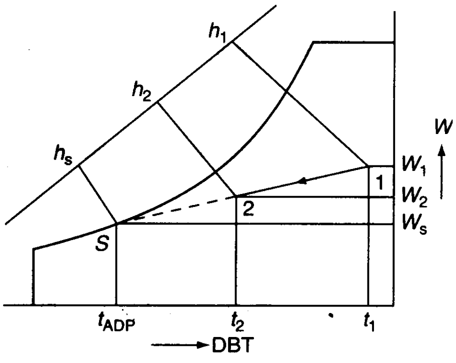


Fig. Ex. 15.11

From the psychrometric chart, for $h_2 = 35.61$ kJ/kg d.a. and $W_2 = 6.77$g water vapour/kg d.a.,

$$t_2 = 18.6°\text{C}, t' = 12.5°\text{C (WBT)}. \qquad \textit{Ans.}$$

Coil bypass factor

$$X = \frac{h_2 - h_s}{h_1 - h_s} = \frac{35.61 - 17.7}{52.5 - 17.7} = 0.515 \qquad \textit{Ans.}$$

Example 15.12

An auditorium has to be air-conditioned first by cooling and dehumidifying and then heating for summer when the outdoor conditions are: DBT 35°C, RH 70%. The desired indoor conditions are: DBT 20°C, RH 60%. The cooling coil dew point temperature is 10°C. The amount of free air to be circulated is 300 cmm. Estimate (a) the capacity of cooling coil and its bypass factor, (b) the capacity of the heating coil and its surface temperature when the bypass factor is 0.25, and (c) the mass of water vapour removed.

Solution

Point 1(*o*): DBT 35°C RH 70%

$h_1 = 98$ kJ/kg d.a.

$w_1 = 0.0246$ kg vap./kg d.a.

$v_1 = 0.907$ m^3/kg d.a.

Point 3(*c*): DBT 20°C, RH 60%,

$h_3 = 42$ kJ/kg d.a., $W_3 = 0.0088$ kg vap./kg d.a.

Point(*s*) $t_s = 10$°C.

$h_2 = 34$ kJ/kg d.a., $h_s = 30$ kJ/kg d.a.,

$t_2 = 12$°C.

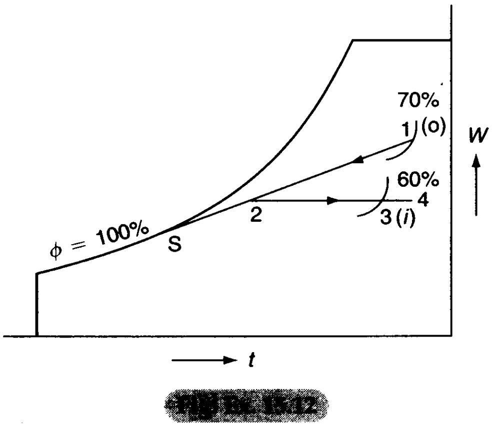


Fig. Ex. 15.12

$$G = \text{mass flow rate of dry air} = \frac{300}{0.907}$$

$$= 330.76 \text{ kg/min}$$

$$\text{Capacity of the cooling coil} = G(h_1 - h_2)$$

$$= 330.76\,(98 - 34)/60 \times 3.5$$

$$= 100.8 \text{ tonnes of refrigeration}$$ *Ans.*

$$\text{Cooling coil bypass factor} = \frac{h_2 - h_s}{h_1 - h_s} = \frac{34 - 30}{98 - 30} = 0.059$$ *Ans.*

$$\text{Capacity of the heating coil} = G(h_3 - h_2) = \frac{330.76}{60}(42 - 34) = 44.1 \text{ kW}$$

$$\text{Bypass factor of the heating coil} = 0.25 = \frac{t_4 - t_3}{t_4 - t_2} = \frac{t_4 - 20}{t_4 - 12}$$ *Ans.*

$$\therefore \quad t_4 = 22.67°\text{C} = \text{surface temperature of the heating coil}$$ *Ans.*

$$\text{Mass of water vapour removed} = G(W_1 - W_3) = 330.76\,(0.0246 - 0.0088)$$

$$= 5.23 \text{ kg/min.}$$ *Ans.*

Example 15.13

Water from a cooling system is itself to be cooled in a cooling tower at a rate of 2.78 kg/s. The water enters the tower at 65°C and leaves a collecting tank at the base at 38°C. Air flows through the tower, entering the base at 15°C, 0.1 MPa, 55% RH, and leaving the top at 35°C, 0.1 MPa, saturated. Make-up water enters the collecting tank at 14°C. Determine the air flow rate into the tower in m³/s and the make-up water flow rate in kg/s.

Solution Figure Ex. 15.13 shows the flow diagram of the cooling tower. From the steam tables.

at 15°C, $p_{sat} = 0.01705$ bar, $h_g = 2528.9$ kJ/kg

at 35°C, $p_{sat} = 0.05628$ bar, $h_g = 2565.3$ kJ/kg

$$\phi_1 = \frac{p_w}{(p_{sat})_{15°C}} = 0.55$$

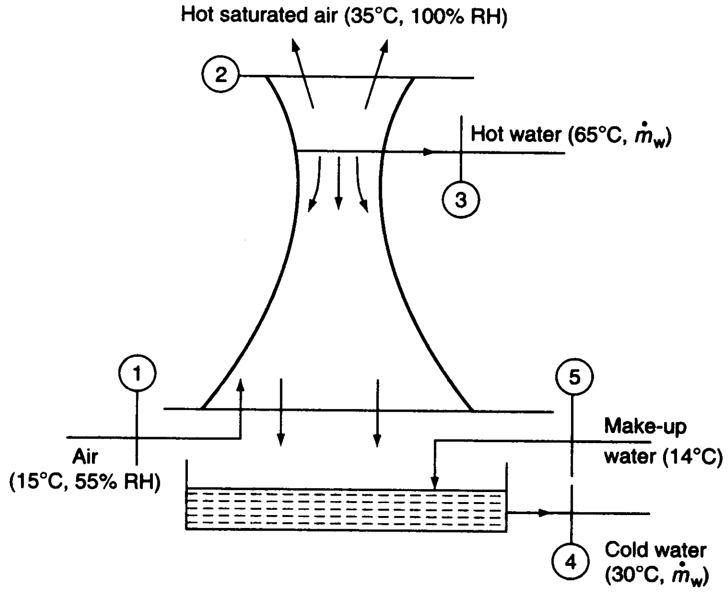
$$\therefore \quad p_{w1} = 0.55 \times 0.01705 = 0.938 \times 10^{-2} \text{ bar}$$

$$\phi_2 = \frac{p_w}{(p_{sat})_{35°C}} = 1.00$$

$$\therefore \quad p_{w2} = 0.05628 \text{ bar}$$

$$W_1 = 0.622\,\frac{p_w}{p - p_w} = 0.622 \times \frac{0.938 \times 10^{-2}}{1.00 - 0.00938} = 0.00589 \text{ kg vap./kg dry air}$$

$$W_2 = 0.622 \times \frac{0.05628}{1.00 - 0.05628} = 0.0371 \text{ kg vap./dry air}$$



[redacted]

$\therefore$ Make-up water $= W_2 - W_1 = 0.0371 - 0.00589 = 0.03121$ kg vap./kg dry air

Energy balance gives

$$H_2 + H_4 - H_1 - H_3 - H_5 = 0$$

For 1 kg of dry air

$$c_{pa}(t_2 - t_1) + W_2 h_2 - W_1 h_1 + \dot{m}_w (h_4 - h_3) - (W_2 - W_1) h_5 = 0$$

$$\therefore \quad 1.005\,(35 - 15) + 0.0371 \times 2565.3 - 0.00589 \times 2528.9$$

$$+ \dot{m}_w (-35)\,4.187 - 0.03121 \times 4.187 \times 14 = 0$$

or

$$146.55\,\dot{m}_w = 98.54$$

$$\therefore \quad \dot{m}_w = 0.672 \text{ kg water/kg dry air}$$

Since water flow rate is 2.78 kg/s

$$\therefore \text{ Rate of dry air flow} = \frac{2.78}{0.672} = 4.137 \text{ kg/s}$$

$\therefore$ Make-up water flow rate $= 0.03121 \times 4.137 = 0.129$ kg/s *Ans.*

Rate of dry air flow $= 4.137$ kg/s

Rate of wet air flow $= 4.137\,(1 + W_1) = 4.137 \times 1.00589 = 4.16$ kg/s

$\therefore$ Volume flow rate of air $= \dfrac{\dot{m}_a RT}{p} = \dfrac{4.16 \times 0.287 \times 288}{100} = 3.438$ m^3/s *Ans.*

Review Questions

15.1 What do you mean by air conditioning?

15.2 What is moist air? Name the constituents of dry air and its composition.

15.3 What is Gibbs theorem? State the molecular mass of atmospheric air.

15.4 What do you understand by psychrometry?

15.5 What do you mean by saturated air and unsaturated air?

15.6 What is specific humidity? When does it become maximum? Show that specific humidity is a function of partial pressure of water vapour.

15.7 What do you mean by dew point temperature?

15.8 What is degree of saturation? What are its limiting values?

15.9 What is relative humidity? How is it defined as a ratio of two partial pressures?

15.10 Show that the relative humidity of air given by

$$\phi = \frac{\mu}{1-(1-\mu)p_s/p}$$

15.11 What is enthalpy of moist air? Show that it is given by

$$h = 1.005\, t + W(2500 + 1.88\, t) \text{ kJ/kg d.a.}$$

15.12 What do your mean by wet bulb temperature? Is it a thermodynamic property?

15.13 When do the DBT, DPT and WBT become equal?

15.14 What is a sling psychrometer?

15.16 Explain the adiabatic saturation process. What is thermodynamic wet-bulb temperature?

15.17 Show that the enthalpy of air-vapour mixture remains constant during an adiabatic saturation process.

15.18 Explain with a neat sketch the constant property lines in a psychrometric chart.

15.19 What do you mean by enthalpy deviation?

15.20 What are the psychrometric processes encountered in airconditioning practice?

15.21 What is sensible heating or cooling?

15.22 Explain SHL, LHL and total heat load.

15.23 Define sensible heat factor (SHF).

15.24 What is humid specific heat?

15.25 Show that

$$\text{SHF} = \frac{0.0204\,(\text{cmm})\,\Delta t}{0.0204\,(\text{cmm})\,\Delta t + 50\,(\text{cmm})\,\Delta W} e^{i\theta}$$

where cmm is m^3/min.

15.26 What do you mean by cooling and dehumidification? Explain it with flow diagram and psychrometric charts.

15.27 Explain the process of heating and humidification.

15.28 Explain the process of adiabatic mixing of two air streams.

15.29 What do you mean by chemical dehumidification? Why does the DBT of air increase?

15.30 What is adiabatic evaporative cooling?

15.31 Explain the operation of a cooling tower. What is the minimum temperature to which warm water can be cooled in a cooling tower?

15.32 How is a cooling tower specified? Define the approach and range.

15.33 What do you mean by bypass factor? What is contact factor?

15.34 Explain the operation of an air washer with sketches. How can it be used for year-round airconditioning?

15.35 Explain with a sketch a simple airconditioning system. Define RSH and RLH.

15.36 Explain with sketches summer air-conditioning schemes with and without ventilation air.

15.37 Explain the terms GSHF and RSHF. What are OASH and OALH?

15.38 Explain with sketches the schemes of winter air conditioning.

15.39 Explain the external and internal heat gains. What is occupancy load?

15.40 What is product load? What do you mean by heat of respiration?

15.41 Explain the applications of air conditioning in cold storages and typical industries.

15.42 What is comfort air conditioning? What do you mean by effective temperature? What are comfort charts?

15.43 State the optimum inside design conditions of air recommended for summer and winter air conditioning.

15.44 Explain the importance of ventilation air in a conditioned space.

Problems

15.1 An air-water vapour mixture at 0.1 MPa, 30°C, 80% RH has a volume of 50 m^3. Calculate the specific humidity, dew point, wbt, mass of dry air, and mass of water vapour.

If the mixture is cooled at constant pressure to 5°C, calculate the amount of water vapour condensed.

15.2 A sling psychrometer reads 40°C dbt and 36°C wbt. Find the humidity ratio, relative humidity, dew point temperature, specific volume, and enthalpy of air.

15.3 Calculate the amount of heat removed per kg of dry air if the initial condition of air is 35°C, 70% RH, and the final condition is 25°C, 60% RH.

15.4 Two streams of air 25°C, 50% RH and 25°C, 60% RH are mixed adiabatically to obtain 0.3 kg/s of dry air at 30°C. Calculate the amounts of air drawn from both the streams and the humidity ratio of the mixed air.

15.5 Air at 40°C dbt and 27°C wbt is to be cooled and dehumidified by passing it over a refrigerant-filled coil to give a final condition of 15°C and 90% RH. Find the amounts of heat and moisture removed per kg of dry air.

15.6 An air-water vapour mixture enters a heater-humidifier unit at 5°C, 100 kPa, 50% RH. The flow rate of dry air is 0.1 kg/s. Liquid water at 10°C is sprayed into the mixture at the rate of 0.002 kg/s. The mixture leaves the unit at 30°C, 100 kPa. Calculate (a) the relative humidity at the outlet, and (b) the rate of heat transfer to the unit.

15.7 A laboratory has a volume of 470 m^3, and is to be maintained at 20°C, 52.5% RH. The air in the room is to be completely changed once every hour and is drawn from the atmosphere at 1.05 bar, 32°C, 86% RH, by a fan absorbing 0.45 kW. This air passes through a cooler which reduces its temperature and causes condensation, the condensate being drained off at 8°C. The resulting saturated air is heated to room condition. The total pressure is constant throughout. Determine (a) the temperature of the air leaving the cooler, (b) the rate of condensation, (c) the heat transfer in the cooler, and (d) the heat transfer in the heater.
Ans. (a) 10°C, (b) 10.35 kg/h, (c) 11.33 kW, (d) 1.63 kW

15.8 In an air conditioning system, air is to be cooled and dehumidified by means of a cooling coil. The data are as follows:

Initial condition of the air at inlet to the cooling coil: dbt = 25°C, partial pressure of water vapour = 0.019 bar, absolute total pressure = 1.02 bar

Final condition of air at exit of the cooling coil: dbt = 15°C, RH = 90%, absolute total pressure = 1.02 bar.

Other data are as follows:

Characteristic gas constant for air = 287 J/kg K

Characteristic gas constant for water vapour = 461.5 J/kg K

Saturation pressure for water at 15°C = 0.017 bar

Enthalpy of dry air = 1.005 *t* kJ/kg

Enthalpy of water vapour = (2500 + 1.88 *t*) kJ/kg where *t* is in °C

Determine (a) the moisture removed from air per kg of dry air, (b) the heat removed by the cooling coil per kg of dry air. *Ans.* (a) 0.0023 kg/kg d.a. (b) 16.1 kJ/kg d.a.

15.9 Air at 30°C, 80% RH is cooled by spraying in water at 12°C. This causes saturation, followed by condensation, the mixing being assumed to take place adiabatically and the condensate being drained off at 16.7°C. The resulting saturated mixture is then heated to produce the required conditions of 60% RH at 25°C. The total pressure is constant at 101 kPa. Determine the mass of water supplied to the sprays to provide 10 m^3/h of conditioned air. What is the heater power required? *Ans.* 2224 kg/h, 2.75 kW

15.10 An air-conditioned room requires 30 m^3/min of air at 1.013 bar, 20°C, 52.5% RH. The steady flow conditioner takes in air at 1.013 bar, 77% RH, which it cools to adjust the moisture content and reheats to room temperature. Find the temperature to which the air is cooled and the thermal loading on both the cooler and heater. Assume that a fan before the cooler absorbs 0.5 kW, and that the condensate is discharged at the temperature to which the air is cooled. *Ans.* 10°C, 25 kW, 6.04 kW

15.11 An industrial process requires an atmosphere having a RH of 88.4% at 22°C, and involves a flow rate of 2000 m^3/h. The external conditions are 44.4% RH, 15°C. The air intake is heated and then humidified by water spray at 20°C. Determine the mass flow rate of spray water and the power required for heating, if the pressure throughout is 1 bar. *Ans.* 23.4 kg/h, 20.5 kW

15.12 Cooling water enters a cooling tower at a rate of 1000 kg/h and 70°C. Water is pumped from the base of the tower at 24°C and some make-up water is added afterwards. Air enters the tower at 15°C, 50% RH, 1.013 bar, and is drawn from the tower saturated at 34°C, 1 bar. Calculate the flow rate of the dry air in kg/h and the make-up water required per hour. *Ans.* 2088 kg/h, 62.9 kg/h

15.13 A grain dryer consists of a vertical cylindrical hopper through which hot air is blown. The air enters the base at 1.38 bar, 65°C, 50% RH. At the top, saturated air is discharged into the atmosphere at 1.035 bar, 60°C.

Estimate the moisture picked up by 1 kg of dry air, and the total enthalpy change between the entering and leaving streams expressed per unit mass of dry air. *Ans.* 0.0864 kJ/kg air, 220 kJ/kg air

15.14 Air enters a counterflow cooling tower at a rate of 100 m^3/s at 30°C dbt and 40% relative humidity. Air leaves at the top of the tower at 32°C and 90% relative humidity. Water enters the tower at 35°C and the water flow rate is 1.2 times the mass flow rate of air. Make-up water is supplied at 20°C. What are the range and approach of the tower? At what rate is heat absorbed from the load by the stream of water on its way back to the top of the tower? What percentage of the water flow rate must be supplied as make-up water to replace the water evaporated into the air stream? *Ans.* Range = 8.7°C, Approach = 6.3°C, Q = 5005 kW, % make-up = 1.39%

15.15 Moist air at standard atmospheric pressure is passed over a cooling coil the inlet conditions are: DBT 30°C, 50% RH. The outlet conditions are: DBT 15°C, RH 80% show the process on a psychrometric chart. Estimate the amount of heat and moisture removed per kg of dry air. *Ans.* (–27.23 kJ/kg d.a., –0.00482 kg/kg d.a.)

15.16 Moist air enters a chamber at 5°C DBT and 2.5°C WBT at a rate of 90 cmm. While passing through the chamber, the air absorbs sensible heat at the rate of 40.7 KW and picks up 40 kg/h of saturated steam at 110°C. Determine the DBT and WBT of leaving air. *Ans.* 26.5°C 18.1°C

15.17 An air-conditioned room is maintained at 27°C DBT and 50% RH. The ambient conditions are 40°C DBT and 27°C WBT. The room has a sensible heat gain of 14 kW. Air is supplied to the room at 7°C saturated. Determine (a) mass of moist air supplied to the room is kg/h, (b) latent heat gain of room in KW, (c) cooling load of the air washer in KW if 30% of the air supplied to the room is fresh, the remainder being recirculated.
Ans. (a) 2482 kg/h, (b) 8.57 kw, (c) 28.71 kw

15.18 The outdoor summer design condition for a bank for 100 persons at a place is DBT 310 K and WBT 300 K. The required inside conditions are DBT 295 K and 60% RH. The room sensible heat gain is 400,000 kJ/h. and the latent heat gain is 200,000 kJ/h. Ventilation air required is 0.0047 m^3/s per person. Estimate (a) the grand total heat load, (b) SHF, (c) apparatus dew point, (d) volume flow rate of dehumidified air
Ans. (a) 5,70,480 kJ/h, (b) 0.6622, (c) 282.5K, (d) 532.7 m^3/min.

15.19 A class room of seating capacity 50 persons (Sensible heat gain per person 100 W, latent hear gain per person 25 W, other heat gains are 3000W) is to be maintained at DBT 15°C, 50% RH. The ambient conditions are 40°C DBT and 27°C WBT. Air is supplied to the room at 7°C, 100% RH. Calculate (a) the mass of moist air supplied to the room, (b) the cooling load of the air washer in kW, if 30% of the air supplied to the room is fresh and the remainder being recirculated. *Ans.* (a) 85.38 kg/min, (b) 6.97 tonnes.

CHAPTER 16

Reactive Systems

In this chapter we shall study the thermodynamics of mixtures that may be undergoing chemical reaction. With every chemical reaction is associated a chemical equation which is obtained by balancing the atoms of each of the atomic species involved in the reaction. The initial constituents which start the reaction are called the *reactants*, and the final constituents which are formed by chemical reaction with the rearrangement of the atoms and electrons are called the *products*. The reaction between the reactants, hydrogen and oxygen, to form the product water can be expressed as

$$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O \tag{16.1}$$

The equation indicates that one mole of hydrogen and half a mole of oxygen combine to form one mole of water. The reaction can also proceed in the reverse direction. The coefficients 1, $\frac{1}{2}$, 1 in the chemical Eq. (16.1) are called *stoichiometric coefficients.*

16.1 DEGREE OF REACTION

Let us suppose that we have a mixture of four substances, A_1, A_2, A_3 and A_4, capable of undergoing a reaction of the type

$$\nu_1 A_1 + \nu_2 A_2 \rightleftharpoons \nu_3 A_3 + \nu_4 A_4$$

where the ν's are the stoichiometric coefficients.

Starting with arbitrary amounts of both initial and final constituents, let us imagine that the reaction proceeds completely to the right with the disappearance of at least one of the initial constituents, say, A_1. Then the original number of moles of the initial constituents is given in the form

$$n_1\text{ (original)} = n_0\,\nu_1$$
$$n_2\text{ (original)} = n_0\,\nu_2 + N_2$$

where n_0 is an arbitrary positive number, and N_2 is the residue (or excess) of A_2, i.e., the number of moles of A_2 which cannot combine. If the reaction is assumed to proceed completely to the left with the disappearance of the final constituent A_3, then

$$n_3\text{ (original)} = n'_0\,\nu_3$$
$$n_4\text{ (original)} = n'_0\,\nu_4 + N_4$$

where n'_0 is an arbitrary positive number and N_4 is the excess number of moles of A_4 left after the reaction is complete from right to left.

For a reaction that has occurred completely to the left, there is a maximum amount possible of each initial constituent, and a minimum amount possible of each final constituent, so that

$$n_1(\text{max}) = n_0\,\nu_1 \qquad + \qquad n'_0\,\nu_1$$

(Original number of moles of A_1) (Number of moles of A_1 formed by chemical reaction)

$$(n'_0\,\nu_3 A_3 + n'_0\,\nu_4 A_4 \rightarrow n'_0\,\nu_1 A_1 + n'_0\,\nu_2 A_2)$$

$$= (n_0 + n'_0)\,\nu_1$$

$$n_2\,(\text{max}) = \underset{\text{(Original number of moles of } A_2\text{)}}{(n_0\,\nu_2 + N_2)} + \underset{\text{(Number of moles of } A_2 \text{ formed by chemical reaction)}}{n'_0\,\nu_2}$$

$$= (n_0 + n'_0)\,\nu_2 + N_2$$

n_3 (min) = 0 (The constituent A_3 completely disappears by reaction)

n_4 (min) = N_4 (The excess number of moles of A_4 that are left after the reaction is complete to the left)

Similarly, if the reaction is imagined to proceed completely to the right, there is a minimum amount of each initial constituent, and a maximum amount of each final constituent, so that

$$n_1\,(\text{min}) = 0$$

$$n_2\,(\text{min}) = N_2$$

$$n_3\,(\text{max}) = \underset{\text{(Original amount)}}{n'_0\,\nu_3} + \underset{\text{(Amount formed by chemical reaction)}}{n_0\,\nu_3}$$

$$(n_0\,\nu_1\,A_1 + n_0\,\nu_2\,A_2 \rightarrow n_0\,\nu_3\,A_3 + n_0\,\nu_4\,A_4)$$

$$= (n_0 + n'_0)\nu_3$$

$$n_4\,(\text{max}) = (n_0 + n'_0)\,\nu_4 + N_4$$

Let us suppose that the reaction proceeds partially either to the right or to the left to the extent that there are n_1 moles of A_1, n_2 moles of A_2, n_3 moles of A_3, and n_4 moles of A_4. The *degree* (or *advancement*) *of reaction* ε is defined in terms of any one of the initial constituents, say, A_1, as the fraction

$$\varepsilon = \frac{n_1(\text{max}) - n_1}{n_1(\text{max}) - n_1(\text{min})}$$

It is seen that when $n_1 = n_1$ (max), $\varepsilon = 0$, the reaction will start from left to right. When $n_1 = n_1$ (min), $\varepsilon = 1$, reaction is complete from left to right.

The degree of reaction can thus be written in the form

$$\varepsilon = \frac{(n_0 + n'_0)\nu_1 - n_1}{(n_0 + n'_0)\nu_1}$$

Therefore

$$n_1 = (n_0 + n'_0)\,\nu_1 - (n_0 + n'_0)\,\nu_1\varepsilon$$

$= n$ (at start) $- n$ (consumed)

= Number of moles of A_1 at start − number of moles of A_1 consumed in the reaction

$$= (n_0 + n'_0)\,\nu_1(1 - \varepsilon)$$

$n_2 = n$ (at start) $- n$ (consumed)

$$= (n_0 + n'_0)\,\nu_2 + N_2 - (n_0 + n'_0)\,\nu_2\varepsilon$$

$$= (n_0 + n'_0)\,\nu_2\,(1 - \varepsilon) + N_2$$

$n_3 = n$ (at start) $+ n$ (formed)

$$= 0 + (n_0 + n'_0)\,\nu_3\varepsilon$$

$$= (n_0 + n'_0)\,\nu_3\varepsilon$$

$n_4 = n$ (at start) $+ n$ (formed)

$$= N_4 + (n_0 + n'_0)\,\nu_4\varepsilon$$

$$= (n_0 + n'_0)\,\nu_4\varepsilon + N_4 \tag{16.2}$$

The number of moles of the constituents change during a chemical reaction, not independently but restricted by the above relations. These equations are the *equations of constraint*. The n's are functions of ε only. In a homogeneous system, in a given reaction, the mole fraction x's are also functions of ε only, as illustrated below.

Let us take the reaction

$$H_2 + \frac{1}{2} O_2 \rightleftharpoons H_2O$$

in which n_0 moles of hydrogen combine with $n_0/2$ moles of oxygen to form n_0 moles of water. The n's and x's as functions of ε are shown in the table given below.

Table 16.1

A	ν	n	x
$A_1 = H_2$	$\nu_1 = 1$	$n_1 = n_0(1-\varepsilon)$	$x_1 = \frac{n_1}{\sum n} = \frac{2(1-\varepsilon)}{3-\varepsilon}$
$A_2 = O_2$	$\nu_2 = \frac{1}{2}$	$n_2 = \frac{n_0}{2}(1-\varepsilon)$	$x_2 = \frac{1-\varepsilon}{3-\varepsilon}$
$A_3 = H_2O$	$\nu_3 = 1$	$n_3 = n_0\varepsilon$	$x_3 = \frac{2\varepsilon}{3-\varepsilon}$
		$\sum n = \frac{n_0}{2}(3-\varepsilon)$	

If the reaction is imagined to advance to an infinitesimal extent, the degree of reaction changes from ε to $\varepsilon + d\varepsilon$, and the various n's will change by the amounts

$$dn_1 = -(n_0 + n'_0)\,\nu_1\,d\varepsilon$$

$$dn_2 = -(n_0 + n'_0)\,\nu_2\,d\varepsilon$$

$$dn_3 = (n_0 + n'_0)\,\nu_3\,d\varepsilon$$

$$dn_4 = (n_0 + n'_0)\,\nu_4\,d\varepsilon$$

or

$$\frac{dn_1}{-\nu_1} = \frac{dn_2}{-\nu_2} = \frac{dn_3}{\nu_3} = \frac{dn_4}{\nu_4} = (n_0 + n'_0)\,d\varepsilon$$

which shows that the dn's are proportional to the ν's.

16.2 REACTION EQUILIBRIUM

Let us consider a homogeneous phase having arbitrary amounts of the constituents, A_1, A_2, A_3 and A_4, capable of undergoing the reaction

$$\nu_1 A_1 + \nu_2 A_2 \rightleftharpoons \nu_3 A_3 + \nu_4 A_4$$

The phase is at uniform temperature T and pressure p. The Gibbs function of the mixture is

$$G = \mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + \mu_4 n_4$$

where the n's are the number of moles of the constituents at any moment, and the μ's are the chemical potentials.

Let us imagine that the reaction is allowed to take place at constant T and p. The degree of reaction changes by an infinitesimal amount from ε to $\varepsilon + d\varepsilon$. The change in the Gibbs function is

$$dG_{T,\,p} = \Sigma \mu_k\, dn_k = \mu_1\, dn_1 + \mu_2\, dn_2 + \mu_3\, dn_3 + \mu_4\, dn_4$$

The equations of constraint in differential form are

$$dn_1 = -(n_0 + n'_0)\,\nu_1\, d\varepsilon, \quad dn_3 = (n_0 + n'_0)\,\nu_3\, d\varepsilon$$

$$dn_2 = -(n_0 + n'_0)\,\nu_2\, d\varepsilon, \quad dn_4 = (n_0 + n'_0)\,\nu_4\, d\varepsilon$$

On substitution

$$dG_{T,\,p} = (n_0 + n'_0)(-\nu_1\mu_1 - \nu_2\mu_2 + \nu_3\mu_3 + \nu_4\mu_4)\, d\varepsilon \tag{16.3}$$

When the reaction proceeds *spontaneously* to the right, $d\varepsilon$ is positive, and since $dG_{T,\,p} < 0$

$$(\nu_1\mu_1 + \nu_2\mu_2) > (\nu_3\mu_3 + \nu_4\mu_4)$$

If $\Sigma\, \nu_k\mu_k = (\nu_3\mu_3 + \nu_4\mu_4) - (\nu_1\mu_1 + \nu_2\mu_2)$, then it is negative for the reaction to the right.

When the reaction proceeds spontaneously to the left, $d\varepsilon$ is negative

$$(\nu_1\mu_1 + \nu_2\mu_2) < (\nu_3\mu_3 + \nu_4\mu_4)$$

i.e., $\Sigma\, \nu_k\mu_k$ is positive.

At equilibrium, the Gibbs function will be minimum, and

$$\nu_1\mu_1 + \nu_2\mu_2 = \nu_3\mu_3 + \nu_4\mu_4 \tag{16.4}$$

which is called the *equation of reaction equilibrium*.

Therefore, it is the value of $\Sigma\, \nu_k\mu_k$ which causes or forces the spontaneous reaction and is called the '*chemical affinity*'.

16.3 LAW OF MASS ACTION

For a homogeneous phase chemical reaction at constant temperature and pressure, when the constituents are *ideal gases*, the chemical potentials are given by the expression of the type

$$\mu_k = \bar{R}T\,(\phi_k + \ln p + \ln x_k)$$

where the ϕ's are functions of temperature only (Article 10.11).

Substituting in the equation of reaction equilibrium (16.4)

$$\nu_1(\phi_1 + \ln p + \ln x_1) + \nu_2(\phi_2 + \ln p + \ln x_2)$$
$$= \nu_3(\phi_3 + \ln p + \ln x_3) + \nu_4(\phi_4 + \ln p + \ln x_4)$$

On rearranging

$$\nu_3 \ln x_3 + \nu_4 \ln x_4 - \nu_1 \ln x_1 - \nu_2 \ln x_2 + (\nu_3 + \nu_4 - \nu_1 - \nu_2)\ln p$$
$$= -(\nu_3\phi_3 + \nu_4\phi_4 - \nu_1\phi_1 - \nu_2\phi_2)$$

$$\therefore \quad \ln\left[\frac{x_3^{\nu_3}\cdot x_4^{\nu_4}}{x_1^{\nu_1}\cdot x_2^{\nu_2}}\right] p^{\nu_3+\nu_4-\nu_1-\nu_2}$$
$$= -(\nu_3\phi_3 + \nu_4\phi_4 - \nu_1\phi_1 - \nu_2\phi_2)$$

Denoting $\quad \ln K = -(\nu_3\phi_3 + \nu_4\phi_4 - \nu_1\phi_1 - \nu_2\phi_2)$

where K, known as the *equilibrium constant*, is a function of temperature only

$$\left[\frac{x_3^{\nu_3}\cdot x_4^{\nu_4}}{x_1^{\nu_1}\cdot x_2^{\nu_2}}\right]_{\varepsilon=\varepsilon_e} p^{\nu_3+\nu_4-\nu_1-\nu_2} = K \tag{16.5}$$

This equation is called the *law of mass action*. K has the dimension of pressure raised to the $(\nu_3 + \nu_4 - \nu_1 - \nu_2)$ power. Here the x's are the values of mole fractions at equilibrium when the degree of reaction is ε_e.

The law of mass action can also be written in this form

$$\frac{p_3^{\nu_3} \cdot p_4^{\nu_4}}{p_1^{\nu_1} \cdot p_2^{\nu_2}} = K$$

where the p's are the partial pressures.

16.4 HEAT OF REACTION

The equilibrium constant K is defined by the expression

$$\ln K = -(\nu_3\phi_3 + \nu_4\phi_4 - \nu_1\phi_1 - \nu_2\phi_2)$$

Differentiating ln K with respect to T

$$\frac{d}{dT}\ln K = -\left(\nu_3\frac{d\phi_3}{dT} + \nu_4\frac{d\phi_4}{dT} - \nu_1\frac{d\phi_1}{dT} - \nu_2\frac{d\phi_2}{dT}\right)$$

Now, from Eq. (10.73) $$\phi = \frac{h_0}{\bar{R}T} - \frac{1}{\bar{R}}\int\frac{\int c_p dT}{T^2}\cdot dT - \frac{s_0}{\bar{R}}$$

Therefore $$\frac{d\phi}{dT} = -\frac{h_0}{\bar{R}T^2} - \frac{\int c_p dT}{\bar{R}T^2}$$

$$= -\frac{1}{\bar{R}T^2}\left(h_0 + \int c_p dT\right) = -\frac{h}{\bar{R}T^2}$$

Therefore $$\frac{d}{dT}\ln K = \frac{1}{\bar{R}T^2}(\nu_3h_3 + \nu_4h_4 - \nu_1h_1 - \nu_2h_2)$$

where the h's refer to the same temperature T and the same pressure p. If ν_1 moles of A_1 and ν_2 moles of A_2 combine to from ν_3 moles of A_3 and ν_4 moles of A_4 at constant temperature and pressure, the heat transferred would be, as shown in Fig. 16.1, equal to the final enthalpy $(\nu_3h_3 + \nu_4h_4)$ minus the initial enthalpy $(\nu_1h_1 + \nu_2h_2)$. This is known as the *heat of reaction*, and is denoted by ΔH.

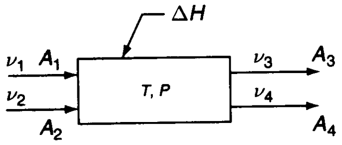


Fig. 16.1 *Heat of reaction*

$$\Delta H = \nu_3h_3 + \nu_4h_4 - \nu_1h_1 - \nu_2h_2 \quad (16.6)$$

Therefore $$\frac{d}{dT}\ln K = \frac{\Delta H}{\bar{R}T^2} \quad (16.7)$$

This is known as the *van't Hoff equation*. The equation can be used to calculate the heat of reaction at any desired temperature or within a certain temperature range.

By rearranging. Eq. (16.7)

$$\frac{\frac{d\ln K}{dT}}{T^2} = \frac{\Delta H}{\bar{R}}$$

$$\frac{d\ln K}{d(1/T)} = -\frac{\Delta H}{\bar{R}}$$

Therefore, $$\Delta H = -2.303\bar{R}\frac{d\log K}{d\left(\frac{1}{T}\right)} = -19.148\frac{d\log K}{d\left(\frac{1}{T}\right)} \text{ kJ/kg mol}$$

If K_1 and K_2 are the equilibrium constants evaluated at temperatures T_1 and T_2 respectively

$$\Delta H = -\ 19.148\ \frac{\log K_1 - \log K_2}{\dfrac{1}{T_1} - \dfrac{1}{T_2}}$$

or

$$\Delta H = 19.148\ \frac{T_1 T_2}{T_1 - T_2} \log \frac{K_1}{K_2}$$

If ΔH is positive, the reaction is said to be *endothermic*. If ΔH is negative, the reaction is *exothermic*.

16.5 TEMPERATURE DEPENDENCE OF THE HEAT OF REACTION

$$\Delta H = \nu_3 h_3 + \nu_4 h_4 - \nu_1 h_1 - \nu_2 h_2$$

$$h = h_0 + \int c_p \mathrm{d}T$$

Therefore

$$\Delta H = \nu_3 h_{03} + \nu_4 h_{04} - \nu_1 h_{01} - \nu_2 h_{02} + \int (\nu_3\, c_{p3} + \nu_4\, c_{p4} - \nu_1\, c_{p1} - \nu_2\, c_{p2}) \mathrm{d}T$$

Denoting

$$\Delta H_0 = \nu_3 h_{03} + \nu_4 h_{04} - \nu_1 h_{01} - \nu_2 h_{02}$$

$$\Delta H = \Delta H_0 + \int (\nu_3 c_{p3} + \nu_4 c_{p4} - \nu_1 c_{p1} - \nu_2 c_{p2}) \mathrm{d}T$$

If c_p is known as a function of temperature and if at any temperature ΔH is known, then at any other temperature, ΔH can be determined for a certain chemical reaction from the above relation.

Some chemical reaction may be expressed as the result to two or more reactions. If ΔH_0 is known for each fo the separate reactions, then the ΔH_0 of the resultant reaction may be calculated. For example,

$$H_2O \rightleftharpoons H_2 + \frac{1}{2} O_2 \qquad \Delta H_0 = 239{,}250 \text{ J/g mol}$$

$$CO_2 \rightleftharpoons CO + \frac{1}{2} O_2 \qquad \Delta H_0 = 279{,}890 \text{ J/g mol}$$

$$CO_2 + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H_0 = -40{,}640 \text{ J/g mol}$$

16.6 TEMPERATURE DEPENDENCE OF THE EQUILIBRIUM CONSTANT

$$\ln K = -(\nu_3 \phi_3 + \nu_4 \phi_4 - \nu_1 \phi_1 - \nu_2 \phi_2)$$

where

$$\phi = \frac{h_0}{\bar{R}T} - \frac{1}{\bar{R}} \int \frac{\int c_p \mathrm{d}T}{T^2} \mathrm{d}T - \frac{s_0}{\bar{R}}$$

On substitution

$$\ln K = \frac{1}{\bar{R}T} (\nu_3 h_{03} + \nu_4 h_{04} - \nu_1 h_{01} - \nu_2 h_{02}) + \frac{1}{\bar{R}} \int \frac{\int (\nu_3 c_{p3} + \nu_4 c_{p4} - \nu_1 c_{p1} - \nu_2 c_{p2}) \mathrm{d}T}{T^2} \cdot \mathrm{d}T + \frac{1}{\bar{R}} (\nu_3 s_{03} + \nu_4 s_{04} - \nu_1 s_{01} - \nu_2 s_{02})$$

If
$$\Delta H_0 = \nu_3 h_{03} + \nu_4 h_{04} - \nu_1 h_{01} - \nu_2 h_{02}$$
$$\Delta S_0 = \nu_3 s_{03} + \nu_4 s_{04} - \nu_1 s_{01} - \nu_2 s_{02}$$
$$\ln K = -\frac{\Delta H_0}{\bar{R}T} + \frac{1}{\bar{R}} \int \frac{\int (\nu_3 c_{p3} + \nu_4 c_{p4} - \nu_1 c_{p1} - \nu_2 c_{p2}) \mathrm{d}T}{T^2} \mathrm{d}T + \frac{\Delta S_0}{\bar{R}} \tag{16.8}$$

This equation is sometimes known as the *Nernst's equation.*

16.7 THERMAL IONIZATION OF A MONATOMIC GAS

One interesting application of Nernst's equation was made by Dr. M.N. Saha to the thermal ionization of a monatomic gas. If a monatomic gas is heated to a high enought temperature (5000 K and above), some ionization occurs, with the electrons in the outermost orbit being shed off, and the atoms, ions, and electrons may be regarded as a mixture of three ideal monatomic gases, undergoing the reaction

$$A \rightleftharpoons A^+ + e$$

Starting with n_0 moles of atoms, it is shown in Table 16.2.
The equilibrium constant is given by

$$\ln K = \ln \left\{ \frac{x_3^{\nu_3} \cdot x_4^{\nu_4}}{x_1^{\nu_1} \cdot x_2^{\nu_2}} \right\}_{\varepsilon_e} \cdot p^{\nu_3 + \nu_4 - \nu_1 - \nu_2}$$

$$\ln K = \frac{\frac{\varepsilon_e}{1+\varepsilon_e} \cdot \frac{\varepsilon_e}{1+\varepsilon_e}}{\frac{1-\varepsilon_e}{1+\varepsilon_e}} \cdot p^{\nu_3 + \nu_4 - \nu_1}$$

or,
$$\ln K = \ln \frac{\varepsilon_e^2}{1-\varepsilon_e^2} \cdot p$$

Since the three gases are monatomic, $c_p = \frac{5}{2}\bar{R}$ which, on being substituted in the Nernst's equation, gives

$$\ln \frac{\varepsilon_e^2}{1-\varepsilon_e^2} \cdot p = -\frac{\Delta H_0}{\bar{R}T} + \frac{5}{2} \ln T + \ln B \tag{16.9}$$

Table 16.2

A	ν	n	x
$A_1 = A$	$\nu_1 = 1$	$n_1 = n_0(1 - \varepsilon_e)$	$x_1 = \frac{1-\varepsilon_e}{1+\varepsilon_e}$
$A_3 = A^+$	$\nu_3 = 1$	$n_3 = n_0\varepsilon_e$	$x_3 = \frac{\varepsilon_e}{1+\varepsilon_e}$
$A_4 = e$	$\nu_4 = 1$	$n_4 = n_0\varepsilon_e$	$x_4 = \frac{\varepsilon_e}{1+\varepsilon_e}$
		$\Sigma n = n_0(1 + \varepsilon_e)$	

where
$$\frac{\Delta S_0}{\bar{R}} = \ln B$$

$$\ln \frac{\varepsilon_e^2}{1-\varepsilon_e^2} \cdot \frac{p}{T^{5/2} \cdot B} = -\frac{\Delta H_0}{\bar{R}T}$$

$$\therefore \quad \frac{\varepsilon_e^2}{1-\varepsilon_e^2} = Be^{-\Delta \mathrm{H}_0/\bar{\mathrm{R}}\mathrm{T}} \cdot \frac{T^{5/2}}{p} \tag{16.10}$$

where ε_e is the equilibrium value of the degree of ionization. This is known as the *Saha's equation*. For a particular gas the degree of ionization increases with an increase in temperature and a decrease in pressure.

It can be shown that ΔH_0 is the amount of energy necessary to ionize 1 gmol of atoms. If we denote the ionization potential ΔH_0 of the atom in volts by E, then

$$\Delta H_0 = \mathrm{E(volts)} \times 1.59 \times 10^{-19} \frac{\text{coulomb}}{\text{electron}} \times 6.06 \times 10^{23} \frac{\text{electron}}{\text{g mol}}$$
$$= 9.6354 \times 10^4 \text{ E J/g mol}$$

Equation (16.9) becomes

$$\mathrm{In}\frac{\varepsilon_e}{1-\varepsilon_e^2} p = -\frac{96354 E}{\bar{R}T} + \frac{5}{2} \mathrm{In}\, T + \mathrm{In}\, B \tag{16.11}$$

Expressing p in atmospheres changing to common logarithms and introducing the value of B from statistical mechanics, Saha finally obtained the equation:

$$\log \frac{\varepsilon_e^2}{1-\varepsilon_e^2} p(\text{atm}) = -\frac{96{,}354\, E}{19.148\, T} + \frac{5}{2} \log T + \log \frac{\omega_i \omega_e}{\omega_a} - 6.491 \tag{16.12}$$

where ω_i, ω_e and ω_a are constants that refer to the ion, electron and atom respectively. The value ω_e for an electron is 2. The value of E. ω_i and ω_a for a few elements are given below:

Table 16.3

Values for E and w

Element	*E, volts*	ω_a	ω_i
Na	5.12	2	1
Cs	3.87	2	1
Ca	6.09	1	2
Cd	8.96	1	2
Za	9.36	1	2

For alkali metals like Cs, Na, K etc., the ionization potential is less. It means less energy is required to ionize one gmol of atoms. So these are used as *seed for magnetohydrodynamic power generation*. Saha applied his Equation (16.12) to the determination of temperature of a stellar atmosphere. The spectrum of a star contains lines which originate from atoms (arc lines) and those which originate from ions (spark lines). A comparison of the intensities of an arc line and a spark line from the same element gives a measure of ε_e. Considering a star as a sphere of ideal gas, the pressure of a star can be estimated. Thus, knowing ε_e, p, E and the ω's, the temperature of the star can be calculated.

16.8 GIBBS FUNCTION CHANGE

Molar Gibbs function of an ideal gas at temperature T and pressure p is equal to (Article 10.11)

$$g = \bar{R}T\ (\phi + \ln p)$$

For the reaction of the type $\nu_1 A_1 + \nu_2 A_2 \rightleftharpoons \nu_3 A_3 + \nu_4 A_4$

the Gibbs function change of the reaction ΔG is defined by the expression

$$\Delta G = \nu_3 g_3 + \nu_4 g_4 - \nu_1 g_1 - \nu_2 g_2 \tag{16.13}$$

where the g's refer to the gases completely separated at T, p. ΔG is also known as the *free energy change*. Substituting the values of the g's

$$\Delta G = \bar{R}T(\nu_3\phi_3 + \nu_4\phi_4 - \nu_1\phi_1 - \nu_2\phi_2) + \bar{R}T \ln p^{\nu_3+\nu_4-\nu_1-\nu_2}$$

But $\qquad \ln K = -\ (\nu_3\phi_3 + \nu_4\phi_4 - \nu_1\phi_1 - \nu_2\phi_2)$

$\therefore \qquad \Delta G = -\ \bar{R}T\ \ln K + \bar{R}T \ln p^{\nu_3+\nu_4-\nu_1-\nu_2}$

If p is expressed in atmospheres and ΔG is calculated from each gas is at a pressure of 1 atm., the second term on the right drops out. Under these conditions ΔG is known as the *standard Gibbs function change* and is denoted by ΔG°

$$\Delta G^\circ = \bar{R}T\ \ln K \tag{16.14}$$

This is an important equation which relates the standard Gibbs function change with temperature and the equilibrium constant. From this the equilibrium constant can be calculated from changes in the standard Gibbs function, or vice versa.

For dissociation of water vapour, $H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$, the value of ln K_{298} is found to be – 93.7. Therefore,

$$\Delta G^\circ_{298} = -8.3143 \times 298 \times (-93.7) = 232{,}157 \text{ J/gmol.}$$

Substituting ln K from Nernst's equation:

$$\Delta G^\circ = \Delta H_0 - T\ \frac{(\nu_3 c_{p_3} + \nu_4 c_{p_4} - \nu_1 c_{p_1} - \nu_2 c_{p_2})\mathrm{d}T}{T^2}\ \mathrm{d}T - T\Delta S_0$$

from which also ΔG° may be calculated directly. Values of ΔH_0, ΔS_0 and ΔG°_{298} for fundamental ideal gas reactions are given in Table 16.4.

Both ΔS_0 and ΔG°_{298} may be added and subtracted in the same manner as ΔH_0. For example.

$$H_2O \rightleftharpoons H_2 + \tfrac{1}{2}O_2 \qquad \Delta G^\circ_{298} = 232{,}545 \text{ J/gmol}$$

$$CO_2 \rightleftharpoons CO + \tfrac{1}{2}O_2 \qquad \Delta G^\circ_{298} = 258{,}940 \text{ J/gmol}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta G^\circ_{298} = -\ 26{,}395 \text{ J/gmol}$$

$$\ln K_{298} = \frac{\Delta G^\circ_{298}}{\bar{R}T} = \frac{26{,}395}{8.3143 \times 298} = 10.653$$

$$K_{298} = 42{,}330$$

From this, the value of the degree of reaction at equilibrium ε_e may be calculated.

Table 16.4

Fundamental Idea Gas Reactions

Reaction	ΔH_0 *J/gmol*	ΔS_0 *J/gmol-K*	ΔG°_{298} *J/gmol*
$H_2 \rightleftharpoons 2H$	427,380	4.90	404,335
$HCl \rightleftharpoons \frac{1}{2}H_2 + \frac{1}{2}Cl_2$	91,760	− 22.25	95,110
$HBr \rightleftharpoons \frac{1}{2}H_2 + \frac{1}{2}Br_2$	50,280	− 24.05	54,050
$HI \rightleftharpoons \frac{1}{2}H_2 + \frac{1}{2}I_2$	5,320	− 21.00	8,380
$NO \rightleftharpoons \frac{1}{2}N_2 + \frac{1}{2}O_2$	− 90,500	− 10.48	− 87,570
$H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$	239,250	14.70	232,545
$H_2S \rightleftharpoons H_2 + \frac{1}{2}S_2$	80,450	6.90	71,230
$CO_2 \rightleftharpoons CO + \frac{1}{2}O_2$	279,890	18.69	258,940
$NO_2 \rightleftharpoons NO + \frac{1}{2}O_2$	59,500	11.44	37,290
$SO_2 \rightleftharpoons \frac{1}{2}S_2 + O_2$	349,025	3.77	329,330
$NH_3 \rightleftharpoons \frac{1}{2}N_2 + \frac{3}{2}H_2$	39,800	40.27	16,380
$SO_3 \rightleftharpoons SO_2 + \frac{1}{2}O_2$	94,690	89.50	67,880
$N_2O_4 \rightleftharpoons 2NO_2$	56,980	174.30	5,030

From Eq. (16.3), if $n_0 = 1$ and $n'_0 = 0$

$$\left(\frac{\partial G}{\partial \varepsilon}\right)_{T,p} = (\nu_3\mu_3 + \nu_4\mu_4 - \nu_1\mu_1 - \nu_2\mu_2)$$

Since $$\mu_k = \bar{R}T\ (\phi_k + \ln p + \ln x_k)$$

and $$g_k = \bar{R}T\ (\phi_k + \ln p)$$

so $$\mu_k = g_k\ \bar{P}T\ \ln x_k$$

Therefore $$\left(\frac{\partial G}{\partial \varepsilon}\right)_{T,p} = \nu_3 g_3 + \nu_4 g_4 - \nu_1 g_1 - \nu_2 g_2 + \bar{R}T\ \ln \frac{x_3^{\nu_3} \cdot x_4^{\nu_4}}{x_1^{\nu_1} \cdot x_2^{\nu_2}}$$

$$= \Delta G + \bar{R}T\ \ln \frac{x_3^{\nu_3}\ x_4^{\nu_4}}{x_1^{\nu_1}\ x_2^{\nu_2}}$$

At $$\varepsilon = 0, x_3 = 0, x_4 = 0$$

$$\left(\frac{\partial G}{\partial \varepsilon}\right)_{\mathrm{T,p}} = -\infty$$

and at $\varepsilon = 1, x_1 = 0, x_2 = 0$

$$\left(\frac{\partial G}{\partial \varepsilon}\right)_{\mathrm{T,p}} = +\infty$$

At $\varepsilon = \frac{1}{2}, x_1 = \frac{\nu_1}{\Sigma\nu}, x_2 = \frac{\nu_2}{\Sigma\nu}$

$$x_3 = \frac{\nu_3}{\Sigma\nu}, x_4 = \frac{\nu_4}{\Sigma\nu}$$

where $\Sigma v = \nu_3 + \nu_4 + \nu_1 + \nu_2$

$$\left(\frac{\partial G}{\partial \varepsilon}\right)_{\substack{\mathrm{T,p}\\ \varepsilon=\frac{1}{2}}} = \Delta G + \bar{R}T \ln \frac{\left(\frac{\nu_3}{\Sigma v}\right)^{\nu_3}\left(\frac{\nu_4}{\Sigma v}\right)^{\nu_4}}{\left(\frac{\nu_1}{\Sigma v}\right)^{\nu_1}\left(\frac{\nu_2}{\Sigma v}\right)^{\nu_2}}$$

If $p = 1$ atm., $T = 298$ K

$$\left(\frac{\partial G}{\partial \varepsilon}\right)_{\substack{p=1\mathrm{atm}\\ T=298\,\mathrm{K}\\ \varepsilon=\frac{1}{2}}} = \Delta G^\circ_{298}$$

because the magnitude of the second term on the right hand side of the equation is very small compared to ΔG°. The slope $\left(\frac{\partial G}{\partial \varepsilon}\right)_{\mathrm{T,p}}$ at $\varepsilon = \frac{1}{2}$ is called the 'affinity' of the reaction, and it is equal to ΔG° at the standard reference state. The magnitude of the slope at $\varepsilon = 1/2$ (Fig. 16.2) indicates the direction in which the reaction will proceed. For water vapour reaction, ΔG°_{298} is a large positive number, which indicates the equilibrium point is far to the left of $\varepsilon = 1/2$, and therefore, ε_e is very small. Again for the reaction $NO \rightleftharpoons \frac{1}{2} N_2 + \frac{1}{2} O_2$, ΔG°_{298} is a large negative value, which shows that the equilibrium point is far to the right of $\varepsilon = 1/2$, and so ε_e is close to unity.

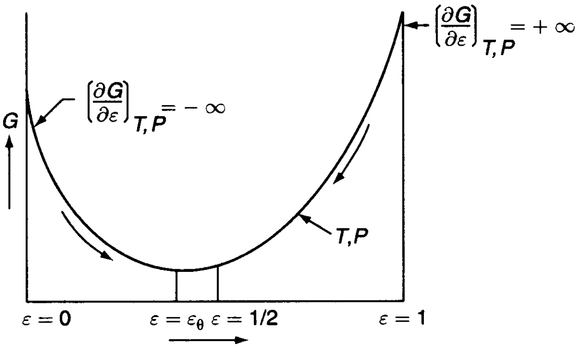


Fig. 16.2 *Plot of G against ε at constants T and p*

16.9 FUGACITY AND ACTIVITY

The differential of the Gibbs function of an ideal gas undergoing an isothermal process is

$$dG = Vdp = \frac{n\bar{R}T}{p}\,dp = n\bar{R}T\ d(\ln p)$$

Analogously, the differential of the Gibbs function for a real gas is

$$dG = n\bar{R}T\ d(\ln f) \tag{16.15}$$

where f is called the *fugacity*, first used by Lewis. The value of fugacity approaches the value of pressure as the latter tends to zero, i.e., when ideal gas conditions apply. Therefore

$$\lim_{p \to 0} \frac{f}{p} = 1$$

For an ideal gas $f = p$. Fugacity has the same dimension as pressure. Integrating Eq. (16.15)

$$G - G^0 = n\bar{R}T \ \ln \frac{f}{f^0}$$

where G^0 and f^0 refer to the reference state when $p_0 = 1$ atm. The ratio f/f^0 is called the *activity*.

Therefore
$$G - G^0 = n\bar{R}T \ \ln a \tag{16.16}$$

For ideal gases, the equilibrium constant is given by $K = \dfrac{p_3^{\nu 3} \cdot p_4^{\nu 4}}{p_1^{\nu 1} \cdot p_2^{\nu 2}}$

For real gases
$$K_{\text{real}} = \frac{f_3^{\nu 3} \cdot f_4^{\nu 4}}{f_1^{\nu 1} \cdot f_2^{\nu 2}}$$

Similarly, it can be shown that
$$\Delta G^0 = -\, n\bar{R}T \ \ln K_{\text{real}}$$

and
$$\frac{\mathrm{d} \ln K_{\text{real}}}{\mathrm{d}T} = \frac{\Delta H^0}{\bar{R}T^2}$$

16.10 DISPLACEMENT OF EQUILIBRIUM DUE TO A CHANGE IN TEMPERATURE OR PRESSURE

The degree of reaction at equilibrium ε_e changes with temperature and also with pressure. From the law of mass action

$$\ln K = \ln \left[\frac{x_3^{\nu_3} \cdot x_4^{\nu_4}}{x_1^{\nu_1} \cdot x_2^{\nu_2}} \right]_{\varepsilon = \varepsilon_e} + (\nu_3 + \nu_4 - \nu_1 - \nu_2) \ln p$$

where $\ln K$ is a function of temperature only and the first term on the right hand side is function of ε_e only. Therefore

$$\left(\frac{\partial \varepsilon_e}{\partial T} \right)_p = \left(\frac{\partial \varepsilon_e}{\partial \ln K} \right)_p \left(\frac{\partial \ln K}{\partial T} \right)_p$$

$$\left(\frac{\partial \varepsilon_e}{\partial T} \right)_p = \frac{\left(\dfrac{\partial \ln K}{\partial T} \right)_p}{\left(\dfrac{\partial \ln K}{\partial \varepsilon_e} \right)_p} = \frac{\Delta H}{\bar{R}T^2 \dfrac{\mathrm{d}}{\mathrm{d}\varepsilon_e} \ln \left[\dfrac{x_3^{\nu_3} \cdot x_4^{\nu_4}}{x_1^{\nu_1} \cdot x_2^{\nu_2}} \right]_{\varepsilon = \varepsilon_e}} \tag{16.17}$$

It can be shown (Example 16.4) that

$$\frac{\mathrm{d}}{\mathrm{d}\varepsilon} \ln \frac{x_3^{\nu_3} \cdot x_4^{\nu_4}}{x_1^{\nu_1} \cdot x_2^{\nu_2}} = \frac{n_0}{\Sigma n_k} \cdot \frac{(\nu_1 + \nu_2)(\nu_3 + \nu_4)}{\varepsilon(1 - \varepsilon)}$$

which is always positive.

Therefore, for endothermic reaction, when ΔH is positive, $\left(\dfrac{\partial \varepsilon_e}{\partial T} \right)_p$ is positive, and for exothermic reaction, when ΔH is negative, $\left(\dfrac{\partial \varepsilon_e}{\partial T} \right)_p$ is negative.

Again,

$$\left(\frac{\partial \varepsilon_e}{\partial p}\right)_T = -\left(\frac{\partial \varepsilon_e}{\partial \ln K}\right)_p \left(\frac{\partial \ln K}{\partial p}\right)_{\varepsilon_e}$$

$$= \frac{-\left(\dfrac{\partial \ln K}{\partial p}\right)_{\varepsilon_e}}{\left(\dfrac{\partial \ln K}{\partial \varepsilon_e}\right)_p}$$

Using the law of mass action

$$\left(\frac{\partial \varepsilon_e}{\partial p}\right)_T = -\frac{\nu_3 + \nu_4 - \nu_1 - \nu_2}{p\dfrac{d}{d\varepsilon_e}\ln\left[\dfrac{x_3^{\nu_3}\cdot x_4^{\nu_4}}{x_1^{\nu_1}\cdot x_2^{\nu_2}}\right]_{\varepsilon=\varepsilon_e}} \tag{16.18}$$

If $(\nu_3 + \nu_4) > (\nu_1 + \nu_2)$, i.e., the number of moles increase or the volume increases due to reaction, $\left(\frac{\partial \varepsilon_e}{\partial p}\right)_T$ is negative. If $(\nu_3 + \nu_4) < (\nu_1 + \nu_2)$, i.e. volume decreases in an isothermal reaction, $\left(\frac{\partial \varepsilon_e}{\partial p}\right)_T$ is positive.

16.11 HEAT CAPACITY OF REACTING GASES IN EQUILIBRIUM

For a reaction of four ideal gases, such as

$$\nu_1 A_1 + \nu_2 A_2 \rightleftharpoons \nu_3 A_3 + \nu_4 A_4$$

the enthalpy of mixture at equilibrium is

$$H = \Sigma n_k h_k$$

where $n_1 = (n_0 + n'_0)\,\nu_1(1 - \varepsilon_e)$, $n_2 = (n_0 + n'_0)\,\nu_2\,(1 - \varepsilon_e) + N_2$

$n_3 = (n_0 + n'_0)\,\nu_3\,\varepsilon_e$, and $n_4 = (n_0 + n'_0)\,\nu_4\,\varepsilon_e + N_4$

Let us suppose that an infinitesimal change in temperature takes place at constant pressure in such a way that equilibrium is maintained.

ε_e will change to the value $\varepsilon_e + d\varepsilon_e$, and the enthalpy will change by the amount

$$dH_p = \Sigma n_k\, dh_k + \Sigma h_k\, dn_k$$

where $dh_k = c_{pk}\, dT,\ dn_k = \pm\,(n_0 + n'_0)\,\nu_k\, d\varepsilon_e$

Therefore $dH_p = \Sigma n_k\, c_{pk}\, dT + (n_0 + n'_0)\,(\nu_3 h_3 + \nu_4 h_4 - \nu_1 h_1 - \nu_2 h_2)\, d\varepsilon_e$

The heat capacity of the reacting gas mixture is

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = \Sigma n_k\, c_{pk} + (n_0 + n'_0)\,\Delta H\left(\frac{\partial \varepsilon_e}{\partial T}\right)_p$$

Using Eq. (16.14)

$$C_p = \Sigma n_k\, c_{pk} + (n_0 + n'_0)\,\frac{(\Delta H)^2}{\bar{R}T^2\dfrac{d}{d\varepsilon}\ln\left[\dfrac{x_3^{\nu_3}\cdot x_4^{\nu_4}}{x_1^{\nu_1}\cdot x_2^{\nu_2}}\right]_{\varepsilon=\varepsilon_e}} \tag{16.19}$$

16.12 COMBUSTION

Combustion is a chemical reaction between a fuel and oxygen which proceeds at a fast rate with the release of energy in the form of heat. In the combustion of methane, e.g.

$$\underset{\text{Reactants}}{CH_4 + 2O_2} \rightarrow \underset{\text{Products}}{CO_2 + 2H_2O}$$

One mole of methane reacts with 2 moles of oxygen to form 1 mole of carbon dioxide and 2 moles of water. The water may be in the liquid or vapour state depending on the temperature and pressure of the products of combustion. Only the initial and final products are being considered without any concern for the intermediate products that usually occur in a reaction.

Atmospheric air contains 21% oxygen, 78% nitrogen, and 1% argon by volume. In combustion calculations, however, the argon is usually neglected, and air is assumed to consist of 21% oxygen and 79% nitrogen by volume (or molar basis). On a mass basis, air contains 23% oxygen and 77% nitrogen.

For each mole of oxygen taking part in a combustion reaction, there are 79.0/21.0 = 3.76 moles of nitrogen. So for the combustion of methane, the reaction can be written as

$$CH_4 + 2O_2 + 2(3.76)N_2 \rightarrow CO_2 + 2H_2O + 7.52N_2$$

The minimum amount of air which provides sufficient oxygen for the complete combustion of all the elements like carbon, hydrogen, etc., which may oxidize is called the *theoretical or stoichiometric air*. There is no oxygen in the products when complete combustion (oxidation) is achieved with this theoretical air. In practice, however, more air than this theoretical amount is required to be supplied for complete combustion. Actual air supplied is usually expressed in terms of percent theoretical air; 150% theoretical air means that 1.5 times the theoretical air is supplied. Thus, with 150% theoretical air, the methane combustion reaction can be written as

$$CH_4 + 2(1.5)\,O_2 + 2(3.76)\,(1.5)N_2$$
$$\rightarrow CO_2 + 2H_2O + O_2 + 11.28N_2$$

Another way of expressing the actual air quantity supplied is in terms of excess air. Thus 150% theoretical air means 50% excess air.

With less than theoretical air supply, combustion will remain incomplete with some CO present in the products. Even with excess air supply also, there may be a small amount of CO present, depending on mixing and turbulence during combustion, e.g., with 115% theoretical air

$$CH_4 + 2(1.15)O_2 + 2(1.15)\,3.76N_2 \rightarrow$$
$$\rightarrow 0.95\,CO_2 + 0.05CO + 2H_2O + 0.325O_2 + 8.65N_2$$

By analyzing the products of combustion, the actual amount of air supplied in a combustion process can be computed. Such analysis is often given on the 'dry' basis, i.e., the fractional analysis of all the components, except water vapour. Following the principle of the conservation of mass of each of the elements, it is possible to make a carbon balance, hydrogen balance, oxygen balance, and nitrogen balance from the combustion reaction equation, from which the actual air-fuel ratio can be determined. It has been illustrated in Ex. 16.4 later.

16.13 ENTHALPY OF FORMATION

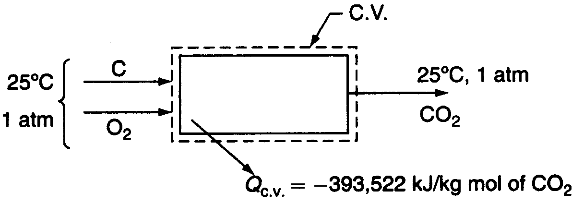


Fig. 16.3 Enthalpy of formation

Let us consider the steady state steady flow combustion of carbon and oxygen to from CO_2 (Fig. 16.3). Let the carbon and oxygen each enter the control volume at 25°C and 1 atm. pressure, and the heat transfer be such that the product CO_2 leaves at 25°C, 1 atm. pressure. The measured value of heat transfer is −393,522 kJ per kg mol of CO_2 formed. If H_R and H_P refer to the total enthalpy of the reactants and products respectively, then the first law applied to the reaction $C + O_2 \rightarrow CO_2$ gives

$$H_R + Q_{C.V.} = H_P$$

For all the reactants and products in a reaction, the equation may be written as

$$\sum_R n_i \bar{h}_i + Q_{C.V.} = \sum_P n_e \bar{h}_e$$

where R and P refer to the reactants and products respectively.

The enthalpy of all the elements at the standard reference state of 25°C, 1 atm. is assigned the value of zero. In the carbon-oxygen reaction, $H_R = 0$. So the energy equation gives

$$Q_{C.V.} = H_p = -393,522 \text{ kJ/kg mol}$$

This is what is known as the *enthalpy of formation of* CO_2 at 25°C, 1 atm., and designated by the symbol, $\bar{h}_f^0$. So

$$\left(\bar{h}_f^0\right)_{CO_2} = -393,522 \text{ kJ/kg mol}$$

In most cases, however, the reactants and products are not at 25°C, 1 atm. Therefore, the change of enthalpy (in the case of constant pressure process or S.S.S.F. process) between 25°C, 1 atm. and the given state must be known. Thus the enthalpy at any temperature and pressure, $\bar{h}_{T,p}$ is

$$\bar{h}_{T,p} = \left(\bar{h}_f^0\right)_{298\text{ K}, 1\text{ atm}} + \left(\Delta\bar{h}\right)_{298\text{ K}, 1\text{ atm} \rightarrow T,p}$$

For convenience, the subscripts are usually dropped, and

$$\bar{h}_{T,p} = \bar{h}_f^0 + \Delta\bar{h}$$

where $\Delta\bar{h}$ represents the difference in enthalpy between any given state and the enthalpy at 298.15 K, 1 atm.

Table 16.5 gives the values of the enthalpy of formation of a number of substances in kJ/kg mol.

Table C in the appendix gives the values of $\Delta\bar{h} = \bar{h}^0 - \bar{h}_{298}^0$ in kJ/kg mol for various substances at different temperatures.

Table 16.5

Enthalpy of Formation, Gibbs Function of Formation, and Absolute Entropy of Various Substances at 25°C, 1 atm. pressure

Substance	*Molecular weight, M*	$\bar{h}_f^0$ *kJ/kg mol*	$\bar{g}_f^0$ *kJ/kg mol*	s^0 *kJ/kg mol K*
CO(g)	28.011	– 110529	– 137150	197.653
CO_2(g)	44.001	– 393522	– 394374	213.795
H_2O(g)	18.015	– 241827	– 228583	188.833
H_2O(l)	18.015	– 285838	– 237178	70.049
CH_4(g)	16.043	– 74873	– 50751	186.256
C_2H_2(g)	26.038	+ 226731	+ 209234	200.958
C_2H_4(g)	28.054	+ 52283	+ 68207	219.548
C_2H_6(g)	30.070	– 84667	– 32777	229.602
C_3H_8(g)	44.097	– 103847	– 23316	270.019
C_4H_{10}(g)	58.124	– 126148	– 16914	310.227
C_8H_{18}(g)	114.23	– 208447	+ 16859	466.835
C_8H_{18}(l)	114.23	– 249952	+ 6940	360.896

16.14 FIRST LAW FOR REACTIVE SYSTEMS

For the S.S.S.F. process as shown in Fig. 16.4 the first law gives

$$H_R + Q_{C.V.} = H_P + W_{C.V.}$$

or

$$\sum_R n_i \bar{h}_i + Q_{C.V.} = \sum_P n_e \bar{h}_e + W_{C.V.}$$

$$\sum_R n_i \left[\bar{h}_f^0 + \Delta \bar{h}\right]_i + Q_{C.V.} = \sum_p n_e \left[\bar{h}_f^0 + \Delta \bar{h}\right]_e + W_{C.V.} \tag{16.20}$$

When the states of reactants and products are not in the standard reference state (298K, 1 atm), then, as shown in Fig. 16.5,

$$\begin{aligned} Q_{C.V.} &= H_P - H_R = (H_P - H_{P_0}) + (H_{P_0} - H_{R_0}) + (H_{R_0} - H_R) \\ &= \sum_p n_e \left(\bar{h}_p - \bar{h}_{p_0}\right) + \Delta \bar{h}\,_{RP}^0 - \sum_R n_i \left(\bar{h}_R - \bar{h}_{R_0}\right) \end{aligned} \tag{16.21}$$

where $\Delta \bar{h}_{PR}^0$ is the enthalpy of reaction at the standard temperature (298 K). The variation of enthalpy with pressure is not significant.

For a constant volume reaction,

$$\begin{aligned} Q_{C.V.} &= U_P - U_R = (U_P - U_{P_0}) + (U_{P_0} - U_{R_0}) + (U_{R_0} - U_R) \\ &= \sum_p n_e \left(\bar{u}_p - \bar{u}_{p_0}\right) + \Delta \bar{u}\,_{RP}^0 - \sum_R n_i \left(\bar{u}_R - \bar{u}_{R_0}\right) \end{aligned} \tag{16.22}$$

where $\Delta \bar{u}\,_{RP}^0$ is the internal energy of reaction at 298 K.

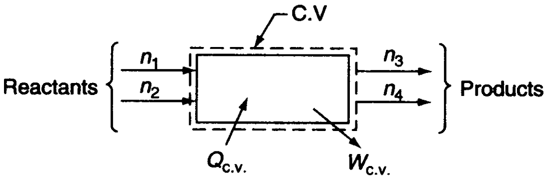


Fig. 16.4 *First law for a reactive system*

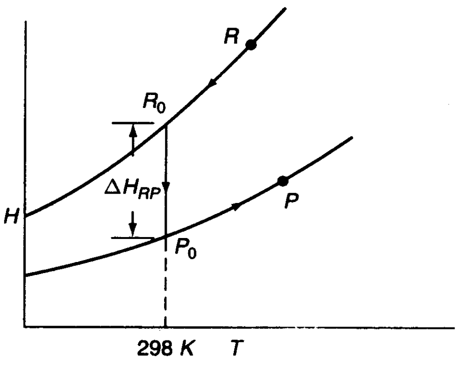


Fig. 16.5 *Enthalpy of reactants and products varying with temperature*

16.15 ADIABATIC FLAME TEMPERATURE

If a combustion process occurs adiabatically in the absence of work transfer or changes in K.E. and P.E. then the energy equation becomes

$$H_R = H_P$$

or

$$\sum_R n_i \bar{h}_i = \sum_p n_e \bar{h}_e$$

or

$$\sum_R n_i \left[\bar{h}_f^0 + \Delta \bar{h}\right]_i = \sum_P n_e \left[\bar{h}_f^0 + \Delta \bar{h}\right]_e \tag{16.23}$$

For such a process, the temperature of the products is called the *adiabatic flame temperature* which is the maximum temperature achieved for the given reactants. The adiabatic flame temperature can be controlled by the amount of excess air supplied; it is the maximum with a stoichiometric mixture. Since the maximum permissible temperature in a gas turbine is fixed from metallurgical considerations, close control of the temperature of the products is achieved by controlling the excess air.

For a given reaction the adiabatic flame temperature is computed by trial and error. The energy of the reactants H_R being known, a suitable temperature is chosen for the products so that the energy of the products at that temperature becomes equal to the energy of the reactants.

16.16 ENTHALPY AND INTERNAL ENERGY OF COMBUSTION: HEATING VALUE

The *enthalpy of combustion* is defined as the difference between the enthalpy of the products and the enthalpy of the reactants when complete combustion occurs at a given temperature and pressure.

Therefore

$$\bar{h}_{RP} = H_P - H_R$$

or

$$\bar{h}_{RP} = \sum_P n_e[\bar{h}_f^0 + \Delta \bar{h}]_e - \sum_R n_i[\bar{h}_f^0 + \Delta \bar{h}]_i \tag{16.24}$$

where $\bar{h}_{RP}$ is the enthalpy of combustion (kJ/kg or kJ/kg mol) of the fuel.

The values of the enthalpy of combustion of different hydrocarbon fuels at 25°C, 1 atm. are given in Table 16.6.

The *internal energy of combustion*, u_{RP}, is defined in a similar way.

Table 16.6

Enthalpy of Combustion of Some Hydrocarbons at 25°C

		Liquid H_2O in Products (Negative of Higher Heating Value)		Vapour H_2O in Products (Negative of Lower Heating Value)	
Hydrocarbon (1)	Formula (2)	Liquid Hydrocarbon kJ/kg fuel (3)	Gaseous Hydrocarbon kJ/kg fuel (4)	Liquid Hydrocarbon kJ/kg fuel (5)	Gaseous Hydrocarbon kJ/kg fuel (6)
Paraffin Family					
Methane	CH_4		– 55496		– 50010
Ethane	C_2H_6		– 51875		– 47484
Propane	C_3H_8	– 49975	– 50345	– 45983	– 46353
Butane	C_4H_{10}	– 49130	– 49500	– 45344	– 45714
Pentane	C_5H_{12}	– 48643	– 49011	– 44983	– 45351
Hexane	C_6H_{14}	– 48308	– 48676	– 44733	– 45101
Heptane	C_7H_{16}	– 48071	– 48436	– 44557	– 44922
Octane	C_8H_{18}	– 47893	– 48256	– 44425	– 44788
Decane	$C_{10}H_{22}$	– 47641	– 48000	– 44239	– 44598
Dodecane	$C_{12}H_{26}$	– 47470	– 47828	– 44100	– 44467
Olefin Family					
Ethene	C_2H_4		– 50296		– 47158
Propene	C_3H_6		– 48917		– 45780
Butene	C_4H_8		– 48453		– 45316
Pentene	C_5H_{10}		– 48134		– 44996
Hexene	C_6H_{12}		– 47937		– 44800
Heptene	C_7H_{14}		– 47800		– 44662
Octene	C_8H_{16}		– 47693		– 44556
Nonene	C_9H_{18}		– 47612		– 44475
Decene	$C_{16}H_{20}$		– 47547		– 44410
Alkylbenzene Family					
Benzene	C_6H_6	– 41831	– 42266	– 40141	– 40576
Methylbenzene	C_7H_8	– 42473	– 42847	– 40527	– 40937
Ethylbenzene	C_8H_{10}	– 42997	– 43395	– 40924	– 41322
Propylbenzene	C_9H_{12}	– 43416	– 43800	– 41219	– 41603
Butylbenzene	$C_{10}H_{14}$	– 43748	– 44123	– 41453	– 41828

$$\bar{u}_{RP} = U_P - U_R = \sum_{p} n_e \left[\bar{h}_f^0 + \Delta\bar{h} - p\bar{v}\right]_e - \sum_{R} n_i \left[\bar{h}_f^0 + \Delta\bar{h} - p\bar{v}\right]_i$$

If all the gaseous constituents are considered ideal gases and the volume of liquid and solid considered is assumed to be negligible compared to gaseous volume

$$\bar{u}_{RP} = \bar{u}_{RP} - \bar{R}T(n_{\text{gaseous products}} - n_{\text{gaseous reactants}}) \tag{16.25}$$

In the case of a constant pressure or steady flow process, the negative of the enthalpy of combustion is frequently called the *heating value at constant pressure*, which represents the heat transferred from the chamber during combustion at constant pressure.

Similarly, the negative of the internal energy of combustion is sometimes designated as the *heating value at constant volume* in the case of combustion, because it represents the amount of heat transfer in the constant volume process.

The *higher heating value* (HHV) or higher calorific value (HCV) is the heat transferred when H_2O in the products is in the liquid state. The *lower heating value* (LHV) or lower calorific value (LCV) is the heat transferred in the reaction when H_2O in the products is in the vapour state.

Therefore

$$\text{LHV} = \text{HHV} - m_{H_2O} \cdot h_{fg}$$

where m_{H_2O} is the mass of water formed in the reaction.

16.17 ABSOLUTE ENTROPY AND THE THIRD LAW OF THERMODYNAMICS

So far only the first law aspects of chemical reactions have been discussed. The second law analysis of chemical reactions needs a base for the entropy of various substances. The entropy of substances at the absolute zero of temperature, called absolute entropy, is dealt with by the third law of thermodynamics formulated in the early twentieth century primarily by W.H. Nernst (1864–1941) and Max Planck (1858–1947). The third law states that the entropy of a perfect crystal is zero at the absolute zero of temperature and it represents the maximum degree of order. A substance not having a perfect crystalline structure and possessing a degree of randomness such as a solid solution or a glassy solid, has a finite value of entropy at absolute zero. The third law (see Chapter 11) provides an absolute base from which the entropy of each substance can be measured. The entropy relative to this base is referred to as the absolute entropy. Table 16.3 gives the absolute entropy of various substances at the standard state 25°C, 1 atm. For any other state

$$\bar{s}_{T,\,p} = \bar{s}_T^0 + (\Delta\bar{s})_{T,\,1\,\text{atm},\,\to T,\,p}$$

where $\bar{s}_T^0$ refers to the absolute entropy at 1 atm. and temperature T, and $(\Delta\bar{s})_{T,\,1\,\text{atm},\,\to T,\,p}$ refers to the change of entropy for an isothermal change of pressure from 1 atm. to pressure p (Fig. 16.6). Table C in the appendix gives the values of $\bar{s}^0$ for various substances at 1 atm. and at different temperatures. Assuming ideal gas behaviour $(\Delta\bar{s})_{T,\,1\,\text{atm},\,\to T,\,p}$ can be determined (Fig. 16.6)

$$\bar{s}_2 - \bar{s}_1 = -\bar{R}\ln\frac{p_2}{p_1}$$

or $$(\Delta\bar{s})_{T,\,1\,\text{atm},\,\to T,\,p} = -\bar{R}\ln p$$

where p is in atm.

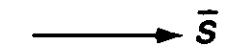


Fig. 16.6 *Absolute entropy*

16.18 SECOND LAW ANALYSIS OF REACTIVE SYSTEMS

The reversible work for a steady state steady flow process, in the absence of changes in K.E. and P.E., is given by

$$W_{\text{rev}} = \sum n_i (h_i - T_0 s_i) - \sum n_e (h_e - T_0 s_e)$$

For an S.S.S.F. process involving a chemical reaction

$$W_{\text{rev}} = \sum_{\text{R}} n_i [\bar{h}_f^0 + \Delta \bar{h} - T_0 \bar{s}]_i - \sum_{\text{P}} n_e [\bar{h}_f^0 + \Delta \bar{h} - T_0 \bar{s}]_e \qquad (16.26)$$

The irreversibility for such a process is

$$I = \sum_{P} n_e T_0 \bar{s}_e - \sum_{\text{R}} n_i T_0 \bar{s}_i - Q_{\text{C.V.}}$$

The availability, ψ, in the absence of K.E. and P.E. changes, for an S.S.S.F. process is

$$\psi = (h - T_0 s) - (h_0 - T_0 s_0)$$

When an S.S.S.F. chemical reaction takes place in such a way that both the reactants and products are in temperature equilibrium with the surroundings, the reversible work is given by

$$W_{\text{rev}} = \sum_{\text{R}} n_i \bar{g}_i - \sum_{\text{P}} n_e \bar{g}_e \qquad (16.27)$$

where the $\bar{g}$*'s* refer to the Gibbs function. The *Gibbs function for formation*, $\bar{g}_f^0$, is defined similar to enthalpy of formation, $\bar{h}_f^0$. The Gibbs function of each of the elements at 25°C and 1 atm. pressure is assumed to be zero, and the Gibbs function of each substance is found relative to this base. Table 16.1 gives $\bar{g}_f^0$ for some substances at 25°C, 1 atm.

16.19 CHEMICAL EXERGY

In Chapter 8, it was stated that when a system is at the dead state, it is in thermal and mechanical equilibrium with the environment, and the value of its exergy is zero. To state it more precisely, the *thermomechanical* contribution to exergy is zero. However, the contents of a system at the dead state may undergo chemical reaction with environmental components and produce additional work.

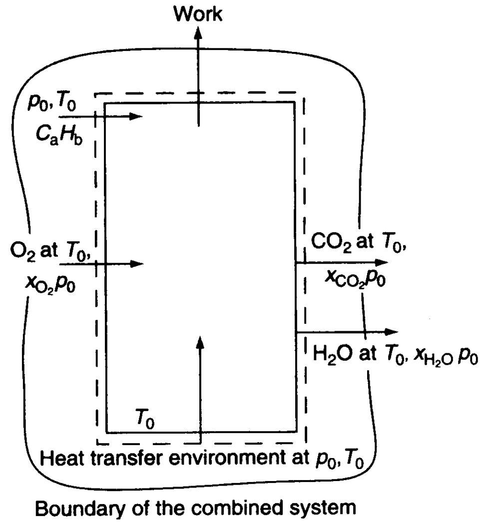


Fig. 16.7 *Fuel exergy concept*

We will here study a combined system formed by an environment and a system having a certain amount of fuel at T_0, p_0. The work obtainable by allowing the fuel to react with oxygen from the environment to produce the environmental components of CO_2 and H_2O is evaluated. The *chemical exergy* is thus defined as the maximum theoretical work that could be developed by the combined system. Thus for a given system at a specific state:

Total exergy = Thermomechanical exergy + Chemical exergy

Let us consider a hydrocarbon fuel (C_aH_b) at T_0, p_0 reacting with oxygen from the environment (Fig. 16.7) which is assumed to be consisting of an ideal gas mixture at T_0, p_0. The oxygen that reacts with the fuel is at a partial pressure of x_{0_2}, p_0, where x_{0_2} is the mole fraction of oxygen in the environment. The fuel and oxygen react completely to produce CO_2 and H_2O, which exit in separate streams at T_0 and respective partial pressures of $x_{CO_2} \cdot p_0$ and $x_{H_2O} \cdot P_0$. The reaction is given by:

$$C_aH_b + \left(a + \frac{b}{4}\right)O_2 \longrightarrow aCO_2 + \frac{b}{2}H_2O$$

At steady state, the energy balance gives

$$\dot{Q}_{\text{C.V.}} + \dot{n}H_R = \dot{W}_{\text{C.V.}} + \dot{n}H_P$$

or,
$$\frac{\dot{W}_{\text{C.V.}}}{\dot{n}} = \frac{\dot{Q}_{\text{C.V.}}}{\dot{n}} + H_R - H_P$$

$$= \frac{\dot{Q}_{\text{C.V.}}}{n} + \left(\bar{h}_f^0 + \Delta\bar{h}\right)C_aH_b + \left(a + \frac{b}{4}\right)\bar{h}_{O_2} - a\bar{h}_{CO_2} - \frac{b}{2}\bar{h}_{H_2O} \tag{16.28}$$

where $\dot{n}$ is the rate of fuel flow in moles, and K.E. and P.E. effects are neglected.

An entropy balance for the control volume gives:

$$0 = \frac{\dot{Q}_{\text{C.V.}}/\dot{n}}{T_0} + \bar{s}_{C_aH_b} + \left(a + \frac{b}{4}\right)\bar{s}_{O_2} - a\bar{s}_{CO_2} - \frac{b}{2}\bar{s}_{H_2O} + \frac{\dot{s}_{\text{gen}}}{\dot{n}} \tag{16.29}$$

Eliminating $\dot{Q}_{\text{C.V.}}$ between Eqs (16.28) and (16.29),

$$\frac{\dot{W}_{\text{C.V.}}}{\dot{n}} = \left[\bar{h}_{C_aH_b} + \left(a + \frac{b}{4}\right)\bar{h}_{O_2} - a\bar{h}_{CO_2} - \frac{b}{2}\bar{h}_{H_2O}\right]$$
$$-T_0\left[\bar{s}_{C_aH_b} + \left(a + \frac{b}{4}\right)\bar{s}_{O_2} - a\bar{s}_{CO_2} - \frac{b}{2}\bar{s}_{H_2O}\right] - \frac{T_0\,\dot{s}_{\text{gen}}}{\dot{n}} \tag{16.30}$$

The specific enthalpies in Eq. (16.30) can be determined knowing only the temperature T_0 and the specific entropies can be determined knowing T_0, p_0 and the composition of the environment.

For maximum work, $\dot{I} = \dfrac{T_0\,\dot{s}_{\text{gen}}}{n} = 0$

Therefore, the chemical exergy $\bar{a}_{\text{ch}}$ can be expressed as

$$\bar{a}_{\text{ch}} = \left[\bar{h}_{C_aH_b} + \left(a + \frac{b}{4}\right)\bar{h}_{O_2} - a\bar{h}_{CO_2} - \frac{b}{2}\bar{h}_{H_2O}\right]$$
$$-T_0\left[\bar{s}_{C_aH_b} + \left(a + \frac{b}{4}\right)\bar{s}_{O_2} - a\bar{s}_{CO_2} - \frac{b}{2}\bar{s}_{H_2O}\right] \tag{16.31}$$

The specific entropies for O_2, CO_2 and H_2O are written from (Eq. 16.22),

$$\bar{s}_i\,(T_0, x_i p_0) = \bar{s}_i\,(T_0, p_0) - \bar{R}\,\ln x_i \tag{16.32}$$

where the first term on the right is the absolute entropy at T_0 and p_0, and x_i is the mole fraction of component i in the environment. Therefore, Eq. (16.31) becomes,

$$\bar{a}_{\text{ch}} = \left[\bar{h}_{C_aH_b} + \left(a + \frac{b}{4}\right)\bar{h}_{O_2} - a\bar{h}_{CO_2} - \frac{b}{2}\bar{h}_{H_2O}\right] (\text{at } T_0, p_0)$$
$$-T_0\left[\bar{s}_{C_aH_b} + \left(a + \frac{b}{4}\right)\bar{s}_{O_2} - a\bar{s}_{CO_2} - \frac{b}{2}\bar{s}_{H_2O}\right] (\text{at } T_0, p_0)$$
$$+\bar{R}T_0 \ln \frac{\left(x_{O_2}\right)^{a+b/4}}{\left(x_{CO_2}\right)^{a}\left(x_{H_2O}\right)^{b/2}} \tag{16.33}$$

In terms of Gibbs functions of respective substances,

$$\bar{a}_{\text{ch}} = \left[\bar{g}_{C_aH_b} + \left(a + \frac{b}{4}\right)\bar{g}_{O_2} - a\bar{g}_{CO_2} - \frac{b}{2}\bar{g}_{H_2O}\right] (\text{at } T_0, p_0)$$

$$+\bar{R}T_0 \ln \frac{\left(x_{O_2}\right)^{a+b/4}}{\left(x_{CO_2}\right)^{a}\left(x_{H_2O}\right)^{b/2}} \tag{16.34}$$

where $\bar{g}(T_0, p_0) = \bar{g}_f^0 + \Delta\bar{g}_{T_0,\, p_0 \to T_{ref},\, P_{ref}}$

For the special case when T_0 and p_0 are the same as T_{ref} and p_{ref}, $\Delta\bar{g}$ will be zero.

The chemical exergy of pure CO at T_0, p_0 where the reaction is given by:

$$CO + \frac{1}{2}O_2 \longrightarrow CO_2$$

$$(\bar{a}_{ch})_{CO} = \left[\bar{g}_{CO} + \frac{1}{2}\bar{g}_{O_2} - \bar{g}_{CO_2}\right] \text{(at } T_0, p_0\text{)}$$

$$+\bar{R}T_0 \ln \frac{\left(x_{O_2}\right)^{1/2}}{x_{CO_2}}$$

Water is present as a vapour within the environment, but normally is a liquid at T_0, p_0. The chemical exergy of liquid water is

$$H_2O(l) \longrightarrow H_2O(g)$$

$$(\bar{a}_{ch})_{H_2O(l)} = \left[\bar{g}_{H_2O(l)} - \bar{g}_{H_2O(g)}\right] \text{(at } T_0, p_0\text{)}$$

$$+\bar{R}T_0 \ln \frac{1}{x_{H_2O(g)}}$$

The specific exergy of system is

$$a = a_{\text{thermo-mech}} + a_{\text{chem}}$$

$$= (u - u_0) + p_0(v - v_0) - T_0(s - s_0) + \frac{V^2}{2} + gz + a_{ch} \tag{16.35}$$

and the specific flow exergy is given by:

$$a = (h - h_0) - T_0(s - s_0) + \frac{V^2}{2} + gz + a_{ch} \tag{16.36}$$

Between two states of a system of constant composition, a_{ch} cancels, leaving just the thermomechanical contribution. For example, to find the chemical exergy of liquid octane, the reaction is:

$$C_8H_{18}(l) + 12.5O_2 \longrightarrow 8CO_2 + 9H_2O(g)$$

Assume the composition of the environment on molar basis be:
N_2 75.67%, O_2 20.35%, H_2O 3.12%, CO_2 0.03%, others 0.83%. Then,

$$\bar{a}_{ch} = \left[\bar{g}_{C_8H_{18}(l)} + 12.5\,\bar{g}_{O_2} - 8\bar{g}_{CO_2} - 9\bar{g}_{H_2O(g)}\right] \text{(at } T_0, p_0\text{)}$$

$$+\bar{R}T_0 \ln \frac{\left(x_{O_2}\right)^{12.5}}{\left(x_{CO_2}\right)^{8}\left(x_{H_2O}\right)^{9}}$$

Using the values given in Table 16.1

$$(\bar{a}_{ch})\, C_8H_{18}(l) = 6610 + 12.5(0) - 8(-394, 380) - 9(-228, 590)$$

$$+ 8.3143\ (298.15) \ln \frac{(0.2035)^{12.5}}{(0.0003)^8\,(0.0312)^9}$$

$$= 5{,}407{,}843 \text{ kJ/kg mol} = 47{,}346 \text{ kJ/kg}$$

16.20 SECOND LAW EFFICIENCY OF A REACTIVE SYSTEM

For a fuel at T_0, p_0, the chemical exergy is the maximum theoretical work that could be obtained through reaction with environmental substances. However, due to various irreversibilities like friction and heat loss, the actual work obtained is only a fraction of this maximum theoretical work. The second law efficiency may thus be defined as the ratio of:

$$\eta_{\text{II}} = \frac{\text{Actual work done}}{\text{Maximum theoretical work}} = \frac{W_{\text{C.V.}}}{m_{\text{fuel}} \times a_{\text{ch}}} \tag{16.37}$$

The associated irreversibilities and the consequent exergy losses require to be reduced to enhance the second law efficiency, which in turn, reduces the fuel consumption and also increases the cost. The trade off between the fuel savings and the additional costs must be carefully weighed.

16.21 FUEL CELLS

Fuel cells are receiving prominent attention as clean, efficient and affordable alternative energy technologies for the future. A *fuel cell* is a direct energy conversion device in which fuel and an oxidizer undergo a controlled chemical reaction, producing products and supplying electrical current directly to an external circuit. The fuel and oxidizer react in stages on two separate electrodes, a positive electrode called *cathode*, and a negative electrode called *anode*. The two electrodes are separated by an electrolyte. The rates of reaction are limited by the time it takes for diffusion of chemical species through the electrodes and the electrolyte and by the reaction kinetics.

Fuel cells are of various kinds. One type, the hydrogen-oxygen fuel cell, is shown schematically in Fig. 16.8. The fuel is hydrogen, which diffuses through the porous anode and reacts on the anode surface with OH^- ions, forming water and yielding free electrons according to:

$$H_2 + 2OH^- \longrightarrow 2H_2O + 2e^-$$

The electrons flow into the external circuit, and the water passes on to the electrolyte. On the cathode surface, oxygen fed into the cell combines with water from the electrolyte and electrons from the external circuit to produce OH^- ions and water according to:

$$\frac{1}{2}O_2 + 2H_2O + 2e^- \longrightarrow 2(OH)^- + H_2O$$

The electrolyte separating the electrodes transports the OH^- ions, completing, the circuit, and the water (products) is removed from the cell. The overall reaction is:

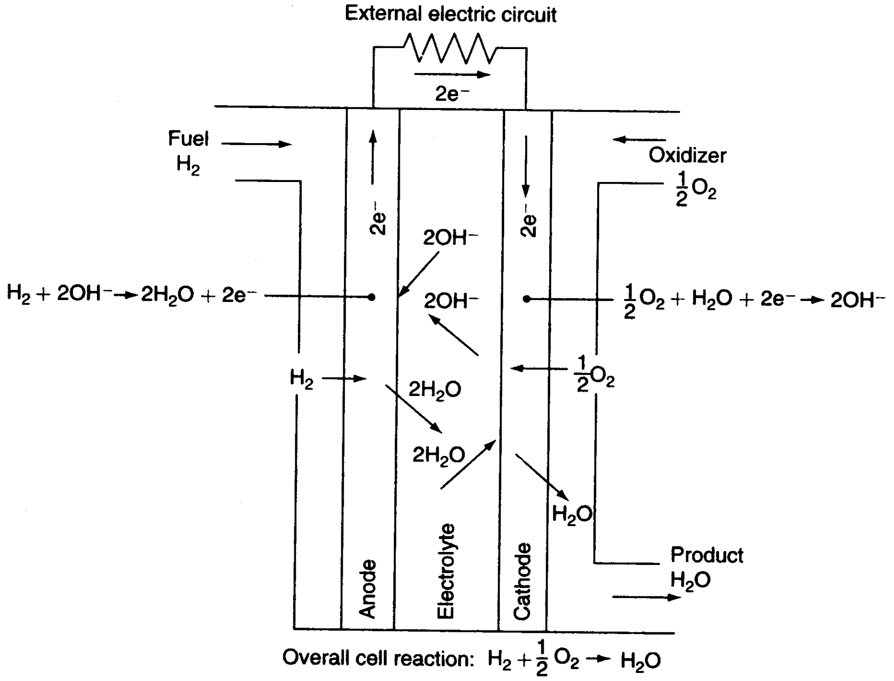
$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$$

which is the same as the equation for the highly exothermic combustion reaction. However, in a fuel cell, only a relatively small amount of heat transfer between the cell and its surroundings takes place, and the temperature rise is also relatively much smaller.

Energy is removed from the fuel cell as electrical energy, whereas energy is removed from a combustion reaction as heat or as heat and work together. Because the fuel cell operates almost isothermally and continuously, the extent of its conversion of chemical energy to electrical energy is not limited by second law of thermodynamics.

In a fuel cell, there is a continuous supply of the reactants. The overall reaction, as stated, is divided into two reactions that occur on separate electrodes. The fuel and the oxidizer do not come directly into contact with each other, because direct contact would generally involve a non-isothermal (exothermic) reaction as in a normal combustion process.

One reaction, occuring on the surface of one electrode, ionizes the fuel and sends released electrons into an external electric circuit. On the surface of the other electrode, a reaction occurs that accepts electrons from



Hydrogen-oxygen fuel cell

the external circuit and when combined with the oxidizer creates ions. The ions from each reaction are combined in the electrolyte to complete the overall reaction. The electrolyte between the electrodes is necessary to transport ions, and it is not electrically conductive, thus, not allowing the flow of electrons through it.

The maximum work obtainable in a fuel all is given by Eq. (16.27),

$$W_{\max} = -\Delta G = \sum_{R} n_i \bar{g}_i - \sum_{P} n_e \bar{g}_e$$

where

$$\bar{g} = g_f^0 + \Delta\bar{g}$$

Also, from Eq. (16.2),

$$W_{\max} = W_{\text{rev}} = \sum_{R} n_i \left[\bar{h}_f^0 + \Delta\bar{h} - T_0\bar{s}\right]_i$$

$$-\sum_{P} n_e \left[\bar{h}_f^0 + \Delta\bar{h} - T_0\,\bar{s}\right]_e$$

$$= \Delta H - T_0 \left[\sum_{R} n_i \bar{s}_i - \sum_{P} n_e \bar{s}_e\right]$$

The fuel cell efficiency is defined as:

$$\varepsilon = \Delta G/\Delta H \tag{16.38}$$

which can be less than, equal to, or greater than unity. The work done in a fuel cell can be written as:

$$W_{\max} = \text{moles of reactant} \times \frac{\text{molecules}}{\text{kgmol}} \times \frac{\text{electrons}}{\text{molecule}} \times \frac{\text{charge}}{\text{electron}} \times \text{voltage}$$

$$= n \times (6.023 \times 10^{26})\text{j}\,(1.6022 \times 10^{19})V = \mathcal{F} n j V,$$